

TOXICOLOGY ASPECTS OF THE DECOMPOSITION OF DIURON BY ADVANCED OXIDATION PROCESSES

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Diuron is a phenylurea-based residual herbicide with toxic and endocrine disrupting effects. The aims of the present work were the comparison of the efficiency of various advanced oxidation processes, such as direct ultraviolet photolysis, ozonation, their combination, and heterogeneous photocatalysis from the point of view of the transformation rate of diuron, rate of mineralisation and dehalogenation, formation of aromatic intermediates, and ecotoxicological effects of the formed multicomponent solutions during the treatments. The initial rates of transformation of diuron are in the order of ozonation < heterogeneous photocatalysis < UV photolysis < combination of UV photolysis and ozonation. Each method provided similar tendencies in the decrease of the concentration of organically bound chlorines (AOX) since, until the diuron was completely degraded, the concentration of AOX decreased almost to zero in each case. However, only heterogeneous photocatalysis was found to be effective in terms of mineralisation. Ecotoxicological results showed that in each case, except for ozonation, the toxicity of the treated solutions changed through a maximum during the transformation of diuron. The maximum value was found to be lower in the case of heterogeneous photocatalysis. Thus, the formation and decomposition of by-products of relatively higher toxicity than diuron can be supposed. Our results confirmed that the amount of the formed (aromatic) intermediates, their quality and specific toxicity strongly depend on the applied processes.

Keywords: phenylurea, ozonation, ultraviolet photolysis, heterogeneous photocatalysis, *Daphnia magna*, *Vibrio fischeri*

1. Introduction

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, *Fig. 1*) is a phenylurea-type residual herbicide that is widely used throughout the world. It is registered in the European Union's pesticide database, in the U.S. EPA, and the Australian APVMA. Its use is strictly controlled due to its known toxic and presumed endocrine disrupting effects.

It has a broad spectrum of uses, mainly as a total herbicide in non-agricultural areas (roads and railways) for the pre- and post-emergence control of weed-type plants, but it also has plant protection purposes in the case of certain species (e.g. sugar cane and corn) [1]. Another application is as an antifouling agent, either in aquariums or in paint, to prevent algal growth on hulls of boats for example [2]. Diuron has a relatively low water solubility of 42 mg dm⁻³ at 25 °C. It is quite

persistent in soil with a typical half-life of 75.5 days and in water-sediment of 48 days [3]. Based on these data and other investigations [4], it can be concluded that this compound and its metabolites pollute the environment over an extended period of time, by leaching and run-off into ground and surface waters. This causes concerns regarding the ecosystem, mainly for aquatic plants (as the main method of action of the compound is to block photosynthesis), but also lower aquatic animals, and later presumably even more advanced organisms in the wild as well as the human body. Therefore, contaminated soils and waters have to be treated in an efficient and environmentally friendly

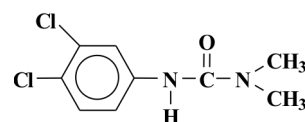


Figure 1. Schematic chemical structure of diuron (N-(3,4-dichlorophenyl)-N,N-dimethylurea).

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manner. For water treatment purposes advanced oxidation processes (AOPs) seem to be sensible choices as secondary treatments, as they are effective, environmentally friendly and economical methods for the elimination of pollutants such as pesticides. These treatments are based mainly on the generation of highly reactive hydroxyl radicals that can induce the degradation of organic matter. The transformation of the target substance can be induced by direct photolysis given that the target molecule is able to absorb irradiating light. It can also be induced by ozonation, which is used as an industrial scale supplementary water treatment method. Alternatively, heterogeneous photocatalysis, the Fenton-reaction or a combination of all the above can also be used [5–9]. Benítez et al. [10] investigated the transformation of phenylurea herbicides during the ozonation of natural waters and determined the reaction rate constants of diuron with both ozone ($16.5 \pm 0.6 \text{ mol dm}^{-3} \text{ s}^{-1}$) and the hydroxyl radical ($6.6 \pm 0.1 \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$).

