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PHOTODEGRADATION OF DIMETHENAMID-P IN DEIONISED AND GROUND WATER

Article Highlights
- Photocatalytic degradation of dimethenamid-P herbicide is presented
- Degradation was studied in deionised and ground water under different conditions
- Photocatalytic degradation of dimethenamid-P is much faster in ground water
- HPLC showed almost complete removal of herbicide after 90 min in both water
- TOC showed herbicide was mineralized 64% in deionised and 50% in ground water

Abstract

The study of photodegradation of dimethenamid-P herbicide was performed in deionised and ground water using TiO₂ as a catalyst under UV light. The effect of electron acceptor (H₂O₂), scavenger of •OH radicals (C₂H₅OH) and scavenger of holes (NaCl and Na₂SO₄) as well as solution pH was analyzed. The photodegradation of dimethenamid-P was followed by HPLC. The formation of transformation products was followed using high performance liquid chromatography-electrospray mass spectrometry. Ion chromatography and total organic carbon measurements were used for the determination of the mineralization level. HPLC analysis showed the almost complete removal of herbicide after 90 min in deionised and ground water, while total organic carbon analysis showed that dimethenamid-P was mineralized 64 and 50% in deionised and ground water, respectively. The ion chromatography results showed that the mineralization process leads to the formation of chloride, sulphate and nitrate anions during the process. Transformation products were identified and the degradation mechanism was proposed.

Keywords: salt effect; ion chromatography; liquid chromatography-electrospray mass spectrometry; photocatalysis; titanium dioxide.

Modern agricultural production in the last decade involves the use of pesticides to a large extent. Dimethenamid-P (2-chloro-*N*-(2,4-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl) acetamide, DMA-P) belongs by its chemical properties and structure to the group of chloroacetamides and plays an important role in the crop protection of broadleaf weeds and annual grasses in row crops [1], primarily in corn, soybean and sorghum [2]. These components include highly toxic and persistent substances and due to exceptional reactivity threaten to jeopardize the aquatic environment through agricultural circle and washing [3-5]. The European Union has stipulated that the
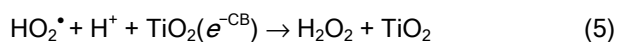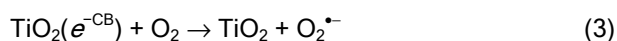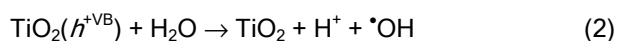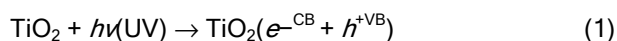
levels of pesticides in drinking water should not exceed 0.1 mg dm⁻³ for the individual components, *i.e.*, for some of their transformation products concentration should not exceed 0.5 mg dm⁻³ [6]. Within the strategy of protection of environmental resources, heterogeneous photocatalysis has proved to be one of the most effective techniques for the degradation of organic pollutants [7]. It involves fotoinduction reaction accelerated by a solid catalyst [8].

TiO₂ as a photocatalytic semiconductor is the most suitable chemical compound for removal of harmful substances from the environment by photocatalytic process. Its chemical inertness, stability to the photo and chemical corrosion, as well as low price are its advantages as a catalyst [9]. Photocatalytic degradation is based on the irradiation of UV light, which results in the generation of oxidative species that are characterized by high and non-selective reactivity, so they can easily attack and decompose the

molecules of organic pollutants. Photon has energy which is greater or equal to the band gap energy of semiconductor (TiO_2). In that way electron (e^-) from the valence band (VB) excitates to the conduction band (CB), leaving a positive hole ($h+$) behind. The energy level at the bottom of the valence zone effectively reduces the potential of photoelectrons, while the peak energy of the valence zone creates its ability to oxidize. Electrons and cavities migrate to the surface of the catalyst and reduce species present on its surface. Photogenerated cavities may oxidize organic molecules or react with OH^-, or H_2O, oxidising them to $^•OH$. Photogenerated electrons can also react with oxygen, translating it into superoxide anion $O_2^{-•}$ radical. This reaction leads to additional formation of $^•OH$. These radicals as very strong oxidative agents having the ability to oxidize organic pollutants adsorbed on the surface of TiO_2 to mineral products [10]. Redox reactions including photons can be presented by Eqs. (1)-(5):

$$TiO_2 + h\nu(UV) \rightarrow TiO_2(e^{-CB} + h^{+VB}) \tag{1}$$

$$TiO_2(h^{+VB}) + H_2O \rightarrow TiO_2 + H^+ + {}^•OH \tag{2}$$

$$TiO_2(e^{-CB}) + O_2 \rightarrow TiO_2 + O_2^{•-} \tag{3}$$

$$O_2^{•-} + H^+ \rightarrow HO_2^• \tag{4}$$

$$HO_2^• + H^+ + TiO_2(e^{-CB}) \rightarrow H_2O_2 + TiO_2 \tag{5}$$

Conclusively, photocatalytic degradation of pesticides can be presented in simplified form by Eqs. (6)-(8):

$$Pesticide + h^{+VB} \rightarrow oxidation\ products \tag{6}$$

$$Pesticide + e^{-CB} \rightarrow reduction\ products \tag{7}$$

$$Pesticide + {}^•OH \rightarrow transformation\ products \tag{8}$$

In order to get higher yield, agriculture relies on the application of pesticides. The negative effects of pesticides on the quality of ground and surface water are well known [5]. The environmental issues concerning pesticides comprehend: inadequate control of the usage (excessive concentrations of pesticides), non-biodegradability, long decomposition time and high mobility in different eco-systems. Dimethenamid--P belongs to the group of chloroacetamides which are persistent organic pollutants. Its specific feature is the migration from the soil to the ground and groundwater [2].

