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Comparison of advanced oxidation processes in the decomposition of diuron and monuron – efficiency, intermediates, electrical energy per order and the effect of various matrices

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The decomposition of diuron and monuron, widely used phenylurea pesticides, *via* UV-induced photolysis (UV_{254nm}), ozonation (O_3), their combination (UV_{254nm}/O_3) and heterogeneous photocatalysis (TiO_2/UV) were investigated and compared. The UV_{254nm}/O_3 and TiO_2/UV methods proved to be effective from the aspects of both the transformation and the mineralization. The transformation rates changed in the order: $O_3 \ll TiO_2/UV < UV_{254nm} < UV_{254nm}/O_3$. Comparing the electric energy per order (E_{EO}^c) values calculated for the transformation, the most efficient method was UV_{254nm}/O_3. However, the lowest E_{EO}^{TOC} value calculated for the mineralization was obtained using TiO_2/UV. Identification of the aromatic intermediates revealed that the first step in the decomposition involves transformation of the aliphatic chain, in parallel with dechlorination and hydroxylation of the aromatic ring. The amount and quality of the intermediates formed depends strongly on the method applied. Matrices such as natural waters (from the River Tisza and thermal water from Kistelek) and inorganic salts exert significant effect on the transformation rates only in the case of TiO_2/UV. Humic acids behave as "light filter" and consequently decrease the rate of photoinitiated transformation using UV_{254nm} and UV_{254nm}/O_3 methods, whereas they slightly enhance the effect of ozonation, most likely because humic acids and/or their intermediates promote the decomposition of ozone and increase the radical concentration. Regarding this parameter, the most sensitive method was heterogeneous photocatalysis, most likely because the well adsorbed humic acid strongly inhibits the formation of hydroxyl radical.

Water impact

Pollution of the environment by pesticide is a complex problem with widespread ecological consequences. The present study aimed to investigate and compare the UV photolysis, ozonation, their combination and heterogeneous photocatalysis for the transformation, mineralization and dechlorination of diuron and monuron. The study partly focused on the investigations of the effects of the matrices on the photooxidation of the herbicides in different types of waters, such as river and thermal waters.

1. Introduction

Pollution of the environment with pesticides is a complex problem with widespread ecological consequences. The contamination of surface waters and waste waters by pesticide residues, mainly resulting from agricultural activities and pesticide manufacturing plants has increased significantly during recent decades. The water supply industry is facing a difficult problem, since pesticides have been detected not only in waste waters[1] and natural waters,[2–5] but also in drinking water,[6–8] and are probably responsible for a number of health problems.[9] Although the amount detected in drinking water is generally lower than the limits set by the European Union, wastewaters from agricultural and/or industrial activities often contain excessively high levels of contamination.

Phenylurea derivatives, such as diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), and monuron (3-(4-chlorophenyl)-1,1-dimethylurea) (Fig. 1) are reported to be amongst the most

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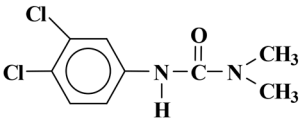
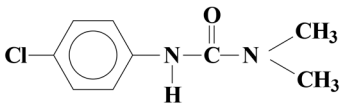


Diuron (*3*-(3,4-dichlorophenyl)-*1,1*-dimethylurea)



Monuron (*3*-4-chlorophenyl)-*1,1*-dimethylurea)

Fig. 1 Molecular formulae of diuron and monuron.

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widely used herbicides in agriculture. Both have a broad spectrum of uses, mainly as total herbicides in non-agricultural areas (roads and railways) for the pre- and post-emergence control of weeds, but also for plant protection purposes in the case of certain species (*e.g.* sugar cane and maize).[10]

The widely investigated advanced oxidation processes (AOPs), which are based on the generation of various reactive radicals, can offer a solution for the treatment of waters contaminated with pesticides, including phenylurea herbicides.[11,12] Numerous investigations have focused on the decomposition of these target substances using conventional water treatment methods,[13,14] membrane technologies[15] and various AOPs,[16] including direct UV photolysis,[17–20] ozonation,[21–24] heterogeneous photocatalysis,[18,25–27] and/or combinations of these methods. Considerable effort has been devoted to research involving ozone in association with other oxidation processes,[28–31] in which non-selective hydroxyl radical oxidation is believed to play a key role in the mineralization of organic substances. Other studies have focused on the identification of the main by-products, and proposals have been put forward relating to the reaction mechanisms.[18,21,32–34] Investigations of the toxicity of the intermediates[33,35] have revealed that this often exceeds that of the parent compounds.

AOPs based on light emission can be used successfully as post-treatment process when the aim is the decomposition of organic compounds which cannot be eliminated easily *via* biological processes. Post treatment is important when these persistent compounds are toxic, carcinogen or endocrine disrupting substances. The application of AOPs might be limited for the treatment of multicomponent industrial wastewater because of the negative effect of the matrix. The matrices can contain various types of components (mainly dissolved inorganic salts and natural organic matter (NOM)), which are able to affect the transformation of target substances by several possible pathways.[17,20,24,36] The main components of NOM are humic substances. A fraction of humic substances, humic acids (HA) have been known to have several effects on drinking water, like aesthetic problems (colour, smell, taste). They are one of the main precursor materials of disinfection by-products, forming further harmful by-products during chlorination. Moreover they are able to increase the potential of the trihalomethanes (THM) formation after chlorination of treated waters.[37] Thus, their removal requires additional chemical treatment.[38] The formation of complexes with metals and organic pollutants may also have significant environmental importance.[39]

During AOP-treatment of humic acid containing waters, the effect of these substances depends on both the method and reaction parameters. In the case of UV light based technology, due to the wide absorption spectrum of humic acids, they can act as a light filter and reduce the light intensity absorbed by the target substances, due to competitive light absorption. They are able to increase the reactivity of various substances through the complex formation and/or partly due to the photosensitization.[40] Humic acids exert an acceleration effect on the hydrolysis rate of pesticides too.[41] In the case of ozonation, organic compounds may initiate the degradation of ozone resulting in increased hydroxyl radical formation and degradation performance.[42] Beside this, humic acids can act as a radical scavenger and cause negative effect on the efficiency of methods based on radical formation.

In the case of heterogeneous photocatalysis the reactions take place on the surface of the photocatalyst, consequently adsorption has a crucial role.[43] Moreover, the presence of various inorganic ions and the ionic strength of the matrix can change the surface potential and the formation rate of hydroxyl radical, too.[44] As humic acids have amphiphil properties, they show significant adsorption on the surface of TiO_2 photocatalyst,[45] changing its surface properties.[46] The adsorbed humic acids cause a negative surface charge, and their adsorption is highly dependent on the pH and ionic strength of the suspension. The change of the surface properties has effect on the rate of aggregation and the size of aggregates.[45,47] Consequently, the complex reaction mechanisms, like the adsorption of target pollutants, the formation of reactive species and the relative contribution of the radical based reaction and direct charge transfer depend strongly on this reaction parameter.

Dissolved inorganic salts may also have an important effect on the degradation of organic pollutants, as they may act as radical transfers *via* certain ions, like HCO_3^-, NO_2^-, PO_4^{3-}. Their effect can be especially significant in the case of heterogeneous photocatalysis,[48–50] as their adsorption on the catalyst surface and the change in the ionic strength of the suspension can significantly change the reaction rates and mechanisms. It has been reported, that inorganic anions inhibit the adsorption of certain organic pollutants.[51] Under visible light irradiation, humic acids were able to act as a sensitizer and inject electrons to the conduction band of TiO_2, and subsequently transformed and decolorized through a series of electron transfer reactions.[52]

The present study focuses on the comparison of the efficiencies of four different AOPs (UV-photolysis, ozonation,

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their combination, and heterogeneous photocatalysis) in the transformation of two hazardous phenylurea herbicides, monuron and diuron using various matrices. Previously authors presented a publication[53] about the efficiency of several combinations of various AOPs in the transformation of diuron, monuron and fenuron in distilled water. As that was mentioned previously, the application of AOPs might be limited significantly *via* presence of various component of the matrix. The present work focuses on the investigation of the effect inorganic salts and humic acids. The measurements are performed in distilled water spiked with NaCl, $NaHCO_3$, $NaNO_3$, and humic acid and in two other matrices, like river water and thermal water. Moreover, the efficiency of applied methods is compared not only based the transformation, mineralization, and dehalogenation rate, but also on the electric energy consumption (electric energy per order). The aromatic intermediates formed during the oxidative transformation are identified, too.