During the oxidative transformation of diuron several aromatic by-products form. The main attack sites for hydroxyl radicals are the aromatic ring and the methyl group, leading to de-chlorinated or demethylated derivatives. In some cases, the reaction with the hydroxyl radical can lead to ring opening by-products. The most important intermediates are 1-(3,4-dichlorophenyl)-3-methylurea, N'-(3-chlorophenyl)-N,N-dimethylurea, 1-(3,4-dichlorophenyl)urea and 3,4-dichloroaniline [4].

Toxicological studies regarding diuron and its metabolites showed that the parent compound is usually less toxic than a multicomponent solution containing its metabolites; however, total toxicity decays with treatment time [4]. The mode of action of diuron is to block the Hill reaction during photosynthesis. Two of its metabolites, 1-(3,4-dichlorophenyl)-3-methyl-urea and N'-(3-chlorophenyl)-N,N-dimethylurea, retain this specific effect; however, the demethylation of diuron decreases its ability to bind to photosystem II [11].

The aim of the present work was the comparison of the efficiencies of various advanced oxidative processes, such as direct ultraviolet (UV) photolysis, ozonation, the combination of these and heterogeneous photocatalysis. This comparison was made regarding the rate of transformation of diuron, the rate of mineralisation and dehalogenation, the formation of aromatic intermediates and the ecotoxicological effects of the multicomponent solutions formed as a result of the treatments.

2. Experimental

2.1. The Light Sources and Experimental Apparatus

For ozonation and its combination treatment, the light source was a low-pressure mercury vapour lamp, which emits 254 nm ultraviolet (UV) and 185 nm vacuum ultraviolet (VUV) light (UV/VUV lamp). This lamp

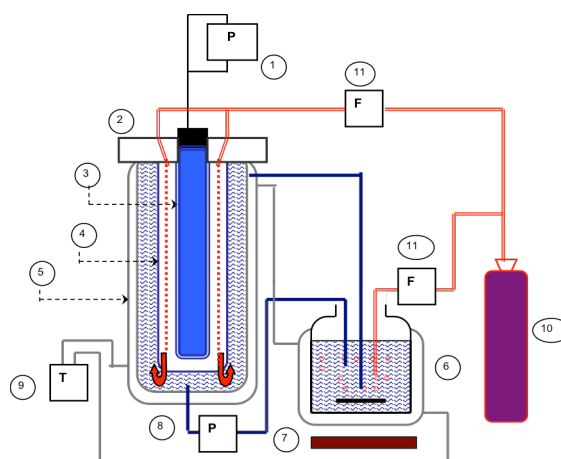


Figure 2. The experimental apparatus. 1: power supply; 2: teflon packing ring; 3: light source with sleeve; 4: envelope; 5: reactor; 6: reservoir; 7: magnetic stirrer; 8: pump; 9: thermostat; 10: air bottle; 11: flow meter from Ref. [13].

(GCL307T5VH/CELL, LightTech, Hungary) was covered with a high purity quartz sleeve, which transmits both 185 nm VUV and 254 nm UV light. Ozone was generated by the VUV photolysis of pure molecular oxygen in the gas phase. For direct UV photolysis, the sleeve of the same low-pressure mercury vapour lamp made of commercial quartz (GCL307T5/CELL, LightTech, Hungary), which transmits 254 nm UV light and absorbs 185 nm VUV light (UV lamp). Another light source, a specific fluorescent UV lamp (LighTech, Hungary) emitting between 300 and 400 nm (maximum intensity at 365 nm) was applied during heterogeneous photocatalysis.

The electric (15 W electric input) and geometric parameters (227 mm arc length, 307 mm length and 20.5 mm external diameter of the sleeves) of the different light sources corresponded to each other. The emitted photon fluxes were determined by ferrioxalate actinometry [12] and were found to be $8.10 \pm 0.65 \times 10^{-6} \text{ mol photon}(254\text{nm})\text{s}^{-1}$ for low-pressure mercury vapour lamps (UV/VUV and UV) and $1.20 (\pm 0.06) \times 10^{-5} \text{ mol photon}(300\text{--}400\text{nm})\text{s}^{-1}$ for the specific fluorescent lamp.