In this work, the study on the photocatalytic behavior of DMA-P in aquatic environment is presented for the first time. the influence of various parameters on the photocatalytic process, such as the initial concentration of catalyst, initial DMA-P concentration, the concentration of added H_2O_2, C_2H_5OH,

NaCl, and Na_2SO_4 as well as pH value of water solution in two different types of water (deionised and ground water) were studied. HPLC/MS (high performance liquid chromatography-electrospray mass spectrometry) were applied for qualitative identification of transformation products.

EXPERIMENTAL

Materials

DMA-P (purity higher than 99%) was supplied by Riedel de-Haen (Seelze-Hannover, Germany). Titanium dioxide (TiO_2) labeled as P25 supplied by Evonik was used in experimental part of the work. All other chemicals were p.a. or higher grade. Deionized water (DW) was obtained from a Millipore water purification system. Ground water (GW) was obtained from public-utility company Water supply and sewage treatment in Novi Sad, as alluvium of Danube. The ground water contains 269.6 mg dm^{-3} of HCO_3^-/CO_3^{2-}, 57.5 mg dm^{-3} of SO_4^{2-}, 20 mg dm^{-3} of Cl^-, 1.496 mg dm^{-3} of NO_3^-, 0.343 mg dm^{-3} of Mn^{2+}, 0.600 mg dm^{-3} of NH_3, 84 mg dm^{-3} of Ca^{2+}, 17.5 mg dm^{-3} of Mg^{2+} and 2.810 mg dm^{-3} of Fe (total). Conductivity of deionized and ground water was 0.55 and 58.5 μS cm^{-1} while pH was 5.9 and 7.20, respectively.

Photocatalytic experiment

The photodegradation of DMA-P was investigated in two different types of water, in the deionised and ground water, with pesticide concentration of 34.5 mg dm^{-3}. All the reactions were performed in an open reactor, thermostated at 25 °C [11]. For the irradiation an Osram Ultra Vitalux® 300 W lamp was used, with ratio of UV-A and UV-B lights 13.6:3. The position of lamp was 40 cm from the surface of the reaction mixture. The temperature of solution changed for 2 °C after 90 min of irradiation. For every experimental cycle 25 cm^3 of the solution was placed into the reactor and stirred for 30 min in the dark. Continuous stirring was maintained during the reaction. The aliquots were taken at defined time intervals (after 10, 20, 30, 60 and 90 min from the beginning of the reaction). All the aliquots were filtrated by 0.45 μm Cronus 13 mm Nylon Syringe filters, in order to remove the suspended TiO_2 particles before the analysis. All the experiments were done in triplicate.

Analytical procedures

During 90 min of irradiation time, the samples were taken from the suspension. The concentration of herbicide was determined by HPLC (high performance liquid chromatography) analysis. All analysis were performed at room temperature.

The HPLC determinations were carried out with HPLC instrument Agilent 1100 Series equipped with Zorbax Eclipse XDB-C18 (Agilent). The analyses were performed in isocratic mode using water/methanol/acetic acid (200:300:5 *V*/*V*/*V*), the mobile phase had flow rate of 0.8 cm^3 min^{-1} and the column temperature was 25 °C. The injection volume was 5 μL and UV detection was carried out at 240.4 nm.

The pH value of the samples was adjusted by the addition of 0.1 mol dm^{-3} NaOH or HCl and the determination of pH value was performed on pH metar Inolab pH 730 (Germany).

The chromatographic separations were followed by an MS analyzer, Hypersil Gold Thermo Scientific (Bremen, Germany) (50 mm×2.1 mm, 3 mm particle size) termostated at 25 °C using a Thermo survey (USA) HPLC instrument. Injection volume was 50 μL and flow rate was 0.2 cm^3 min^{-1}. The mobile phases were: A (0.10% acetic acid/99.9% water) and B (0.10% acetic acid/99.9% acetonitrile). The analyses were performed in isocratic mode. A LCQ Deca mass spectrometer equipped with an atmospheric pressure interface and an ESI ion source was used as a detector. The LC column effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas. The tuning parameters adopted for ESI source were: capillary voltage 45 V, capillary temperature 275 °C, spray voltage 6 kV and gas flow was 20 arbitrary units. The analysis was performed in positive ion mode. Mass spectra were recorded across the range 100−400 *m*/*z*.

Ion chromatographic (IC) analysis was performed on a Dionex DX-300 ion chromatograph at ambient temperature (25 °C) with a suppressed conductivity detector. Ion chromatograph was equipped with a Dionex IonPac AS14 column.

Total organic carbon (TOC) was measured using a Zellweger LabTOC 2100 instrument.

RESULTS AND DISCUSSION

Preliminary experiments

In the beginning of the photocatalytic study, three different experiments have been carried out in aqueous environmental matrices with the aim to evaluate adsorption and photolysis of the studied DMA-P. These experiments were conducted under the following conditions:

a) investigation of DMA-P adsorption on the TiO_2 in the dark (C_{kat}: 2.0 g dm^{-3}, $C_{(DMA-P)\,0}$: 34.5 mg dm^{-3}, *V*: 25 cm^3, *T*: 25 °C),

b) investigation of DMA-P degradation under UV light, in the absence of TiO_2 (photolysis) ($C_{(DMA-P)\,0}$: 34.5 mg dm^{-3}, *V*: 25 cm^3, *T*: 25 °C),

c) heterogeneous photocatalysis of DMA-P solution under UV light and a catalyst (C_{kat}: 2.0 g dm^{-3}, $C_{(DMA-P)\,0}$: 34.5 mg dm^{-3}, *V*: 25 cm^3, *T*: 25 °C).