2. Materials and methods

2.1. Experimental parameters

For the UV photolysis, a low-pressure mercury vapour lamp (GCL307T5VH/CELL, LightTech, Hungary, 227 mm arc length) with main output at 254 nm, but with 6% of the total intensity of irradiation at 185 nm, was applied as light source, with a high-purity silica sleeve which transmits both 254 and 185 nm light. This lamp can be applied to generate ozone from oxygen in the gas phase due to the 185 nm light. The electric input of the lamp is 15 W and the effective power output in the UV range is 4.0 W. The photon flow emitted by the light source was determined by potassium ferrioxalate actinometry[54] to be $8.10(\pm0.65) \times 10^{-6}$ Einstein per s. The fluorescent UV lamp used for photocatalytic experiments had the same electric input and geometric parameters, and emits photons between 300 and 400 nm wavelength, with a maximum at 365 nm. The photon flux is $1.2(\pm0.06) \times 10^{-5}$ Einstein per s.

The UV lamps with their envelope (320 mm long and 28 mm in internal diameter) were centered in a water-cooled, tubular glass reactor (length 340 mm, inner diameter 46 mm). Oxygen or air (855 ml min^{-1}) was led through the Teflon packing ring between the wall of the lamp and the envelope, which separates the gas phase and the aqueous solution.[55]

The formation of ozone from oxygen in the gas phase is due to the absorption of 185 nm light. The ozone-containing oxygen or air was bubbled through the perforated envelope into the aqueous solution. Depending on the construction of the envelope and the light source, ozonation (low-pressure mercury vapour lamp and perforated glass envelope), UV photolysis (low-pressure mercury vapour lamp and non-perforated quartz envelope) their combination (combined method, low-pressure mercury vapour lamp and perforated quartz envelope), and heterogeneous photocatalysis (fluorescent UV lamp and non-perforated quartz envelope) were investigated. Thus, the efficiency of these processes could be compared at the same energy consumption.

In the photocatalytic experiments the photocatalyst was TiO_2 Aeroxide P25 commercialized by Evonik Industries (73–85% anatase, 14–17% rutile, surface area: a^S_{BET} = 35–65 $m^2\ g^{-1}$, particle size: $d_{anatáz} \sim 25$ nm, $d_{rutil} \sim 40$ nm), which was suspended by sonication. The suspension contained 1.0 g dm^{-3} TiO_2 in each case. The selection of the TiO_2 concentration is based on data presented in the previous paper of the same authors.[53] The transformation rate of target substances reached maximum at 0.5 g dm^{-3} TiO_2 and slightly decreased when 1.0 g dm^{-3} TiO_2 load was applied. However, 1.0 g dm^{-3} TiO_2 load was chosen because at this concentration the photons must be fully absorbed by the irradiated layer of the suspension. The treated samples were centrifuged and filtered before analysis.

The thermostated (25 ± 0.5 °C) aqueous solution (500 ml) was circulated (375 ml min^{-1}) continuously and stirred with a magnetic stirrer bar in the reservoir. Before each experiment, nitrogen, air or oxygen was bubbled through the solution for at least 10 min. The kinetic measurements were started by switching on the light source.

2.2. Methods

The concentration of diuron or monuron was measured with an Agilent 1100 type HPLC equipped with diode array detector (DAD) and a Lichrospher RP 18 column, methanol/water (v/v = 50/50) mixture serving as eluent. The flow rate was 1.0 ml min^{-1}. Samples were analysed at 210 nm and at the absorption maximum of diuron and monuron (248 nm and 245 nm, respectively). The organic acids formed during the irradiation were determined by using a GROM-RESIN ZH column with 0.01 M sulfuric acid as eluent in the same HPLC system (λ = 206 nm). Calibrations were carried out by using standard solutions of known concentrations. The determination of monuron and diuron concentration was based on the linear regression of the calibration curve (R^2 = 0.995) presenting the integrated peak areas of the chromatograms measured by HPLC-DAD. Kinetic curves show the ratio of the actual and the initial concentrations (c/c_0, $c_0 = 1.7 \times 10^{-4}$ mol dm^{-3}). The transformation of herbicides were characterized by the initial rate (r_0), which was obtained from linear regression fits of the decay curves corresponding to 20% of transformation.

The intermediates were identified by HPLC-MS (Agilent 1200) after preconcentration by means of solid-phase extraction, on octadecyl cartridges (7020-01 from J. T. Baker). The solid phase extraction was achieved according to the modified method of Shankar *et al.*[56] The cartridges were first conditioned with 5.0 ml methanol and 5.0 ml water. Typically, 200 ml of treated diuron or monuron solution were percolated at 5 ml min^{-1} and the cartridge was completely dried by using a Baker spe-12G apparatus (J. T. Baker) connected to a vacuum system. After rising with 1.0 ml

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distilled water the phase was dried for 15 min under a nitrogen flow and subsequently eluted with 2 × 2.0 ml methanol. LC-atmospheric pressure chemical ionization-MS (LC-APCI-MS) was used in the negative ion mode of operation, with a 90 V fragmentor.

The concentration of the sum of the H_2O_2, methyl- and ethyl-hydroperoxides was measured by a modified literature method[57,58] involving the horseradish peroxidase (Sigma)-catalysed transformation of leuco crystal violet (Aldrich, Hungary) in tartrate buffer (pH = 4.0). The absorbance of the solution was measured at 592 nm with a Hewlett-Packard (HP8452A) diode array spectrophotometer. The molar absorptivity of the crystal violet formed from the leuco crystal violet was 75 600 M^{-1} cm^{-1}.

The concentration of ozone in the gas phase was measured with the same spectrophotometer *via* the absorbance at 254 nm (ε_{254nm} = 2952 M^{-1} s^{-1}),[59] and was found to be 1.37 × 10^{-5} M when oxygen was used and 4.04 × 10^{-6} M on the use of air. The concentration of dissolved ozone in the aqueous phase was determined by the indigo method[60,61] in phosphate-buffered solution.

The absorption spectra of the treated samples were detected by spectrophotometry. The adsorption of monuron, diuron and humic acid on the TiO_2 surface was determined by the same method. The suspensions were left in dark and stirred until the adsorption equilibrium.

The total organic carbon (TOC) and adsorbable organic halogens (AOX) concentration of 100 μl sample solutions were measured with Euroglass 1200 TOC apparatus.

Diuron and monuron were from Sigma (98%). $NaHCO_3$ (Riedel-de Haën, 99.7%), NaCl (VWR, ≥99%) and $NaNO_3$ (VWR, 99.2%) were used in 1 × 10^{-2} M concentration to investigate the effects of individual inorganic salts on the degradation processes. For the humic acid experiments sodium-humate was used (Aldrich, tech. grade). The effects of the matrix were investigated through comparison of the kinetic curves measured in Milli-Q bidistilled water, in filtered water from the River Tisza (sampled in Szeged, Hungary) and in thermal water (sampled in Kistelek, Hungary), containing a relatively high total mineral content (1390 mg dm^{-3}) and $NaHCO_3$ concentration (360 mg dm^{-3}).

2.3. Calculation of electrical energy per order (E_{EO})

The electrical energy per order (E_{EO}) is a useful concept for comparing the performance of UV-based AOPs for the degradation of organic contaminants. The parameter was introduced in 2001 by Bolton, *et al.* in a report published by the IUPAC Photochemistry Commission.[62] When choosing the best method for wastewater treatment, the economic factor is often seen as the most relevant. Calculation is based on the amount of electric energy required to decrease the concentration of pollutant by one order of magnitude. The effectiveness of each process was evaluated based on these E_{EO} values, reflecting the electric energy in kilowatt hours [kW h] required to treat 1 m^3 of contaminated water. E_{EO} values [kW h m^{-3} per order] are calculated for a batch system, using the following formula:

$$E_{EO}^{c} = \frac{P \times t \times 1000}{V \times \lg(c_i/c_f)} \quad \text{and} \quad E_{EO}^{TOC} = \frac{P \times t \times 1000}{V \times \lg(TOC_i/TOC_f)}$$

where P is the rated power [kW] of the AOP system, V is the volume [dm^3] of the treated water, t [h] is the time required to decrease the concentration of pollutant (c_i and c_f are the initial and final concentrations of monuron [mol dm^{-3}], while TOC_i and TOC_f are the initial and final TOC content [mol dm^{-3}]) by one order of magnitude, and lg is the symbol for the decadic logarithm. In the present work the power (P) was calculated by the electric power required for the UV lamp (15 W). Ozone was generated by 185 nm VUV light and did not required excess of electrical energy.