All experiments were performed in the same photoreactor (Fig.2). The light source, surrounded by an envelope was centred in a water-cooled, tubular glass reactor (340 mm length, 46 mm inner diameter). In the course of the measurements, envelopes (320 mm length and 28 mm internal diameter) made of various materials were used. The thermostat controlled ($25 \pm 0.5 \text{ }^\circ\text{C}$) solution of pesticide (500 cm^3 , $c_0 = 1.7 \times 10^{-4} \text{ mol dm}^{-3}$) was circulated ($375 \text{ cm}^3 \text{ min}^{-1}$) continuously and stirred with a magnetic stirrer bar in the reservoir. Before each experiment, air was bubbled through the solution at least for 10 min. The injection of the air was continued throughout the experiment. The kinetic measurements were initiated by switching on the light source.

Ozonation, UV photolysis or the combination of these methods could be applied by the careful selection of the light source and apparatus envelope. Ozonation

was performed using a UV/VUV lamp and perforated glass envelope. Oxygen flowed through the Teflon packing ring between the wall of the lamp and envelope, which separates the gas phase and aqueous solution, as shown in Fig.2. The ozone was generated by the direct VUV photolysis of molecular oxygen and bubbled through the perforated envelope into the solution.

Using a UV lamp and non-perforated quartz envelope, UV photolysis at 254 nm could be investigated. In the case of the combination of UV photolysis with ozonation, a perforated quartz envelope was used. When heterogeneous photocatalysis was applied, the specific fluorescent lamp and non-perforated glass envelope were used. Thus, the efficiency of these processes could be compared using the same energy consumption.

2.2. Analytical Methods and Materials

The concentration of diuron was determined using an HPLC system (Merck Hitachi L-7100 with L-4250 UV-Vis detector). The separation of aromatic compounds was achieved with an RP-18 column (Licrospher 100), using 60 % methanol and 40 % water as eluents, with a flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$. The quantification wavelength for UV detection was 210 nm.

Spectra (200 to 400 nm) of the samples during each degradation measurement were acquired on an Agilent 8453 spectrophotometer using 2 mm cuvettes. The concentration of ozone in the gas phase was measured using the same spectrophotometer in a flow cell at 254 nm ($\epsilon(254 \text{ nm}) = 2,952 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [14]), and was found to be $1.37 \times 10^{-5} \text{ M}$, using oxygen gas.

The adsorbable organic halogen (AOX) content was recorded using an AOX analyser, which consisted of an Analytik Jena multiX 2500 AOX sample unit and an APU2 sample preparation unit. Samples were adsorbed on active carbon, transferred into the AOX furnace and burned at $950 \text{ }^\circ\text{C}$ under an oxygen flow. Chlorine was quantified using a micro-coulometric method. The total organic carbon (TOC) content was determined using a multi N/C 3100 analyser (Analytik Jena).

The toxicity towards *Daphnia magna* was determined using Daphtoxkit FTM magna (MicroBioTests Inc.) tests according to the ISO Standard 6341. The ephippia were used after 72–90 h of hatching time at $21 \text{ }^\circ\text{C}$, applying 6000 lx bottom illumination and after 2 h of pre-nourishment. The zooplankton containing samples were incubated under the same conditions for 48 h, and 8–10 neonates were added to each sample. The number of the neonates was counted using a $3 \times 8 \times$ table-gooseneck magnifier (VWR). Mortality values were given as the percentage of the dead and/or immobilised neonates compared to their initial number.