DMA-P concentrations have not changed significantly in the case of adsorption and photolysis. The results of the adsorption experiment show slight decrease in herbicide concentration (less than 5%) during a period of 90 min, indicating only slight adsorption on the TiO_2 surface. Photolysis results show insignificant fall of the initial concentration of DMA-P. On the other hand, photocatalysis shows almost complete destruction of this active substance (more than 99% determined by HPLC) both in deionised and ground water. The comparison of photocatalysis and adsorption processes implies that stirring of suspension for 30 min in the dark prior to the photocatalysis process is an important step for reaching the adsorption equilibrium [9].

To determine the optimum concentration of TiO_2 for the photodegradation of DMA-P, experiments were conducted by varying the initial concentration of TiO_2 from 0.5 to 3.0 g dm^{-3}, while keeping other parameters constant. It was found out that the maximum removal efficiency of the chloroacetamide has been achieved with the catalyst concentration of 2.0 g dm^{-3}, and, therefore, this concentration of TiO_2 has been selected as the optimum one. Further increase of the catalyst concentration decreases the rate of photodegradation, and reduces the efficiency of degradation process. Theoretically, the increase of the catalyst concentration above an optimum value should not have effect on the photodegradation rate since all the light available is already utilized. However, higher mass concentrations of TiO_2 Evonik P25 led to the aggregation of its particles and thus to a decrease of contact surface between the substrate and the photocatalyst. This caused a decrease in the number of active sites and a lower rate of photodegradation. When the concentration of catalyst is exceeded, a part of the UV light is not utilized because of the increased turbidity of solution and increased light scattering by the photocatalyst particles, and therefore the overall performance decreases [12].

Initial concentration of DMA-P affects the rate of its photocatalytic degradation. The increase of the initial substrate concentration on the catalyst surface number of molecules/ions that react with •OH increases and the rate of degradation decreases. The increase of the initial substrate concentration above an optimum value leads to the decrease of the effi-

ciency of the photocatalytic process. the substrate molecules may adsorb on the catalyst surface instead of OH⁻ and water molecules, which then result in the generation of fewer •OH [7,9]. But since very small adsorption was observed, the reduced photoactivity of semiconductor may be due to the absorbtion of light by organic molecules [13].

The effect of the pH value

The influence of pH value on the photocatalytic degradation can be explained by electrostatic interactions between the surface of TiO_2, solvent molecules, substrate and electrically charged radicals formed during the process. At pH values above the value of point of zero charge (PZC) of TiO_2 (6.8), the surface will remain negatively charged. For pH < PZC the surface will remain positively charged [14]. For the influence of pH value on the photocatalytic degradation five different pH values were analyzed. The adjustments of acidic medium (pH 2.0 and 4.0) and alkaline medium (pH 9.0 and 11.0) were made with diluted HCl or NaOH. Before any adjustments the pH value of pesticide solution in DW and GW was measured and the obtained values were 6.33 and 7.34 for DW and GW, respectively. The photocatalytic degradation rate of DMA-P in DW and GW as a function of pH value is shown in Figure 1. Lower degradation rate for both aqueous media was at pH values near to PZC. The possible explanation for this phenomenon is the fact that the TiO_2 particles tend to agglomerate and thus decrease the yield of degradation. As reported, at pH values equal to the PZC, aggregate particles are larger, and number of active sites on the catalyst surface is decreased and degradation rate reduced [15,16].
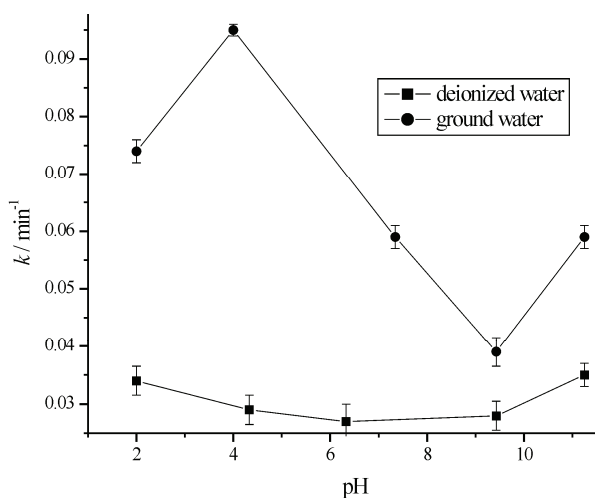

Figure 1. The effect of pH value on the photocatalytic degradation rate of DMA-P (34.5 mg dm⁻³) in deionised and ground water (c_cat 2.0 g dm⁻³).

The difference in DMA-P degradation rate caused by the change of pH value was more significant in ground than in the deionised water. The reaction rate in ground water is decreased in neutral and in the alkaline medium and pH has an insignificant effect on the rate of degradation in deionised water. The explanation for the effect of pH on the photocatalytic reaction might be in the influence of electrically charged surface of the TiO_2 on the physical and chemical properties of the parent molecule. Although DMA-P molecule is electrically neutral it can be repulsed from the negatively charged surface of the photocatalyst at pH value above 6.8 due to unequal distribution of electron density in the substrate molecule when electronegative atom like Cl is present [4].

The disappearance rate in the process of photocatalytic degradation can be described by a pseudo-first kinetic order, as shown by Eqs. (9) and (10):

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{9}$$

$$C = C_0 e^{-kt} \tag{10}$$

where C is the concentration of DMA-P at irradiation time t, and C_0 is the initial concentration of DMA-P.