3. Results and discussion

3.1. Transformation rates of diuron and monuron

UV photolysis proved to be efficient for the transformation of the target substances (Fig. 2a and 3a and Table 1) because of the high molar absorptivities of diuron (16 050 M^{-1} cm^{-1}) and monuron (13 990 M^{-1} cm^{-1}), determined at 254 nm. The data obtained are in accordance with the data reported by Sanches *et al.*[20] and Schöler.[63] In the case of photoionization, dissolved molecular oxygen generally enhances the rate of transformation because of its reaction with the hydrated electron ($k(O_2 + e_{aq}^- \rightarrow O_2^{\bullet-})$ = 1.9 × 10^{10} M^{-1} s^{-1}).[64] This reaction inhibits the recombination of the hydrated electron and the radical ion formed from the organic substance, and consequently dissolved oxygen causes higher rate of transformation.[65] In our cases however, dissolved oxygen has no effect on the rates of transformation (Fig. 3a and d), which suggests that photoionization is insignificant in the UV-initiated transformation of both diuron and monuron. The rates of transformation of monuron (5.29 × 10^{-7} M s^{-1} (oxygen); 4.66 × 10^{-7} M s^{-1} (air); 4.83 × 10^{-7} mol dm^{-3} s^{-1} (nitrogen)) were approximately 2.3–3.3-fold those of diuron (1.76 × 10^{-7} M s^{-1} (oxygen); 1.77 × 10^{-7} M s^{-1} (air); 2.14 × 10^{-7} M s^{-1} (nitrogen)), in spite of the molar absorptivity of diuron exceeding that of monuron. This can be explained by the two times higher quantum yield of the direct photo-initiated transformation of monuron (0.05)[63] than that of diuron (0.019).[17,20]

In the case of ozonation, the concentration of ozone in the gas phase was 1.37 × 10^{-5} M and 4.04 × 10^{-6} mol dm^{-3}, and that of dissolved ozone in pure Milli-Q bidistilled water was 2.3 × 10^{-6} M and 1.04 × 10^{-6} M when oxygen or air was used, respectively. Consequently, on the use of oxygen, the rate of degradation were about 2 times higher (7.0 × 10^{-9} M s^{-1} (diuron); 8.7 × 10^{-9} M s^{-1} (monuron)) than in the case of air (3.2 × 10^{-9} M s^{-1} (diuron); 4.9 × 10^{-9} M s^{-1} (monuron)) (Fig. 2b and 3b and Table 1). In the presence of ozone, transformation of the target substances can be initiated by reaction with molecular ozone or by reaction with radicals formed *via* the decomposition of ozone. During the

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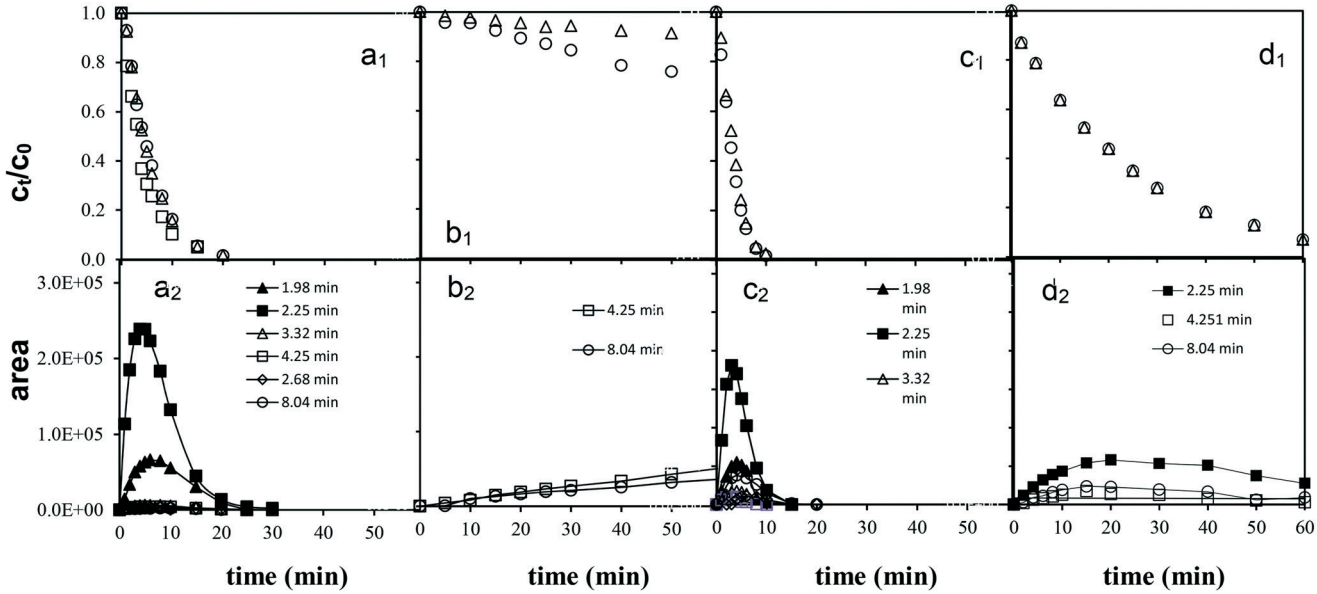

Fig. 2 Relative concentration of diuron (a_1, b_1, c_1, where c_0 is the initial concentration (t = 0 min), while c is the concentration of the treated solution (t)) and the integrated area of the peak of the intermediates (detected by HPLC-DAD), on the use of air (a_2, b_2, c_2; retention time is presented as legend) *versus* duration of treatment, using 1.7×10^{-4} M initial concentration ○: oxygen; △: air; □: nitrogen; a: UV photolysis; b: ozonation; c: combination of UV photolysis and ozonation; d: heterogeneous photocatalysis.

transformation of these compounds, the pH decreased from 6.9 to 3.8 and from 8.3 to 4.1 in the case of monuron and diuron, respectively. The decomposition of ozone in aqueous solution is initiated by the hydroxide ion, but under neutral and acidic conditions a direct reaction with molecular ozone is more expected. The negligible effect of methanol (1.0×10^{-2} M) as hydroxyl radical scavenger also confirmed that, the relative contribution of radical based reaction to the transformation of these pesticides is not considerable. The phenylurea-derived pesticides react slowly or moderately fast with ozone. Moreover the Cl attached to the aromatic ring reduces its reactivity toward the electrophilic attack of O_3 to the aromatic ring. The second-order rate constant for the reaction between diuron and ozone has been reported to be in the range 13.3–16.3 M s^{-1}.[23,24,66] This may be one of the reasons why the rates of transformation during ozonation were found to be more than one magnitude lower than those of direct UV photolysis. Moreover, the ozone was produced *via*

