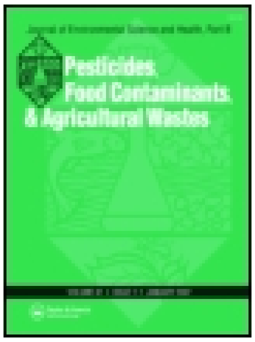

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# Comparison of various advanced oxidation processes for the degradation of phenylurea herbicides

Krisztina Kovács[a,b], János Farkas[a], Gábor Veréb[a], Eszter Arany[a], Gergő Simon[a], Krisztina Schrantz[a,c], András Dombi[a], Klára Hernádi[a,d], and Tünde Alapi[a,c]

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**ABSTRACT**

Various types of advanced oxidation processes (AOPs), such as UV photolysis, ozonation, heterogeneous photocatalysis and their combinations were comparatively examined at the same energy input in a home-made reactor. The oxidative transformations of the phenylurea herbicides fenuron, monuron and diuron were investigated. The initial rates of transformation demonstrated that UV photolysis was highly efficient in the cases of diuron and monuron. Ozonation proved to be much more effective in the transformation of fenuron than in those of the chlorine containing monuron and diuron. In heterogeneous photocatalysis, the rate of decomposition decreased with increase of the number of chlorine atoms in the target molecule. Addition of ozone to UV-irradiated solutions and/or $TiO_2$-containing suspensions markedly increased the initial rates of degradation. Dehalogenation of monuron and diuron showed that each of these procedures is suitable for the simultaneous removal of chlorinated pesticides and their chlorinated intermediates. Heterogeneous photocatalysis was found to be effective in the mineralization.

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**KEYWORDS**
Diuron; monuron; fenuron; ozone; heterogeneous photocatalysis; photolysis

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## Introduction

Directive 2000/60/EC establishes a new framework for a water pollution strategy that includes a list of priority substances which pose a significant risk to the European aquatic environment. Most of these substances are synthetic contaminants, including pesticides. Pesticides have recently become one of the most hazardous environmental pollutants of concern because of their stability, mobility and long-term effects on living organisms.[1,2] The occurrence of pesticides having endocrine-disrupting effects has especially attracted great attention. Pesticides can be detected in soils, surface and groundwater samples[3–6] in which phenylurea pesticides can undergo biotransformation, but some of the metabolites or degradation products proving more harmful than the original compounds.[7,8]

Phenylurea herbicides are generally applied for the pre- and post-emergence control of weeds in many crops and also on non-cultivated areas such as roads and railways. They act as inhibitors of photosynthesis. Because of their relatively long lifetimes in the environment[9,10] these herbicides can be present as contaminants in surface and ground waters.[11] The target substances in this study were fenuron, monuron and diuron phenylurea herbicides, with a very similar chemical structure, with the exception of the numbers of chlorine substituents (Fig. 1).

The most frequently used wastewater treatment techniques can be divided into physical, biological and chemical categories. Urban wastewater is usually treated by physical and biological techniques which reduce the pollution, but are not sufficient to eliminate trace pollutants and their by-products completely.[6] As a consequence of their biorecalcitrant and toxic properties, herbicides cannot be treated directly in conventional wastewater treatment plants based on the activity of a microbiological consortium,[12] and the development of new technologies aimed at the facile degradation of such substances is of practical interest.

Advanced oxidation processes (AOPs), including ozonation, heterogeneous photocatalysis, Fenton and photo-Fenton processes, ultraviolet (UV) photolysis and its combination with the addition of $H_2O_2$ and/or $O_3$, have been shown to be promising solutions for the removal of these compounds in water treatment.[13–15] In the present work the value of ozonation, UV photolysis, heterogeneous photocatalysis and their combinations was investigated in the oxidative transformation of phenylurea pesticides fenuron, monuron and diuron.

Direct UV photolysis is widely used in water disinfection. In the presence of dissolved $O_2$, the UV light-initiated transformation of organic substances is generally influenced by the formation of reactive oxygen-containing species.[16,17] The combination of UV photolysis with the addition of $H_2O_2$ or $O_3$ results in a promising technique for the degradation and mineralization of organic contaminants.

$O_3$ is used, even commercially, as an oxidant for drinking water treatment and disinfection,[18] and also for the elimination of organic micropollutants.[19,20] The combination of ozonation with UV irradiation at 254 nm generally greatly improves the efficiency of the oxidative transformation of organic compounds.[21–24]

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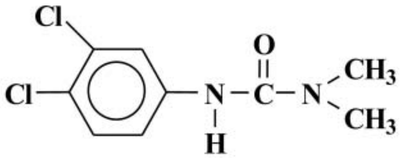
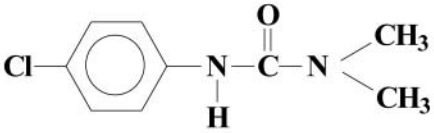
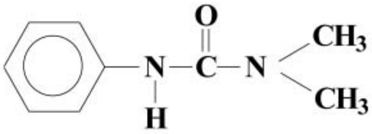


Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea))



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



Fenuron (3-phenyl-1,1-dimethylurea)