The effect of the addition of electron acceptor

When TiO_2 is used as a photocatalyst, one of the problems that arise is the recombination of the e⁻h⁺ pair. This problem is particularly apparent in the absence of appropriate electron acceptors which also reduces the efficiency of photocatalytic reaction [17]. In order to enhance the formation of •OH and inhibit e⁻h⁺ pair recombination, the effect of addition of H_2O_2 as an electron acceptor on the efficiency of photodegradation has been investigated in a number of experiments conducted in both deionised and ground water [17,18]. In this study, a series of experiments has been carried out in both media. The obtained results have shown that for H_2O_2 concentration of up to 0.005 mol dm⁻³ the reaction time is increased by 2 times in deionised water and by 1.6 times in ground water (as shown in Figure 2). This may be due to the increased concentration of •OH. Faster degradation rate in the presence of H_2O_2 may be attributed to the generation of •OH and OH⁻ in the presence of UV radiation, and not to the formation of less powerful $O_2^{•-}$ oxidant by the reduction of O_2 [19]. At higher concentrations (above 0.005 mol dm⁻³), H_2O_2 acts as a "scavenger" of •OH and holes on the catalyst surface, leading to the formation of $HO_2^•$ that react with •OH to generate oxygen and water as illustrated

by Eqs. (11) and (12). As the result, the efficiency of photocatalytic degradation is reduced.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2{}^{\bullet} + H_2O \qquad (11)$$

$$H_2O_2 + h^+ \rightarrow HO_2{}^{\bullet} + H^+ \qquad (12)$$
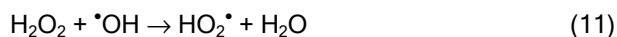
According to some researchers, if reaction products, such as oxygen and H_2O_2 are not present near the surface of TiO_2, electron-hole pairs recombine and adsorbed energy is dissipated as heat. H_2O_2 added in smaller concentrations is able to prevent this reaction [4].
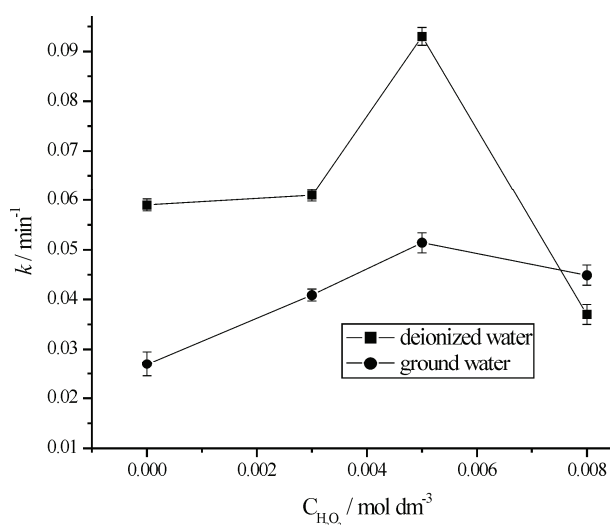

Figure 2. The effect of the added H_2O_2 on the photocatalytic degradation rate of DPA-P (34.5 mg dm^{-3}) in deionised and ground water (c_{cat} 2.0 g dm^{-3}).

The effect of the $^{\bullet}OH$ scavenger

To confirm and to prove if heterogeneous photocatalysis is taking place through $^{\bullet}OH$, the effect of ethanol added in the reaction mixture containing DMA-P and TiO_2 Evonik P25 on the reaction rate has been investigated in both deionised and ground water (Figure 3). It was determined that as the ethanol concentration increases, the degradation rate decreases, compared with the same reaction without addition of this solvent. The obtained result is in agreement with previous research from this field [20]. In the same research the effect of various solvents on the photocatalytic degradation of benzidene yellow was studied. The results showed that the degradation efficiency decreases with the addition of solvents in the following order: hexane < acetonitrile < 2-propanol < < 1-butanol < 2-methyl-2-propanol. The obtained results confirm that alcohols are good $^{\bullet}OH$ scavengers and the products of reaction are weaker oxidants (alkoxy-radicals) that react with the substrate. The results obtained in the present study also show that

the inhibition of catalytic degradation is more pronounced in ground water where gradual addition of ethanol (up to 0.8 mol dm^{-3}) decreases the reaction rate 15 times, while in deionised water the reaction rate decreases 3 times under the same conditions.
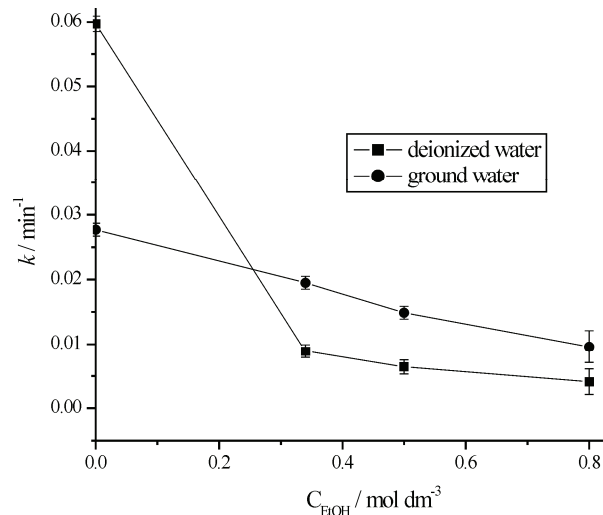

Figure 3. The effect of the added of C_2H_5OH on the photocatalytic degradation rate of DMA-P (34.5 mg dm^{-3}) in deionised and ground water (c_{cat} 2.0 g dm^{-3}).
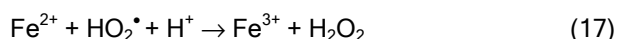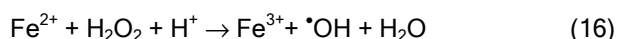
The effect of the inorganic ions