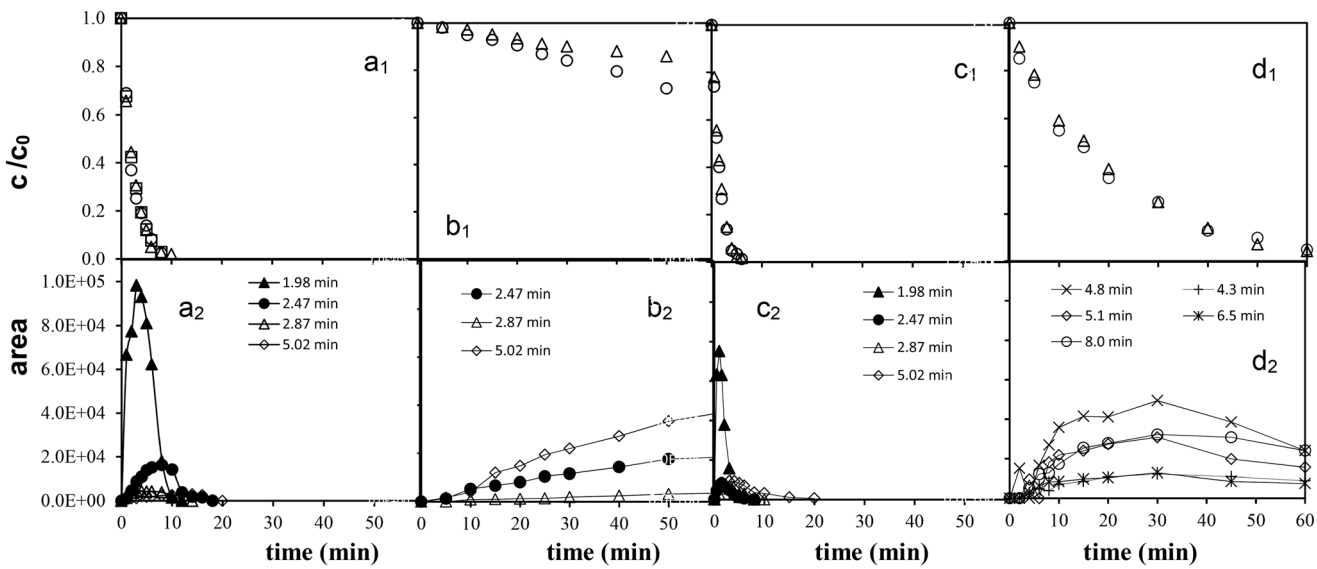

Fig. 3 Relative concentration of monuron (a_1, b_1, c_1, where c_0 is the initial concentration (t = 0 min), while c is the concentration of the treated solution (t)) and the integrated area of the peak of the intermediates (detected by HPLC-DAD), on the use of air (a_2, b_2, c_2; retention time is presented as legend) *versus* duration of treatment, using 1.7×10^{-4} M initial concentration ○: oxygen; △: air; □: nitrogen; a: UV photolysis; b: ozonation; c: combination of UV photolysis and ozonation; d: heterogeneous photocatalysis.

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Table 1 The initial transformation rates (r_0 ($\times 10^{-8}$ M s^{-1})) and treatment time required for the transformation of 50% monuron and diuron ($t_{50\%}$ (min))

	UV photolysis						Ozonation				Combination of UV photolysis with ozonation				Heterogeneous photocatalysis			
	N_2		Air		O_2		Air		O_2		Air		O_2		Air		O_2	
	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$	r_0	$t_{1/2}$
Monuron	48.3	1.5	46.6	1.5	52.9	1.5	0.49	n.d.	0.87	90	75.5	1.0	78.9	1.0	6.76	15	7.05	15
Diuron	21.4	3.5	17.7	4.0	17.6	4.0	0.32	n.d.	0.70	120	24.9	3.0	26.7	3.0	4.33	15	4.15	16

emitted 185 nm VUV light of the lamp and its concentration was relative low. A significant difference between the initial rates of transformation of diuron and monuron was not found in this study, although the value determined for diuron, containing two Cl atoms, was lower than that of monuron containing only one Cl.

The combination of ozonation with UV photolysis resulted in a more effective method and increased the transformation rates comparing to those determined in the case of simple UV photolysis (diuron: $r_0(UV/O_3)/r_0(UV)$ = 1.4–1.5; monuron: $r_0(UV/O_3)/r_0(UV)$ = 1.5–1.6) (Fig. 2 and 3). When these methods are applied simultaneously, the 254 nm light has two functions: (i) initiating the decomposition of the aromatic target substances by direct photolysis, and (ii) enhancing the concentration of oxygen-containing radicals such as hydroxyl radical, due to the photoinitiated decomposition of ozone. A two-step process is proposed involving the light-induced homolysis of ozone and the subsequent production of hydroxyl radical by the reaction of $O(^1D)$ with water.

$$O_3 + h\nu_{<310nm} \rightarrow O_2 + O(^1D) \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2^{\bullet}OH \quad (2)$$

The 254 nm photolysis resulted in the concentration of dissolved ozone being one magnitude lower (3.5×10^{-7} M) than in the case of simple ozonation (2.3×10^{-6} M) because of the UV photolysis of dissolved ozone. Thus, the concentration of hydroxyl radical must be increased. The rate constants of the reactions of the hydroxyl radicals with diuron (4.8×10^9 M s^{-1})[32,67] and monuron (7.3×10^9 M s^{-1})[32,67] considerably exceed those with ozone. Consequently, the relative contribution of radical-based reactions to the decomposition of organic target substances is enhanced and this could be responsible for the higher rate of decomposition comparing to the simple ozonation or UV photolysis. At the same time, similarly to the UV-induced photolysis, there was no significant difference between the rates of transformation in aerated (2.49×10^{-7} M s^{-1} (diuron); 7.55×10^{-7} M s^{-1} (monuron)) and oxygen-saturated solutions (2.67×10^{-7} M s^{-1} (diuron); 7.89×10^{-7} M s^{-1} (monuron)), in part because of the high relative contribution of the direct UV photolysis to the transformation of these organic substances, even in the presence of hydroxyl radicals. This was proved by the effect of methanol. The addition of methanol (1.0×10^{-2} M) as hydroxyl radical scavenger only slightly decreased the transformation rate ($r_0^{monuron}(MeOH)/r_0^{monuron}$ = 0.73 and $r_0^{diuron}(MeOH)/r_0^{diuron}$ = 0.80) confirming the important role of direct UV photolysis, beside hydroxyl radical based reactions, even in the case of the combination of methods.

Using heterogeneous photocatalysis the transformation of organic substances (S) can be initiated by direct charge transfer *via* photogenerated charges (hole (h_{VB}^+))

$$h_{VB}^+ + S \rightarrow S^{\bullet+} \quad (3)$$

and/or hydroxyl radical based reactions. Hydroxyl radicals can form directly from hydroxide ion or adsorbed water

$$h_{VB}^+ + H_2O \rightarrow HO^{\bullet} + H^+ \quad (4)$$

$$h_{VB}^+ + OH^- \rightarrow HO^{\bullet} \quad (5)$$

Another way is the further transformation of superoxide radical ion ($O_2^{\bullet-}$) which is generated *via* direct charge transfer from adsorbed oxygen molecule and photogenerated electron (e_{CB}^-)

$$O_2 + e_{CB}^- \rightarrow O_2^{\bullet-} \quad (6)$$

$$HO_2^{\bullet} \rightleftharpoons H^+ + O_2^{\bullet-} \quad (7)$$

$$HO_2^{\bullet} + O_2^{\bullet-} + H^+ \rightarrow H_2O_2 + O_2 \quad (8)$$

The adsorbed H_2O_2 can transform *via* direct charge transfer and result partly in hydroxyl radical

$$H_2O_2(ads) + e_{CB}^- \rightarrow HO^{\bullet} + OH^- \quad (9)$$

$$H_2O_2(aq) + e_{CB}^- \rightarrow HO^{\bullet} + OH^- \quad (10)$$

$$H_2O_2(ads) + h_{VB}^+ \rightarrow O_2^{\bullet-} + 2H^+ \quad (11)$$

Both herbicides are only negligibly adsorbed.[68,69] At the given initial concentration in 1.0 g dm^{-3} TiO_2 suspension less than 4% of diuron or monuron was adsorbed in the conditions used. The initial rate of transformation of monuron (air: 6.76×10^{-8} M s^{-1}; oxygen: 7.05×10^{-8} M s^{-1}) was higher than diuron (air: 4.33×10^{-8} M s^{-1}; oxygen: 4.15×10^{-8} M s^{-1}), similarly to the rate constants of their reactions with hydroxyl radical. The values reported by Oturan *et al.* are 7.3×10^9 and 4.8×10^9 M s^{-1} for monuron and diuron, respectively.[32] The

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ratio of the initial rates of transformation ($r_0^{monuron}/r_0^{diuron}$ = 1.6–1.7) is similar to the ratio of the reaction rate constants ($k^{monuron}/k^{diuron}$ = 1.5), which confirms that their degradation was initiated by photogenerated hydroxyl radicals. Krýsa *et al.*[69] reported similar consequence in the case of photocatalytic transformation of monuron. The significant negative effect of 1.0×10^{-2} M methanol, as hydroxyl radical scavenger, ($r_0^{monuron}(MeOH)/r_0^{monuron}$ = 0.29 and $r_0^{diuron}(MeOH)/r_0^{diuron}$ = 0.35) confirmed the essential role of hydroxyl radical.

Sharp, nearly linear decrease in the monuron and diuron concentration was observed during UV photolysis, ozonation and their combination until ~70% elimination. In the photocatalytic systems there is exponential-like decrease of the concentration with time during the whole treatment, probably because of the strong competition between diuron/monuron and the formed intermediates, which are adsorb better than the parent compounds and successfully compete for the reactive species.