The toxicity towards *Vibrio fischeri* luminescent bacteria was determined by measuring the natural light emission of these microorganisms using a HACH-LANGE LUMISTox 3000 luminometer. The inhibition of the light emission in the presence of the sample was determined against a non-toxic control. NaCl was added to each sample to obtain a 2 % solution. The samples

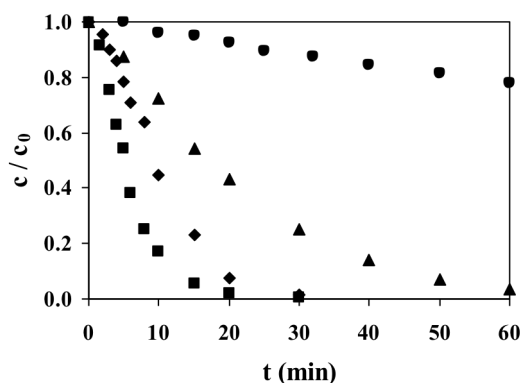


Figure 3. Kinetic curves of the transformation of diuron using ozonation (●), heterogeneous photocatalysis (□), direct UV photolysis (◆) and the combination of UV photolysis with ozonation (■).

were diluted by half with 1.0 mol dm^{-3} NaOH and 1.0 mol dm^{-3} HCl solutions to achieve a pH value of 7 ± 0.2 . Samples containing bacteria were incubated at $15 \text{ }^\circ\text{C}$ for 15 min before the toxicity measurements. Samples for the toxicity tests were taken at the same degradation degrees (0, 12, 25, 50, 75, 100, and above 100 %) of diuron for the treatments.

The decomposition of diuron, as characterised by the initial rate of transformation, which was obtained from linear regression fits to the actual concentration of pesticide versus the time of irradiation, up to 30 % of the concentration of the transformed target compound.

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, purity 98 %) was purchased from Sigma-Aldrich and used without further purification. Ultrapure water obtained from a Millipore Milli-Q System was utilised for the preparation of all stock solutions and HPLC eluents. HPLC-grade methanol was purchased from Hipersolv Chromanorm. The Degussa P25 photocatalyst ($49 \text{ m}^2 \text{ g}^{-1}$ surface area, 90:10 anatase/rutile ratio with 25.4 and 40 nm primary particle size, respectively) with 0.5 g dm^{-3} loading was used during the heterogeneous photocatalytic experiments.

3. Results and Discussion

3.1. The Rate of Transformation of Diuron

In the present work, the initial rate (r_0) of transformation of diuron was determined using various advanced oxidation processes. These can be ranked as ozonation ($r_0 = 1.0 \pm 0.05 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < heterogeneous photocatalysis ($r_0 = 7.9 \pm 0.3 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < UV photolysis ($r_0 = 13.6 \pm 1.2 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) < combination of UV photolysis and ozonation ($r_0 = 27.3 \pm 1.2 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$) (Fig.3).

The rate of direct photolytic transformation is determined by the molar absorbance of the target compound and quantum yield of the photolytic process. The absorption coefficient of diuron at the irradiation wavelength of the lamp (254 nm) was determined by using the Beer-Lambert law, and was found to be $\epsilon = 15,000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. Djebbar et al. [15] determined

the quantum yield of the photolysis of diuron at 254 nm to be 0.0125, insensitive to pH within the range 2–8.5. The apparent quantum yield of the photoinitiated transformation of diuron was calculated on the basis of the absorbed photon flow and initial transformation rate of the target molecule. In the present work, this value was found to be 0.008. At the applied initial concentration ($c_0 = 1.70 \times 10^{-4}$ M), the solution of diuron fully absorbed the emitted photons.

Ozonation was found to be the least effective method (Fig.3). In aqueous solutions, the decomposition of ozone yields reactive oxygen containing species such as hydroxyl radicals, which are generally a stronger oxidising agent than molecular ozone. The decomposition of ozone in an aqueous solution is initiated by hydroxide ions. At a neutral pH and/or under acidic conditions, molecular ozone should be the dominant oxidant species. During the ozonation of diuron the pH strongly decreased from 8.3 to 4.1, consequently, ozone reacts with diuron mainly as molecular ozone and the formation of hydroxyl radicals is irrelevant. Referring to the reaction mechanisms, molecular ozone can react with organic substrates either through cycloaddition to unsaturated bonds or in electrophilic and nucleophilic reactions [16]. Nucleophilic reactions occur at molecular sites exhibiting an electron deficit and, more frequently, on carbons carrying electron-withdrawing groups, such as chlorine.