When comparing the results of the rate of photocatalytic degradation of DMA-P in two types of water, the great difference can be noticed. The rate of decomposition of DMA-P in ground water is two times faster than in deionised water. This could be ascribed to the presence of nitrate ions. Reaction of nitrate ions with photons ends with hydroxyl radicals according to the Eqs (13)-(15) [21]:

$$NO_3{}^- + h\nu \rightarrow NO_2{}^- + O \qquad (13)$$

$$NO_3{}^- + h\nu \rightarrow NO_2{}^{\bullet} + O^{\bullet-} \qquad (14)$$

$$O^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad (15)$$

Taking into account the fact that groundwater from the Danube alluvium is slightly alkaline it can be expected that hydroxyl radicals formed together with photogenerated oxidative species generated with the irradiated TiO_2, have higher degradation rates of DMA-P. Chen *et al.* [21] reported that $NO_3{}^-$ as constituents found in natural waters absorb solar radiation in UV range less than 350 nm with maximum at 302 nm. Photolysis of these anions leads to formation of $^{\bullet}OH$ under influence of UV radiation, as shown by Eqs (13)-(15).

Ground water also contains dissolved metal ions, such as Fe^{3+}, Mn^{2+}, Ca^{2+} and Mg^{2+}. Wei *et al.* indicated another possible explanation for the differ-

ences observed in the kinetics of the process taking place in these two aqueous media [22]. The effect of Fe^{3+} on the photodegradation efficiency of metamidophos was studied by varying amount of Fe^{3+} from 0.001 to 0.8 mmol dm^{-3}. The results showed that when higher Fe^{3+} concentrations were added (up to 0.5 mmol dm^{-3}) its photodegradation efficiency increased rapidly (from 37.3 to 55.0%). When the concentration of this cation exceeds this value, photodegradation efficiency is greatly reduced. It has been concluded that positively charged Fe^{3+} absorbed on surface of the TiO_2 are more easily reduced ($Fe^{3+} + e^- \rightarrow Fe^{2+}$) thus decreasing electron-hole pair recombination. This favours the formation of $^\bullet OH$ and O_2^{2-} on the surface of the TiO_2. The following reactions occur at the same time:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^\bullet OH + H_2O \qquad (16)$$

$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad (17)$$

It has also been shown that the presence of Na^+, K^+, Ca^{2+} and Mg^{2+} has no effect on the photodegradation rate. This is explained by the fact that these ions are in their most stable oxidation state and as such they do not show affinity for bonding photogenerated electrons and holes [23].

Physicochemical composition of groundwater indicates the presence of HCO_3^-. When investigating the previous studies the effects of HCO_3^- on the rate of photocatalytic degradation, showed that concentrations above 0.1 mol dm^{-3} lead to reduced photodegradation efficiency due to the formation of greater number of $CO_3^{\bullet-}$ radical-ions which are less reactive than $^\bullet OH$ [24]. However, in ground water where pH is slightly alkaline, HCO_3^- are present to a greater extent than CO_3^{2-} and their concentration in this medium is below 0.05 mol dm^{-3}, being, according to the findings of Lair *et al.*, the most probable explanation for increased efficiency of herbicide degradation [25].

The effect of the added salts

In addition, the salt effect on the reaction rate (Figure 4) was studied, using NaCl and Na_2SO_4. The salts were used at concentrations of 20 and 200 mmol dm^{-3}, for each of the added salts. As can be seen from Figure 4, the photodegradation reaction is slower in the presence of salts in deionized water. Sodium chloride proved to be the stronger inhibitor than sodium sulfate. While chloride ions have hole scavenging properties, sulfate anions react with positive holes and hydroxyl radicals [26,27]. There is also a competitive adsorption between DMA-P and chlorides and/or sulfates [24]. These influences can be described by the Eqs. (18)-(24) [7,26-29]:
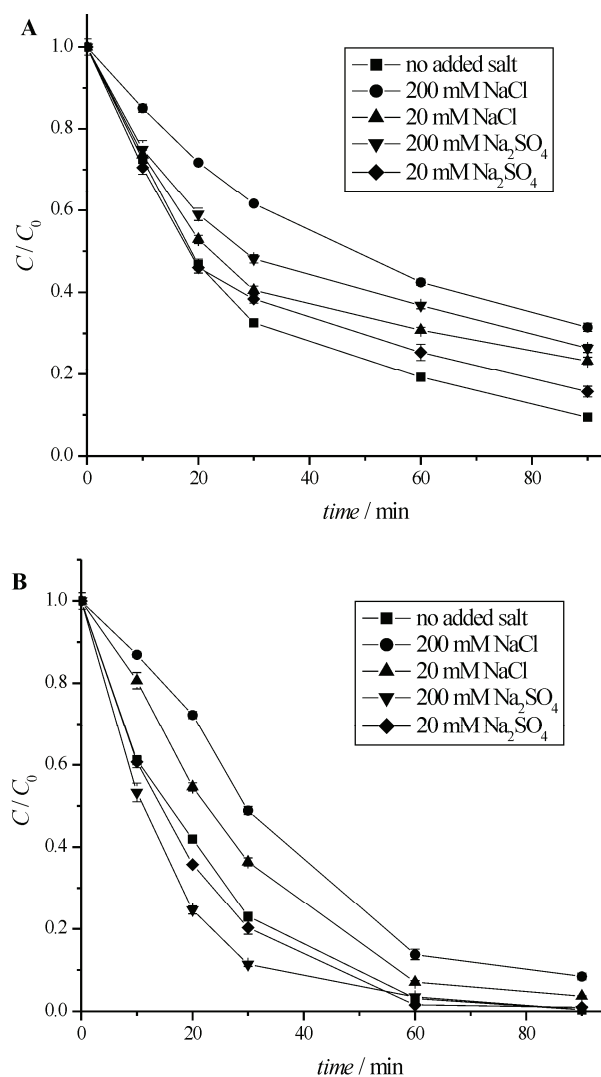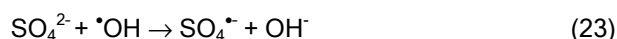
$$Cl^- + h^+ \rightarrow Cl^\bullet \qquad (18)$$