3.2. Aromatic intermediates

3.2.1. Spectrophotometric measurements. The spectra of the UV-irradiated solutions revealed that the absorbance at 277 and 227 nm in the case of diuron (Fig. 4a and b) and at 217 and 270 nm in the case of monuron (Fig. 4d and e) described maximum curves. This proved that aromatic intermediates accumulated and decomposed during the UV initiated transformations. The maximum absorbance was much higher on UV irradiation than in the case of the combination of ozonation with UV photolysis, proving that the addition of ozone strongly enhanced the rates of formation and decomposition of these intermediates, most likely in radical-based reactions, thereby preventing their accumulation. The accumulation of these intermediates and the increase of relative absorbance was not significant using heterogeneous photocatalysis. This could be due to the better adsorption of the intermediates on the surface of TiO_2, enhancing their transformation and preventing their accumulation in the irradiated suspension. At the same time, probably competition occurs between monuron/diuron and well adsorbed intermediates for the hydroxyl radicals. Another important observation is that, the main intermediates (t_{ret} = 1.98 min), which formed in 254 nm irradiated solutions was present only in trace amount in the case of heterogeneous photocatalysis. The significant difference in the quality and quantity of the main aromatic intermediates between 254 nm irradiated solutions and in TiO_2 suspension re-confirm the existence of different main transformation ways (direct UV photolysis and hydroxyl radical based reaction).

In UV irradiated solutions, the absorbance at 248 and 244 nm (the absorbance maximum of diuron and monuron, respectively) decreased in parallel with the concentration of phenylurea pesticides. The time dependence of the relative absorption at 277 and 270 nm suggested the occurrence not only of the formation, but also the decomposition of these aromatic intermediates, in parallel with the decomposition of the parent compounds. After the decomposition of 60–70% of pesticides the concentration of these intermediates

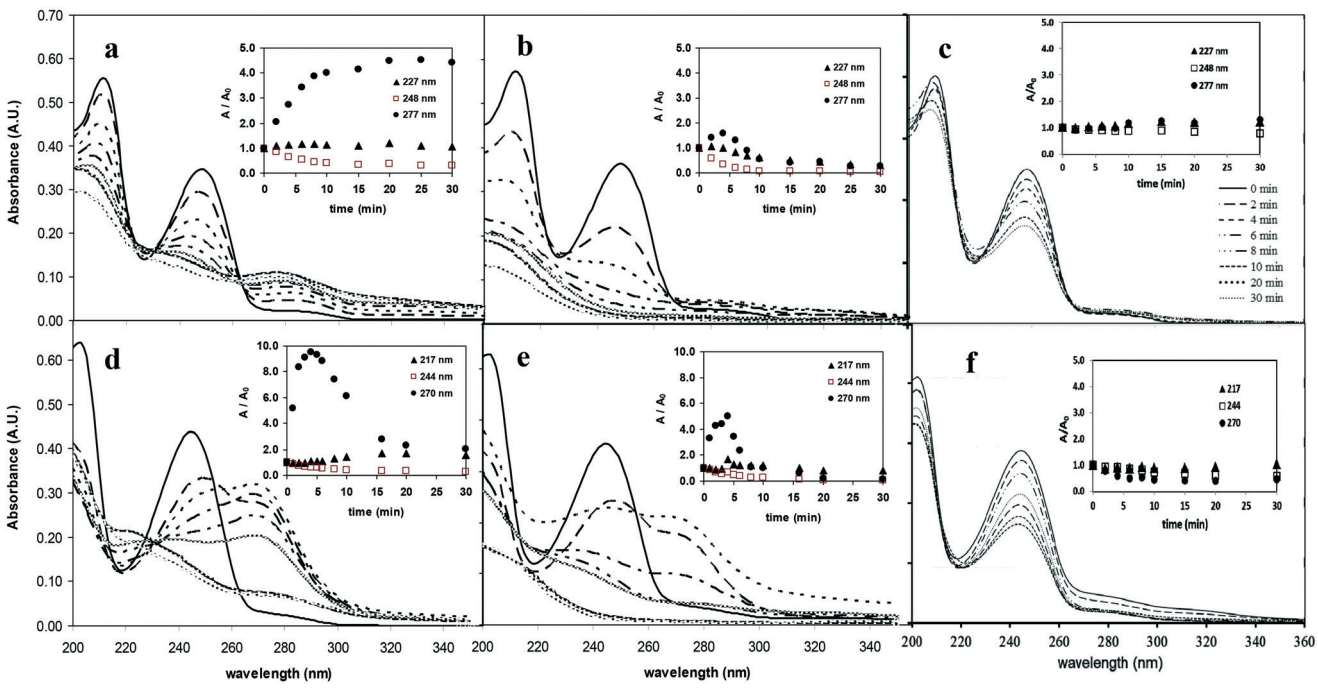

Fig. 4 The spectra and the relative absorbance (inserts, where A_0 is the absorbance of the solution before treatment (t = 0 min), while A is the absorbance of the treated solution (t: 0, 2, 4, 6, 8, 10, 15, 20, 25, 30 min) at the given wavelength) *versus* the duration of treatment in solutions saturated with air a: diuron, UV photolysis; b: diuron, combination of UV photolysis with ozonation; c: diuron, heterogeneous photocatalysis; d: monuron, UV photolysis; e: monuron, combination of UV photolysis with ozonation; f: monuron, heterogeneous photocatalysis.

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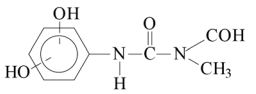
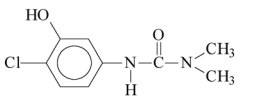
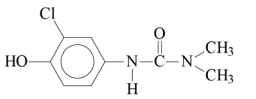
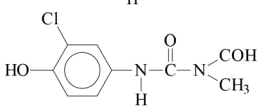
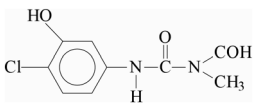
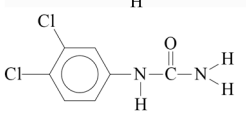
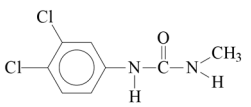
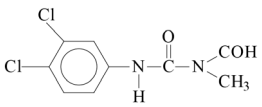
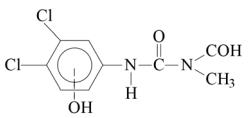
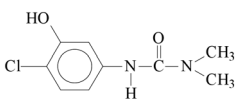
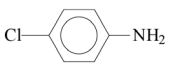
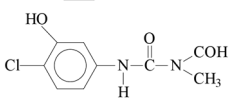
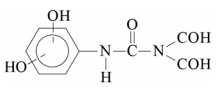
decreased sharply. The transformation of both chlorinated substances by ozonation is a very slow process. The spectra do not change significantly during 30 min of treatment therefore they are not presented here.

The colourless aqueous solution of diuron became yellowish-pink when UV photolysis was applied, while that of monuron became pink. When the combination of UV photolysis with ozonation was employed, the intensity of the colour change was weaker. Each solution became colourless shortly after the decomposition of the target substances. On ozonation and heterogeneous photocatalysis no change in colour was observed, and there was no increase in the absorbance at 277 and 270 nm. During ozonation two main pathways of degradation were suggested for both target compounds: *N*-demethylation and OH-substitution of a Cl atom on the phenyl ring.[21] In addition, the main transformation ways of monuron using heterogeneous photocatalysis include the hydroxylation of the aromatic ring too.[18,25] In the cases of

Table 2 Molecular masses and suggested structures of the aromatic intermediates of diuron (above the thick line) and monuron (below the thick line) identified by LC-MS (+: detected; −: not detected)

Molecular mass (m/z = M^{-1})	Retention time (min)	Assumed structure	UV photolysis	Ozonation	Combination treatment	Heterogeneous photocatalysis
210	1.20		+	−	−	−
214	1.98 and 2.25		+	−	+	+
			+	−	+	+
228	2.68 and 3.32		+	−	+	−
			+	−	+	−
203	5.04		−	−	+	+
218	4.25		+	+	+	+
246	8.04		+	+	+	+
262	7.80		−	+	−	−
214	1.98		+		+	−
127	5.02		−	+	−	+
228	2.68		−	+	−	−
224	2.87		+	+	+	−

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reaction with molecular ozone and hydroxyl radical based transformation probably the formation of ring-opened products are more favourable than the formation of aromatic intermediates.