Based on the values of the initial rate of decomposition, it can be concluded that, by applying the combination of UV photolysis and ozonation, the synergistic effect occurred. The addition of ozone, although in a relatively low concentration, caused the rate of decomposition to double ($r_0(254 \text{ nm} / \text{O}_3) / r_0(254 \text{ nm}) = 2.0$) (Fig.3). Both UV photolysis and ozonation are quite selective methods in the oxidative transformation of organic substances. Their combination via UV photolysis of ozone itself can produce reactive species, mainly hydroxyl radicals. Consequently, the combination of UV photolysis with ozonation generally results in a less selective and more effective method for the oxidative transformation of organic substances. It has to be mentioned, that the relative contribution of direct photolysis to the transformation probably remains high, because of the high molar absorbance of diuron and the relatively low concentration of ozone. Under the employed experimental conditions, light absorption of ozone was negligible compared to that of diuron.

In the present work, the light emitted by the fluorescent lamp was suitable for the excitation of TiO_2 . The direct photolysis of the compound was excluded by the chosen experimental conditions. This was controlled during the measurements. Upon irradiation in the near UV range, electron hole pairs are formed in the TiO_2 nanoparticles. These charges may reach the surface of the catalyst particle, and undergo redox reactions with substrates or dissolved molecular oxygen, producing highly reactive species such as hydroxyl radicals and hydroperoxyl or superoxide radicals, which can efficiently oxidise the organic pollutants. Besides, contaminants adsorbed on the surface of the catalyst

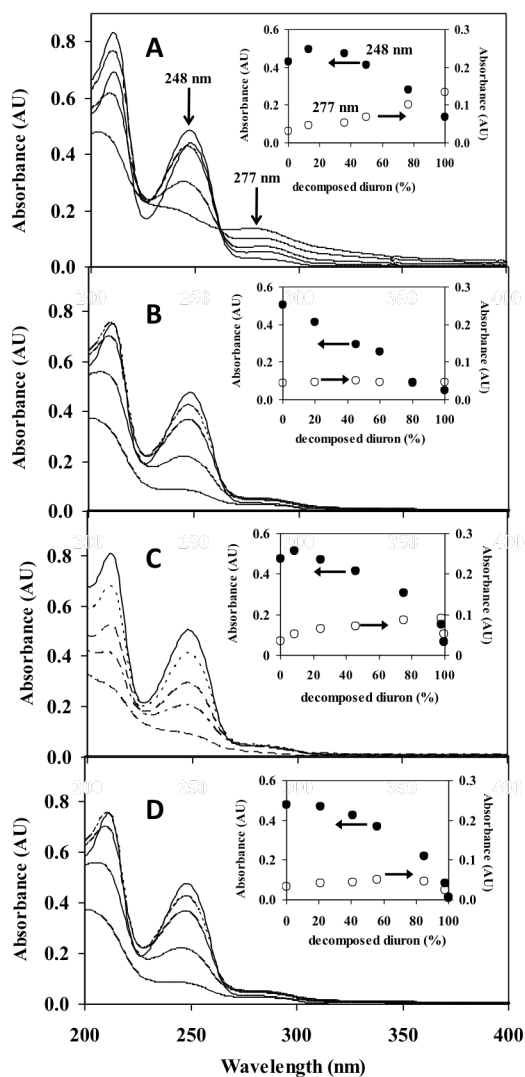


Figure 4. Spectra of the samples treated with UV photolysis (a), ozonation (b), combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 25, 50, 75 and 100 % decomposition of diuron (inserted figures show the absorbances at 248 nm (●) and 277 nm (○) versus the decomposed diuron).

particles can directly react with the photochemically formed holes and electrons, promoting the processes of mineralisation. Comparing the efficiency of heterogeneous photocatalysis to direct photolysis, this method is less efficient, but much more efficient than ozonation in the case of the transformation of diuron (Fig.3).