$$Cl^- + {}^\bullet OH \rightarrow ClOH^{\bullet-} \qquad (19)$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^\bullet + H_2O \qquad (20)$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \qquad (21)$$

$$SO_4^{2-} + h^+ \rightarrow SO_4^{\bullet 2-} \qquad (22)$$

$$SO_4^{2-} + {}^\bullet OH \rightarrow SO_4^{\bullet-} + OH^- \qquad (23)$$

$$SO_4^{\bullet-} + e_{CB}^- \rightarrow SO_4^{2-} \qquad (24)$$

Figure 4. Effect of salt on the photocatalytic degradation of DMA-P (34.5 mg dm^{-3}) in the presence of TiO_2 (c_{cat} 2.0 g dm^{-3}) in deionized water (A) and ground water (B).

Chloride ions inhibit photocatalytic degradation in both of analyzed waters, deionized and ground water. The inhibitor effect of these anions can be explained through electrostatic interactions between surface of photocatalyst and anions. In acidic solution surface of photocatalyst is positively charged and attracts anions, which has influence on the reduced

adsorption of molecules of DMA-P and intermediates and therefore reduced rate of degradation process and mineralization. In alkaline solutions such adsorption would be unlikely because of repulsive electrostatic forces [24]. Sulfate ions inhibit photocatalytic degradation in deionized water (at mildly acidic solution, for pH 6.33), which can be explained by the same inhibitor effect as for chloride ions. In ground water (in mild alkaline solution, for pH 7.34) these anions increase rate of the degradation process which can be explained by oxidative ability of sulfate anions radicals. Although the sulfate anion radical is less reactive than $^\bullet$OH, it may oxidize the DMA-P molecule. At mild alkaline pH, both $SO_4^{\bullet-}$ and $^\bullet$OH are responsible for the degradation of DMA-P [24].

Results of total organic carbon elimination and ion chromatography

The results of ion chromatography (shown in Figure 5) and TOC analysis have been used for the determination of the mineralisation level of DMA-P. Considering that the molecule of DMA-P contains one atom of chlorine, nitrogen and sulphur, Cl^-, SO_4^{2-} and NO_3^- may be separated after their complete mineralization. The degradation results in deionised water show that after 90 min of degradation 95% of chlorine is converted into chloride, while during the same period of irradiation 23% of total nitrogen is converted into NO_3^- and 8% of sulphur is converted into SO_4^{2-} ions. However, mineralisation of the DMA-P in ground water is almost unnoticeable.

The results lead to the conclusion that the formation rates of Cl^-, SO_4^{2-} and NO_3^- are slower compared to the degradation rate of DMA-P, and indicate the formation of intermediates that contain chlorine, sulphur and nitrogen.

The mineralization of DMA-P was studied by the total organic carbon analysis. For the period of 90 min, the TOC elimination was 64% in deionised water and 50% in ground water (Figure 6). This indicates that the TOC removal rate was not proportional to the rate of DMA-P photodegradation and also confirms the formation of the organic intermediates.
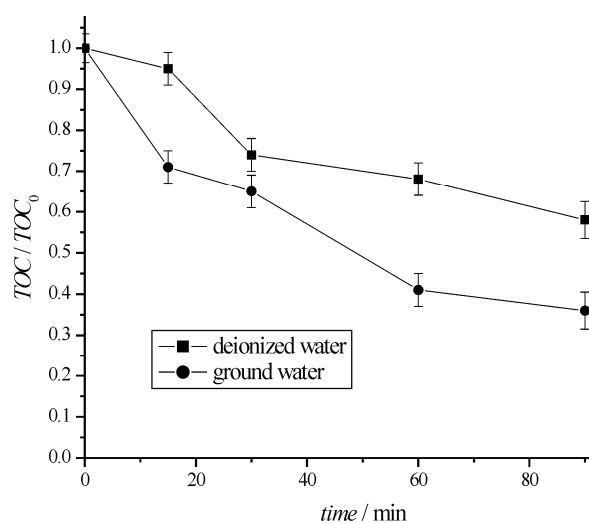
Figure 6. Time dependence of TOC concentration during the photocatalytic degradation of DMA-P (34.5 mg dm^{-3}) in deionised and ground water (c$_{cat}$ 2.0 g dm^{-3}).
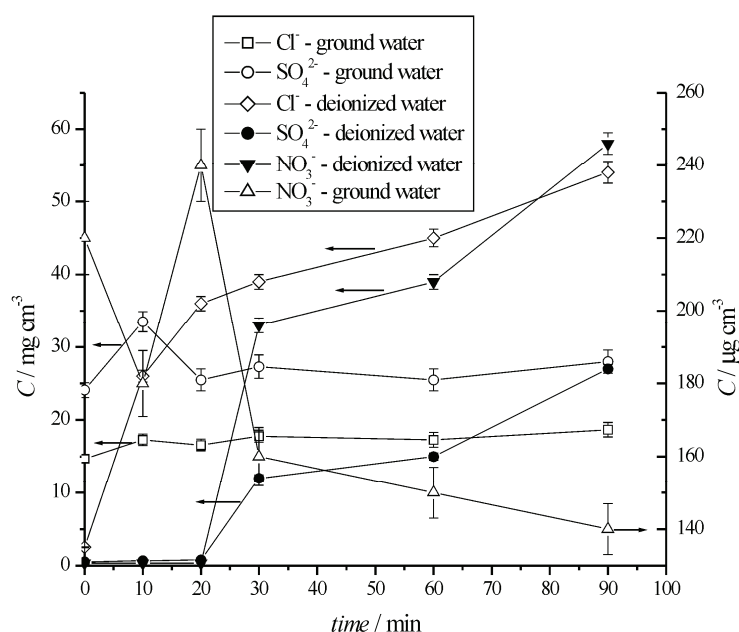
Figure 5. Time dependence of inorganic ions (nitrates, sulphates and chlorides) concentration during the photocatalytic degradation of DMA-P (34.5 mg dm^{-3}) in deionised and ground water (c$_{cat}$ 2.0 g dm^{-3}).