3.2.2. Identification of aromatic intermediates. The oxidative transformation pathways of diuron have been suggested in several studies. The main intermediates of photodegradation have been reported to be 1-(3,4-dichlorophenyl)-3-methylurea, 3,4-dichlorophenylurea and 3,4-dichloroaniline.[10,56] In the reaction with the hydroxyl radical with diuron or monuron, there are two main sites of attack: the methyl groups and the aromatic ring, leading to dehalogenation and/or hydroxylation.[18,21,32,34]

The MS results (Table 2) indicated that the transformations of diuron and monuron commenced with oxidation of the N-terminus group, in parallel with hydroxylation and dehalogenation of the aromatic ring. The time dependence of the areas of the peaks in the chromatograms confirmed the occurrence of the formation and transformation of the aromatic intermediates together with the decomposition of the parent compounds. The addition of ozone to the UV-irradiated solution strongly enhanced the rates of transformation and decomposition of the aromatic substances. These observations are in agreement with the spectrophotometric measurements: relative absorbance determined at 277 nm (diuron) and 270 nm (monuron) increased much sharply in UV-irradiated solution and reached higher value than in the case of combination with ozonation (Fig. 4a, b, d and e).

Quantification of the intermediates demonstrated that, demethylation and oxidation of the N-terminus groups on ozonation was more favorable than dehalogenation of the aromatic ring. Rather than dechlorination, the formation of ring-opened products appeared to be preferred.

3.3. Mineralization and dehalogenation

As a result of the dehalogenation of diuron and monuron, as well as their intermediates, chloride ion was formed (Fig. 5a). There was no significant difference between the rate of accumulation of chloride ion and hence, the rate of dehalogenation between UV photolysis alone and its combination with ozonation. In solutions of diuron treated with these two methods, the concentration of chloride ion reached a maximum after 20 min. During this period, more than 90% of diuron decomposed in both cases. The ozonation alone was less effective in the decomposition of diuron, but dehalogenation also proceeded during the period needed for the transformation of diuron (about 240 min). Similar observations were made in the case of monuron. In all cases the transformation of Cl containing intermediates takes place simultaneously with diuron/monuron and after the transformation of the parent compounds there are no measurable chlorinated organic substances in the treated solution/suspension.

Concerning mineralization, only the combination of UV photolysis with ozonation and heterogeneous photocatalysis were effective methods. In the case of ozonation and UV

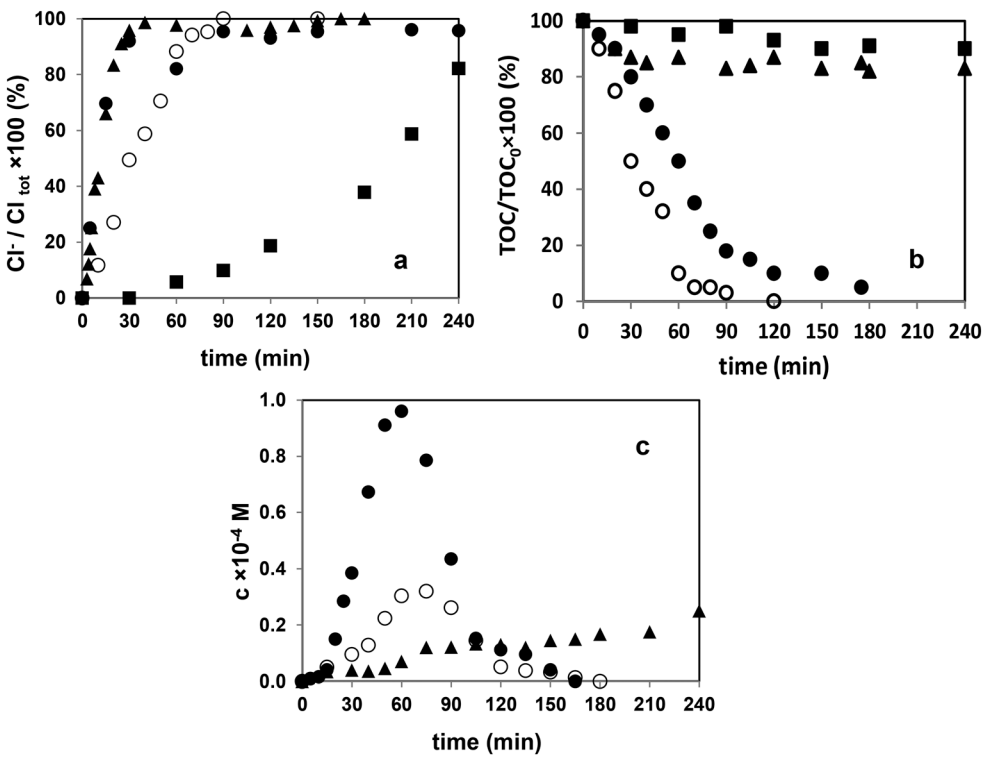

Fig. 5 Relative concentration of Cl^- (a), total organic carbon content (TOC) (b) and sum of the concentration of peroxydes (H_2O_2, methyl- and ethyl-hydroperoxides) (c) in the case of the transformation of diuron in aerated solutions/suspension ■: ozonation; ▲: UV photolysis; ●: combination of UV photolysis with ozonation; ○: heterogeneous photocatalysis.

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photolysis, the TOC concentration decreased only slightly (Fig. 5b). Radical based reactions and mineralization of organic pollutants in the presence of dissolved oxygen generally occurs through the formation of peroxyl radicals.[65,70] Further fragmentation and transformation of peroxyl radicals result in $HO_2^{\bullet}/O_2^{\bullet-}$ having low reactivity towards organic substances. The H_2O_2 mainly forms and accumulates due to the recombination of these species.

In this work, using the method based on catalysed transformation of leuco crystal violet, the sum of the concentration of H_2O_2 and methyl- and ethyl-hydroperoxides was measured. The obtained value was much higher using the combination of methods, than using UV-irradiation, and it was not measurable during ozonation (Fig. 5c). Using heterogeneous photocatalysis the reactions can take place on the TiO_2 surface *via* direct charge transfer. In this case the decomposition of H_2O_2 is highly favored due to its reactions with photogenerated charges (both h_{VB}^+ and e_{CB}^-), which strongly inhibits its accumulation (9–11).

Aliphatic intermediates such as oxalic, fumaric, malic, maleic, acetic, succinic, propionic and tartaric acids were formed during all treatments, confirming the opening of the aromatic ring and further fragmentation (Fig. 6). The time dependence of the oxalic acid concentration is the most characteristic. Relative to UV photolysis or ozonation alone, the concentration of this compound was one magnitude higher when the combination of UV photolysis with ozonation was applied. In the case of single UV photolysis and ozonation only the slow accumulation was observed, while using their combination the time dependence of the oxalic acid concentration showed maximum curve (Fig. 6). Using heterogeneous photocatalysis the transformation of well adsorbed organic acids is quite fast, preventing their accumulation and enhancing the rate of mineralization. Thus, the maximum concentration of oxalic acid was lower comparing to the maximum concentration measured in the case of combination of UV photolysis with ozonation. For a typical reaction system containing photocatalyst, the photocatalytic oxidation of carboxylic acids follows a photo-Kolbe reaction mechanism: the decomposition results in the formation of CO_2 as the primary reaction product and a carbon-centered radical as the primary reaction intermediate.

3.4. Economic efficiency – electrical energy per order (E_{EO})

To compare the economic efficiency of the applied AOPs the values of electrical energy per order (E_{EO}) were calculated for both transformation (E_{EO}^{c}) and mineralization (E_{EO}^{TOC}) of monuron and diuron. The E_{EO}^{c} value was not calculated for ozonation, since its efficiency was negligible. For the same reason, E_{EO}^{TOC} values were calculated only for the combination of UV photolysis with ozonation and heterogeneous photocatalysis.