3.2. Spectrophotometric Measurements

Spectrophotometric measurements were carried out on each treatment experiment. The spectra of solutions show that the absorbance at 277 nm increased during the decomposition of diuron while the absorbance at 248 nm changed according to the maximum curves in UV irradiated solutions (Fig.4a). It has to be mentioned, that the absorbance at 277 nm decreased slowly after the decomposition of diuron. This suggests that aromatic

intermediates accumulated and probably decomposed during the UV initiated transformation.

The maximum value of the absorbance at 277 nm was found to be much higher in UV irradiated solutions (0.145) (Fig.4a) than in the case of the combination of ozonation with UV photolysis (0.09) (Fig.4c). This suggests that the addition of ozone strongly enhanced the rate of formation and decomposition of these intermediates and consequently, hindered their accumulation, most likely due to radical based reactions. The time dependence of the relative absorption at 277 nm suggests that not only the formation, but also the decomposition of these aromatic intermediates took place. This latter process was partly completed in parallel with the transformation of the parent compound, and partly after its transformation. The colour of the aqueous solution of diuron changed from colourless to intensive yellow-pink when UV photolysis was applied. At the same time, when the combination of UV photolysis with ozonation was applied, the change in colour was less intensive. Each solution became colourless after the decomposition of diuron. Using ozonation (Fig.4b) or heterogeneous photocatalysis (Fig.4d) neither the change in colour of the solution, nor increase in absorbance at 277 nm was observed. This suggests that the coloured aromatic intermediates were most probably formed mainly during the direct UV photolysis of diuron. These results and observations also suggest that the amount and quality of the aromatic intermediates strongly depend on the applied process.

3.3. Dehalogenation and Mineralisation

UV photolysis, ozonation, the combination of these and heterogeneous photocatalysis provided similar tendencies with respect to the decrease in concentration of adsorbable organically bound chlorines (AOX), since in each case, until the 100 % transformation of diuron was achieved, the concentration of AOX decreased by almost 100 % (Fig.5a). This means that not only the pesticide itself, but the formed halogenated by-products were also de-chlorinated simultaneously within the timeframe of transformation of the parent substance. It has to be mentioned, that the rate of dechlorination was higher in the case of UV photolysis than heterogeneous photocatalysis, mainly at the beginning of the treatment. Direct UV photolysis is a quite selective method for the transformation of organic substances and can be effective for the transformation of compounds, which highly absorb at 254 nm (such as diuron and probably its aromatic intermediates), mainly by the dissociation of the carbon-halogen bond. On the other hand, in the case of heterogeneous photocatalysis, adsorption has an important role. Competitive adsorption can occur between the aromatic compounds containing chlorine atom(s) and the formed intermediates, which do not contain chlorine atom, and exhibit better adsorptivity (mainly carboxylic acids). Consequently, the formation of these intermediates and their adsorption on the

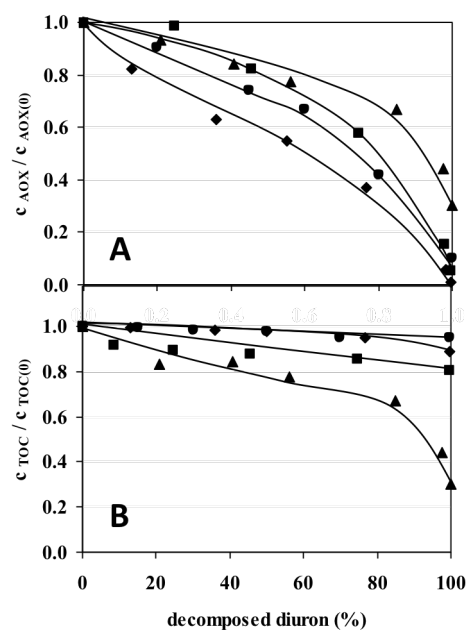


Figure 5. Kinetic curves of the transformation of diuron using ozonation (●), heterogeneous photocatalysis (□), direct UV photolysis (◆) and the combination of UV photolysis with ozonation (■).

surface of the photocatalyst can cause a relatively slow decrease in the rate of dechlorination (Fig.5a).