Results of HPLC/MS analysis

In order to identify intermediates formed during the photocatalytic process, a qualitative analysis of aliquot samples taken at various periods of degradation process was carried out. From the analysis of the obtained peaks identified by the value of *m/z* ratios, based on the molecular weight and the nature of the chemical bond in the molecule of DMA-P, the occurrence of transformation products can be confirmed, which is illustrated in Figure 7. The efficiency of LC-MS hyphenated techniques for the characterization of various photodegradation [30,31] products has been recently reported for chloracetamide herbicide acetochlor, which has similar structure as the investigated dimethenamide-P.
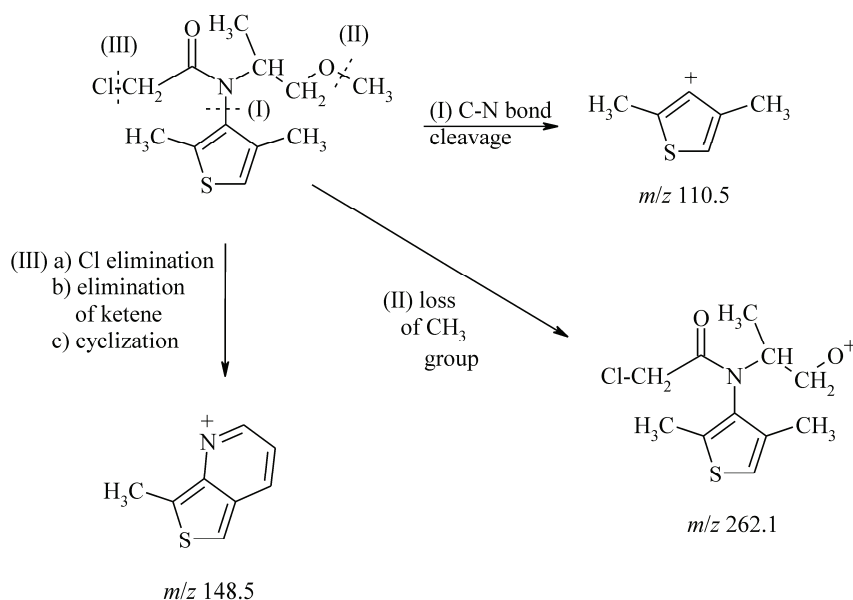
At the end of the photodegradation reaction (90 min) only traces of DMA-P were detected. When DMA-P was electrochemically degradated the major degradation product was formed by C-N bond cleavage, while Cl elimination produced minor degradation product [1].

CONCLUSION

The elimination of DMA-P from water with the mediation of TiO_2 has been studied for the first time in this study. Under optimal conditions almost complete disappearance of 34.5 mg dm^{-3} of herbicide (determined by HPLC) and 50% TOC removal, occurred within 90 min in deionised and ground water, while

Figure 7. The degradation mechanism proposed for DMA-P photocatalytic degradation.

HPLC/MS analysis of the reaction mixture after 10 minutes of the photocatalytic degradation, revealed the presence of one degradation product with *m/z* of 110.5. From the structural analysis of DMA-P it can be assumed that the cleavage of C-N bond occurred (path I) and that the dimethylthiophenyl cation has been formed, as shown in Figure 7.

The existence of ion fragment with *m/z* 262.1 may be explained by ordinary loss of CH_3 group in side chain of a parent molecule (II).

Another abundant degradation product was detected after 30 min of the photocatalytic degradation with *m/z* 148.5 (III). the formation of this structure can be explained by the following subsequent processes: elimination of chlorine and then loss of ketene, followed by rearrangement and cyclization to obtain a bicyclic product (Figure 7).

TOC analysis showed that DMA-P was mineralized 64 and 50% in deionised and ground water, respectively. The ion chromatography results showed that the mineralization process leads to the formation of chloride, sulphate and nitrate anions during the process. DMA-P degradation products were identified by HPLC/MS analysis. They were formed by: C-N bond cleavage (*m/z* 110.5), loss of CH_3 group (*m/z* 262.1), elimination of chlorine and ketene, followed by rearrangement and cyclization (*m/z* 148.5).

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REFERENCES

[1]   O. Glavaški, S. Petrović, D. Mijin, M. Jovanović, A. Dugandžić, T. Zeremski, M. Avramov Ivić, Electroanalysis 26 (2014) 1877-1880

[2]   R.A. Yokley, L.C. Mayer, S.B. Huang, J.D. Vargo, Anal. Chem. 74 (2002) 3754-3759

[3]   J. Fenoll, P. Hellín, C-M. Martínez, P. Flores, S. Navarro, J. Photochem. Photobiol., A 238 (2012) 81-87

[4]   V.A. Sakkas, P. Calza, A.D. Vlachou, C. Medana, C. Minero, T. Albanis, Appl. Catal., B 110 (2011) 238- 250

[5]   E.M. Thurman, E.A. Scribner, in The Triazine Herbicides 50 Years Revolutionizing Agriculture, H.M. LeBaron, J.M. McFarland, O.C. Burnside Eds., Elsevier, San Diego, CA, 2008, pp. 451-475

[6]   Directive 2000/60/EC, EU Official Journal, 2000. L327, Council Directive 2000/60/EC establishing a framework for Community action in the field of water policy (Water Framework Directive), pp. 1-73.