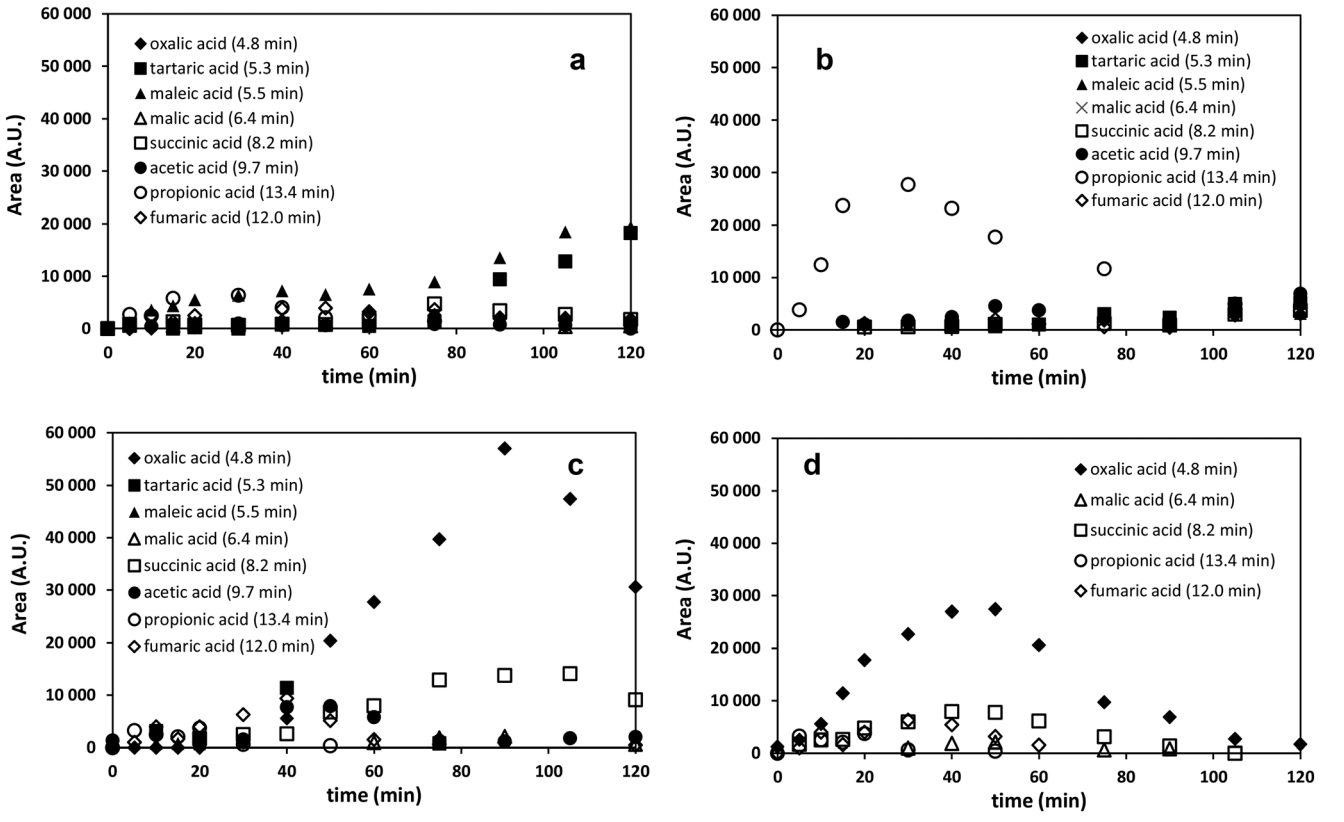

Fig. 6 The area of the chromatographic peaks of acids *versus* the duration of treatment in diuron solutions saturated with air a: ozonation; b: UV photolysis; c: combination of UV photolysis with ozonation; d: heterogeneous photocatalysis.

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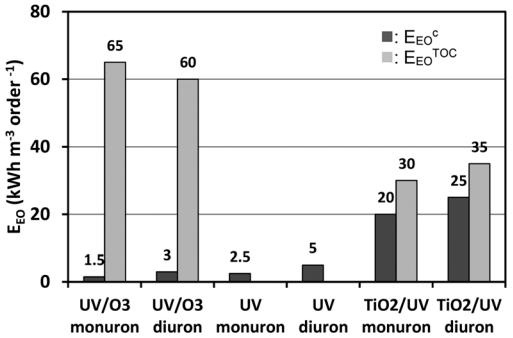

Fig. 7 Values of electrical energy per order (E_{EO}) calculated for transformation (E_{EO}^{c}) and mineralization (E_{EO}^{TOC}) of monuron and diuron.

As the values presented on Fig. 7 show, the energy requirement of UV photolysis and its combination with ozonation is about one magnitude lower than that of heterogeneous photocatalysis. In the respect of mineralization the heterogeneous photocatalysis is definitely the most feasible method, and needs about the half of the energy requirement of the combination of UV photolysis with ozonation. Using heterogeneous photocatalysis the E_{EO}^{c} and E_{EO}^{TOC} values are close to each other. Opposite to this, the E_{EO}^{TOC} value of the combined method is more than one magnitude higher than E_{EO}^{c} value, most probably because UV photolysis is quite inefficient in the transformation of intermediates which do not absorb 254 nm light, while heterogeneous photocatalysis is an unselective method for the transformation of various type of organic substances.

4. The matrix effect

4.1. Influence of inorganic salts and two natural matrices

Addition of inorganic salts has no significant effect in the case of ozonation, UV photolysis and their combination. Even addition of HCO_3^-, which can behave as hydroxyl radical scavenger (k = 8.5 × 10^6 M s^{-1})[73] inhibited only slightly the transformation using the combined method (Fig. 8). The heterogeneous photocatalysis was found to be much more sensitive to the ion concentration. The addition of various salts, even HCO_3^-, increased the transformation rates. Surface properties can be changed strongly by the presence of inorganic ions and ionic strength in the suspension. These parameters affect not only the adsorption properties of the catalyst, but also the formation rate of hydroxyl radicals. Surprisingly, the effect was more significantly manifested in the case of diuron, than monuron.

In this study, treatments were carried out in natural waters such as the water of the River Tisza and in thermal

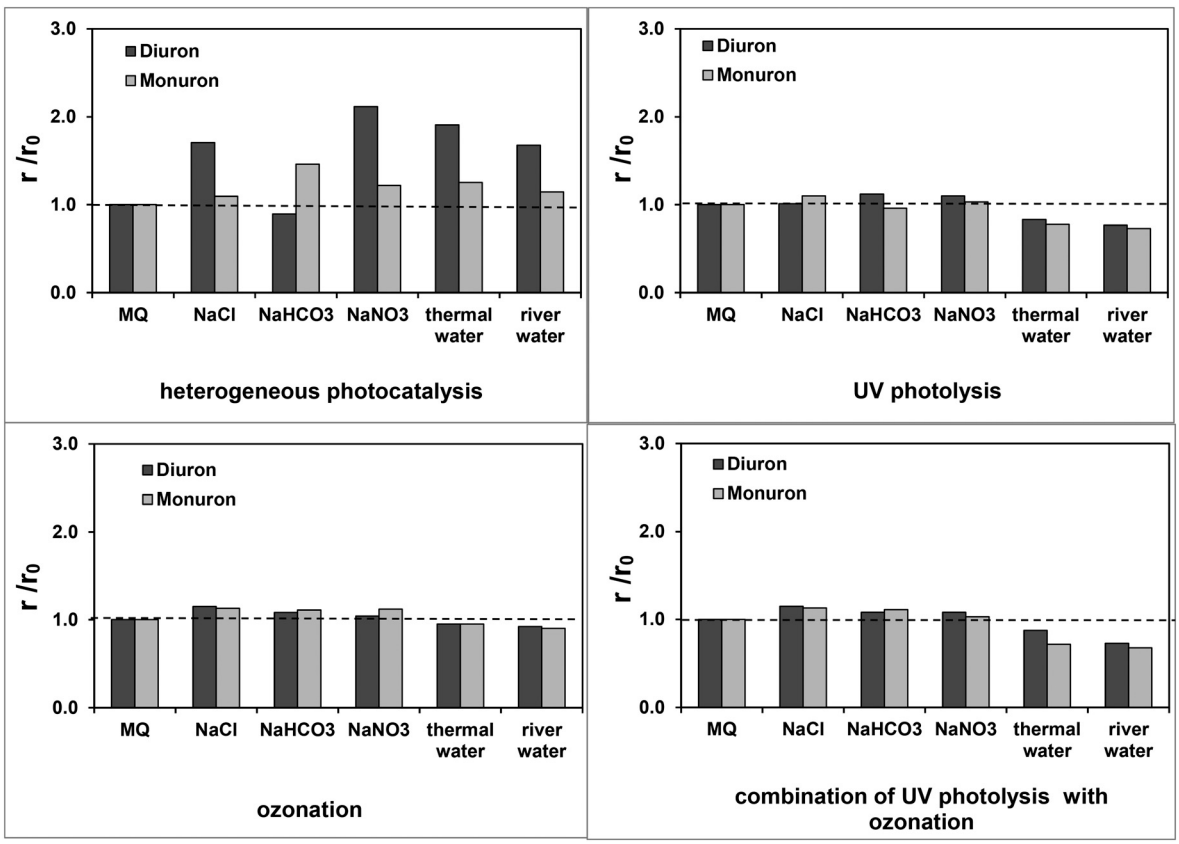

Fig. 8 Relative rate of transformations (r: transformation rate determined in the presence of added salt or in thermal or river water; r_0: transformation rate determined in MilliQ water).