Ozonation is a quite selective method for the transformation of organic substances, similar to direct UV photolysis. These methods are generally not effective in terms of mineralisation, as also observed in this work (Fig.5b). In the case of the combination of these methods the TOC content slightly decreased, most likely because of the hydroxyl radical based reactions. In the case of heterogeneous photocatalysis, the rate of mineralisation was very low at the beginning, but the TOC decreased rapidly in the final stage of decomposition of diuron (Fig.5b). Compared to UV photolysis and ozonation, heterogeneous photocatalysis is a less selective method and generally results in the transformation and, in most cases, the mineralisation of a large variety of organic substances.

However, the transformation of compounds takes place on the surface of TiO_2 particles, thus adsorption has a crucial role in this case, as mentioned previously. It is probable that the superior adsorptivity of aliphatic intermediates (mainly carboxylic acids) is the reason why mineralisation takes place in parallel with the transformation of parent compounds. This explanation is in agreement with the observation that the rate of the change in concentration of AOX increased when mineralisation became dominant (Fig.5).

3.4. Ecotoxicological Measurements

The results obtained from both Daphtoxkit FTM and *Vibrio fischeri* luminescence inhibitory tests showed that the toxicity of the treated solutions changed through a maximum value within the time frame of transformation of diuron in solutions irradiated with 254 nm UV light (Figs.6a and 7a). Consequently, the

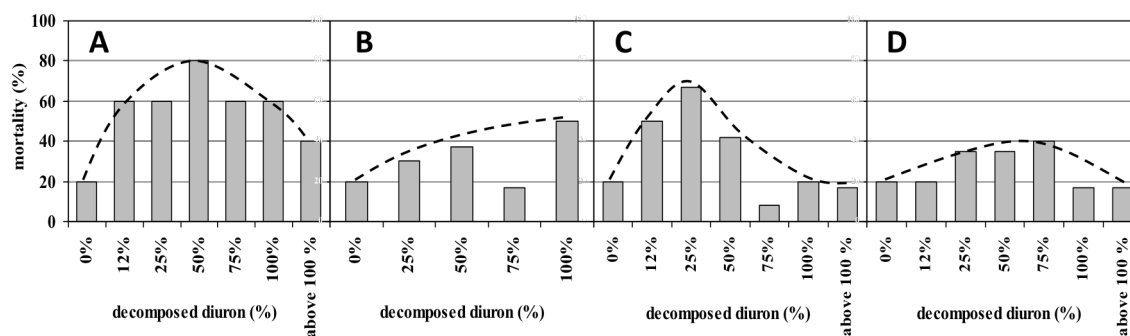


Figure 6. Mortality of *Daphnia magna* after UV photolysis (a), ozonation (b), the combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 12, 25, 50, 75, 100 % and above 100 % (samples taken 10 minutes after total decomposition) decomposition of diuron.

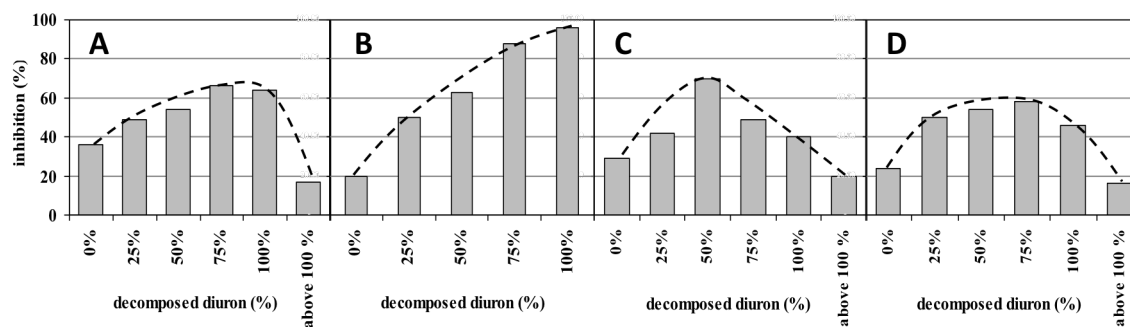


Figure 7. Inhibition values for *Vibrio fischeri* after UV photolysis (a), ozonation (b), the combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d) at 0, 12, 25, 50, 75, 100 % and above 100 % (samples taken 10 minutes after total decomposition) decomposition of diuron.

formation and decomposition of by-products exhibiting relatively higher toxicities than expected from diuron.