[7]   S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, J. Environ. Manage. 92 (2011) 311-330

[8]   N.A. Laoufi, F. Bentahar, Desalin. Water Treat. 52 (2014) 1947-1955

[9]   D.A. Lambropoulou, I.K. Konstantinou, T.A. Albanis, A.R. Fernández-Alba, Chemosphere 83 (2011) 367-378

[10] A. Verma, M. Sheoran, A.P. Toor, Indian J. Chem. Technol. 20 (2013) 46-51

[11] D. Mijin, M. Savić, S. Perović, A. Smiljanić, O. Glavaški, M. Jovanović, S.D. Petrović, Desalination 249 (2009) 286-292

[12] B. Abramović, S. Kler, D. Šojić, M. Laušević, T. Radović, D.Vione, J. Hazard. Mater. 198 (2011) 123-132

[13] A. Nezamzadeh-Ejhieh, S. Moeinirad, Desalination 273 (2011) 248-257

[14] W.Y. Wang, Y. Ku, Colloids Surfaces, A 302 (2007) 261--268

[15] C. Minero, D. Vione, Appl. Catal., B 67 (2006) 257-269

[16] J. Wang, W. Sun, Z. Zhang, X. Zhang, R. Li, T. Ma, P. Zhang, Y. Li, J. Mol. Catal., A: Chem. 272 (2007) 84-90

[17] M. Qamar, M. Muneer, D. Bahnemann, J. Environ. Manage. 80 (2006) 99-106

[18] S. Chen, Y. Liu, Chemosphere 67 (2007) 1010-1017

[19] W. Chu, W.K. Choy, T.Y.So, J. Hazard. Mater. 141 (2007) 86-91

[20] M.R. Sohrabi, M. Davallo, M. Miri, Int. J. ChemTech. Res. 1 (2009) 446-451

[21] Y. Chen, K. Zhang, Y. Zuo, Sci. Total Environ. 463-464 (2013) 802-809

[22] L. Wei, C. Shifu, Z. Wei, Z. Sujuan, J. Hazard. Mater. 164 (2009) 154-160

[23] C. Wang, L. Zhu, M. Wei, P. Chen, G. Shan, Water Res. 46 (2012) 845-853

[24] D.E. Santiago, J. Araña, O. González-Díaz, M.E. Alemán-Dominguez, A.C. Acosta-Dacal, C. Fernandez-Rodríguez, J. Pérez-Peña, M. José, J.M. Doña-Rodríguez, Appl. Catal., B 156-157 (2014) 284-292

[25] A. Lair, C. Ferronato, J.M. Chovelon, J-M. Herrmann, J. Photochem. Photobiol., A 193 (2008) 193-203

[26] Y. Wang, K. Lu, C. Feng, J. Rare Earths 31 (2013) 360-365

[27] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Chemosphere 46 (2002) 1173-1181

[28] C. Hu, J.C. Yu, Z. Hao, P.K. Wong, Appl. Catal., B 46 (2003) 35-37

[29] N. Kashif, F. Ouyang, J. Environ. Sci. 21 (2009) 527-533

[30] S. Bouchonnet, S. Bourcier, Y. Souissi, C.Genty, M. Sablier, P. Roche, V. Boireau, V. Ingrand, J. Mass Spectrom. 47 (2012) 439-452

[31] Y. Souissi, S. Bourcier, S. Ait-Aissa, E. Maillot-Maréchal, S. Bouchonnet, C. Genty, M. Sablier, J. Chromatogr., A 1310 (2013) 98-112.

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NAUČNI RAD

FOTODEGRADACIJA DIMETANAMIDA-P U DEJONIZOVANOJ I PODZEMNOJ VODI

Proučavanje reakcije fotodegradacije herbicida dimetanamida-P, izvršeno je u prisustvu TiO_2 kao katalizatora i pod dejstvom UV zračenja, u dejonizovanoj i podzemnoj vodi. Ispitan je uticaj koncentracije elektron-akceptora (H_2O_2), "hvatača" $^{\bullet}OH$ radikala (C_2H_5OH) i šupljina (NaCl and Na_2SO_4), kao i uticaj pH sredine na brzinu reakcije fotodegradacije. Promena koncentracije dimetanamida-P praćena je pomoću HPLC. Nastajanje degradacionih proizvoda analizirano je pomoću HPLC/MS. Jonska hromatografija kao i metoda određivanja ukupnog organskog ugljenika primenjene su u cilju određivanja nivoa mineralizacije herbicida. HPLC analiza je pokazala da se u toku 90 min herbicid skoro potpuno uklanja u dejonizovanoj i podzemnoj vodi. Metodom određivanja ukupnog organskog ugljenika utvrđeno je da se dimetanamid-P mineralizije 64% u dejonizovanoj, a 50% u podzemnoj vodi. Jonska hromatografija je pokazala da pri degradaciji ispitivanog molekula nastaju hloridni, sulfatni i nitratni anjoni. HPLC/MS analiza ukazala je da pri degradaciji dolazi do raskidanja C-N veze (m/z 110,5), gubitka CH_3 grupe (m/z 262,1), kao i do eliminacije hlora i ketena, praćene premeštanjem i ciklizacijom (m/z 148,5).

Ključne reči: uticaj soli; jonska hromatografija; tečna hromatografija-elektronsprej masena spektrometrija; fotokataliza; titan-dioksid.