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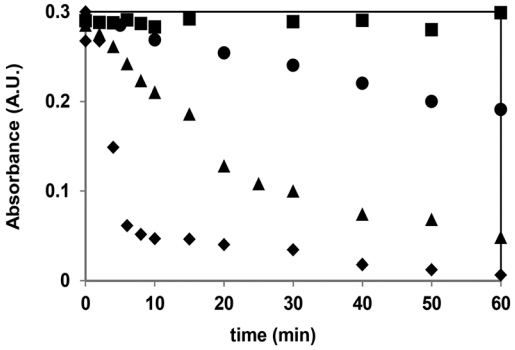

Fig. 9 The absorbance of the humic acid solution/suspension (c_0 = 20 ppm) *versus* the time of treatment using heterogeneous photocatalysis (◆), combination of UV photolysis with ozonation (▲), ozonation (●), and UV photolysis (■).

water. The rates of transformation of both target substances obtained in the mentioned matrices were compared with those measured in Milli-Q bidistilled water. Based on the results, no significant effect of these matrices, expect in the case of heterogeneous photocatalysis (Fig. 8) could be observed. This effect is most probably due to the high ionic strength of the thermal water, having relatively high HCO_3^- concentration. It is manifested in river water too, in spite of the presence of several components (mainly small amount of organic substances), that can behave as radical scavengers.

4.2. Effect of humic acids

Humic acids can impact by several pathways the decomposition and transformation of organic molecules and are able to decrease or increase the rates of transformation of the target substances.[36,71,72] At first, the efficiency of UV radiation, ozonation, their combination and heterogeneous photocatalysis on the elimination of humic acid was investigated. UV irradiation had no effect, in spite of the fact, that humic acid is able to absorb 254 nm UV light. There was no change of the absorbance during 60 min irradiation. In contrast, during ozonation the measured absorbance significantly decreased, proving that the transformation of humic acids (Fig. 9) can be initiated by the direct reaction with ozone, even at the very low ozone concentration applied in this work. The combination of these two methods is more efficient than simple ozonation, because of the well-known formation of the highly reactive hydroxyl radical.

Humic acid is well adsorbed on the TiO_2 surface. Less than 5 ppm humic acid is completely adsorbed in 1.0 g L^{-1} TiO_2 suspension and was not measurable by spectrophotometric method after filtration. Using 20 ppm initial concentration, 13% of humic acid was adsorbed. Heterogeneous photocatalysis was proved to be widely the most effective method in the elimination of humic acid, comparing to other methods investigated in this work ($r_0^{\text{humicacid}}(TiO_2/UV_{300-400nm}) \gg r_0^{\text{humicacid}}(O_3/UV_{254nm}) > r_0^{\text{humicacid}}(UV_{254nm}) > r_0^{\text{humicacid}}(O_3)$) (Fig. 8).

On ozonation, the presence of humic acids slightly increased the rate of transformation (Fig. 10a). The decomposition of ozone was probably positively affected by the humic acid. This effect could be attributed to the reactions of intermediates originated from the ozonation of humic acid, that behaves as a strong promoter of ozone decomposition. Consequently, the relative contribution of radical-based reactions

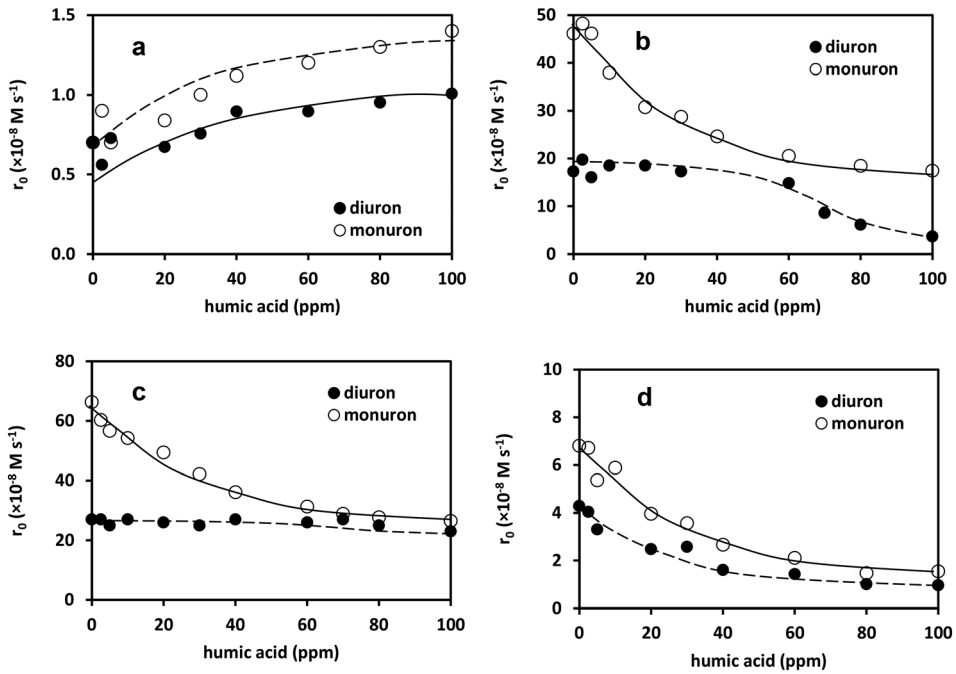

Fig. 10 The effect of humic acid addition on the initial rate of transformation of diuron and monuron *via* ozonation (a), UV photolysis (b), the combination of UV photolysis with ozonation (c) and heterogeneous photocatalysis (d).

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to the transformation of diuron and monuron increased in the presence of humic acid and results in higher transformation rate of pesticides.

In UV-irradiated solutions, the humic acid caused a decrease in the rate of transformation of the pesticides, most likely because of acting as a "UV filter". The resulting competitive light absorption is responsible for the decrease (Fig. 10b). In the case of monuron this negative effect is much more pronounced, most likely because of the higher quantum yield of the UV light irradiated transformation. In diuron solution the negative effect of humic acid was observed only above 60 ppm concentration.

When the combination of ozonation and UV photolysis was applied, the dependence of the initial rate of transformation on the concentration of humic acids was similar to that in the case of UV photolysis (Fig. 10c). With regards to the high molar absorbance of both diuron and monuron, the relative contribution of direct photolysis to the transformation remained dominant in the case of the UV-irradiated ozone-containing solutions. In this case humic acids can behave both as a "UV filter" and hydroxyl radical scavenger. Surprisingly, the negative effect of humic acid was observed only in the case of monuron, when the relative contribution of direct photolysis must be higher than in the case of diuron. Probably any kind of photosensitization is able to compensate the "UV filter" effect of humic acid in the latter case.

The negative effect of humic acid was well manifested in the case of heterogeneous photocatalysis, due to the favored adsorption of humic acid on the TiO_2 surface and its competition with diuron/monuron for the formed hydroxyl radical. The behavior of monuron and diuron in the presence of humic acid is very similar in this case.

5. Conclusions

Decomposition of diuron and monuron by UV-induced photolysis, ozonation, their combination, and heterogeneous photocatalysis was investigated and compared at the same energy input. The UV photolysis was very effective in the transformation of the target pesticides. The addition of ozone enhanced the transformation rates due to the hydroxyl radical formation. However, the direct photolysis remained the dominant pathway for the initialization of transformation in the latter case. Mineralization was significant only using the combined method and heterogeneous photocatalysis. Definitely, heterogeneous photocatalysis was the most efficient and economically most feasible method from the mineralization point of view.

Several aromatic intermediates were detected and identified. Demethylation and oxidation of the aliphatic chain occurred in parallel with the dechlorination and hydroxylation of the aromatic ring. The identified aromatic intermediates suggest that ring opening is more favourable in case of ozonation and heterogeneous photocatalysis than in case of UV photolysis and its combination with ozonation.

Humic acids behaved as "UV filter" and had a negative effect on the transformation rates in UV-irradiated solutions, but a positive effect in the case of ozonation, due to their behaviour as ozone transformation promoter, and consequently due to the increased radical concentration. The effects of natural waters (water of River Tisza and thermal water) as matrix, similarly to the effect of added inorganic salts, were negligible, except in case of heterogeneous photocatalysis, most likely due to the change of surface properties and the formation rate of hydroxyl radical.

Conflicts of interest

There are no conflicts to declare.

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