During ozonation, both the mortality and inhibitory effect increased, which can be explained by the formation and accumulation of intermediates more toxic than the parent compound (Figs.6b and 7b). The tendencies of mortality and the inhibitory effect were similar, although mortality increased slightly, and the inhibitory effect increased strongly during the transformation of diuron. It can be supposed, that *Vibrio fischeri* is more sensitive to the presence of the intermediates formed due to the reaction of molecular ozone with diuron, which can be the reason for this observation.

In the case of the combination of UV photolysis with ozonation, the mortality and inhibitory effect changed through maxima (Figs.6c and 7c), in a similar way to direct UV photolysis. However, in this case the maxima were reached at 25 % and 50 % decomposition of diuron (Figs.6c and 7c), while during UV photolysis the maxima were reached at 50 % and 75 % decomposition of diuron (Figs.6a and 7a).

Using heterogeneous photocatalysis, the mortality and inhibitory effect changed also through maxima (Figs.6d and 7d). At the same time, it has to be mentioned, that in this case, the values of the maxima were found to be lower than those determined in the case of UV photolysis and its combination with ozonation, mainly in the case of results obtained using the Daphtoxkit FTM test. The mortality using heterogeneous photocatalysis did not reach 40 %, while in the case of UV photolysis and its combination with UV photolysis it exceeded 60 %. This confirms that the amount of the aromatic intermediates was less, and/or

their specific toxicity was lower than in the case of UV photolysis and its combination with ozonation.

At this point, a correlation can be established between the results of spectrophotometric measurements and ecotoxicological tests. In the case of UV photolysis, the formation and accumulation of aromatic intermediates were supposed, while in the case of the combined method, their amount was likely to be lower. At the same time, in the case of heterogeneous photocatalysis, their formation was less favourable than in the presence of 254 nm UV light. These observations, together with the results of the ecotoxicological tests, suggest that the toxic intermediates are most likely aromatic by-products.

4. Conclusion

In this work, various advanced oxidation processes, such as UV photolysis at 254 nm, ozonation, their combination and heterogeneous photocatalysis were investigated and compared regarding the oxidative transformation of diuron. The initial rates of transformation were determined at the same electric energy input and exhibited the following order: ozonation < heterogeneous photocatalysis < UV photolysis < combination of UV photolysis and ozonation.

The results obtained from spectrophotometric measurements suggested that aromatic intermediates accumulated during the UV initiated transformation of diuron. The addition of ozone of relatively low concentration strongly enhanced the rate of formation and/or decomposition of these intermediates. Using ozonation or heterogeneous photocatalysis, the amount

of the formed aromatic intermediates was likely to be lower.

UV photolysis, ozonation, their combination and heterogeneous photocatalysis provided similar tendencies in the decrease of the concentration of adsorbable organically bound chlorines (AOX) since, in each case, until the 100% degradation of diuron was achieved, the concentration of AOX decreased by almost 100%. On the other hand, only heterogeneous photocatalysis was found to be effective in terms of mineralisation during the decomposition of diuron. In this case, the rate of mineralisation was low at the beginning, but the total organic carbon content decreased rapidly in the final stage of the decomposition of diuron.

Ecotoxicological measurements were carried out with both Daphtoxkit FTM and *Vibrio fischeri* luminescence inhibitory tests. The results showed that the toxicity of the treated solutions changed through a maximum curve within the time of transformation of diuron in each case, except for with ozonation. Thus, the formation and decomposition of by-products, having relatively higher toxicity than diuron, can be supposed. Using heterogeneous photocatalysis, the mortality and inhibitory effect also changed through maxima, but the values of the maxima were found to be lower than that determined in the case of UV photolysis and its combination with ozonation. Our observations and results confirmed that the aromatic intermediates formed, their quantity, and specific toxicity strongly depend on the applied process.

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