**Figure 1.** Molecular formulae of the investigated pesticides.

Heterogeneous photocatalysis is a further promising technique for the degradation of organic contaminants.[25] $TiO_2$ is generally used as photocatalyst in the view of its chemical and biological inertness, optical and electronic properties, stability and low cost. It is widely presumed that water or hydroxide ion adsorbed on the surface of the photocatalyst interact with positively charged holes, whereby hydroxyl radical ($^\bullet OH$) can be produced.[26] On the other hand, the direct reaction of adsorbed organic substances with photogenerated holes is also possible. The effectiveness of heterogeneous photocatalysis can be improved by the addition of a powerful oxidant, such as $O_3$.[27–29]

There have been a number of studies on the use of various AOPs[14,30] to remove phenylurea herbicides from water, such as UV photolysis,[22,31–35] ozonation,[22,36–38] heterogeneous photocatalysis,[39–43] and either Fenton, photo-Fenton[32,34,44,45] or electro-Fenton reactions[46] which have extended to the determination of the rate of transformation of the target substance under various experimental conditions, the quantum yields of direct photolysis,[31–33] the reaction rate constants with $O_3$[22,37] $^\bullet OH$,[22,37,46] and the qualification[34,36,43] and toxicity of the intermediates.[35]

Chemical oxidation treatments usually involve certain limitations, which may be economical or due to the recalcitrant behavior of the reaction by-products. A suitable combination of AOPs can be more effective for the removal of environmental pollutants. The goal and novelty of the current study is a comparison of a variety of UV photolysis, heterogeneous photocatalysis, ozonation and combinations in the cases of three phenylurea pesticides in many ways (rate of transformation, mineralization and dehalogenation). The AOPs and their combinations were compared in the same reactor, at the same energy input, without the use of an external $O_3$ generator. The efficiencies of the various methods and combinations could therefore be compared easily and directly from the aspect of energy investment.

## Materials and methods

### Materials

The phenylurea herbicides fenuron (3-phenyl-1,1-dimethylurea) (Supelco, Bellefonte, PA, USA), monuron (3-(4-chlorophenyl)-1,1-dimethylurea) (Sigma-Aldrich, St. Louis, MO, USA) and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) (Sigma-Aldrich) were used without further purification. Ultrapure water obtained from a Millipore Milli-Q System with resistance >18 MΩ cm at room temperature was utilized for the preparation of all stock solutions and HPLC eluents. HPLC-grade methanol was purchased from Hipersolv Chromanorm. The Degussa P25 photocatalyst (49 $m^2\ g^{-1}$ surface area, 90:10 anatase:rutile ratio with 25.4 and 40 nm primary particle size, respectively) with 0.5 $g\ L^{-1}$ loading was used during the heterogeneous photocatalytic experiments.

### Experimental apparatus

#### Light sources

In the case of ozonation and its combinations the light source was a low-pressure mercury vapor lamp, which emits 254 nm UV and 185 nm vacuum UV (VUV) light (UV/VUV lamp). This lamp (GCL307T5VH/CELL, LightTech, Hungary) was covered with a high-purity quartz sleeve which transmits both 185 nm and 254 nm light. $O_3$ was generated by the 185 nm photolysis of molecular oxygen in the gas phase.

In direct UV photolysis, the sleeve of the same low-pressure mercury vapor lamp was made of commercial quartz (GCL307T5/CELL, LightTech, Hungary), which emits 254 nm light and absorbs 185 nm (UV lamp).

Another light source, a specific fluorescent lamp (GCL303T5/UVA, LighTech) which emits 300–400 nm (intensity maximum at 365 nm) light, was applied during heterogeneous photocatalysis.

The electric (15 W electric input) and geometric parameters (227 mm arc length, 307 mm long and 20.5 mm external diameter of the sleeve) of the different light sources corresponded to each other. The emitted photon flux determined by ferrioxalate actinometry[31] was found to be $8.10(\pm0.65)\times10^{-6}$ $mol_{photon\ (254\ nm)}\ s^{-1}$ for the low-pressure mercury vapor lamp (UV/VUV and UV) and $1.20(\pm0.06)\times10^{-5}$ $mol_{photon\ (300\text{–}400\ nm)}\ s^{-1}$ for the specific fluorescent lamp.

#### Photoreactor

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

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

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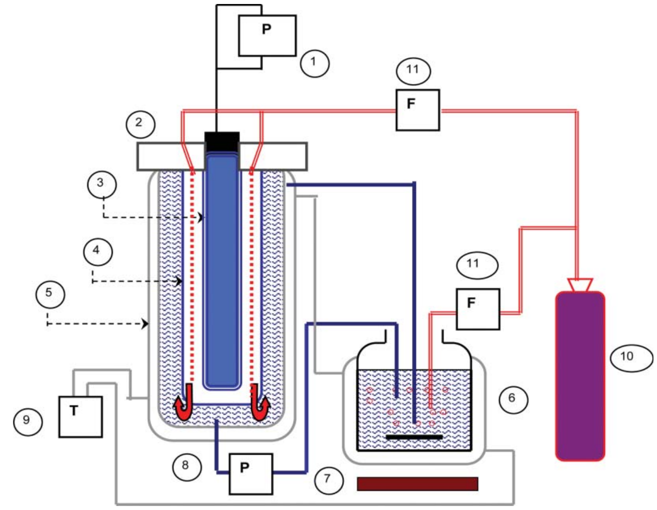

**Figure 2.** The experimental apparatus.[23] 1: power supply; 2: teflon packing ring; 3: light surce (low-pressure mercury vapor lamp or special flurescent lamp) with sleeve; 4: envelope; 5: reactor; 6: reservoir; 7: magnetic stirrer; 8: pump; 9: thermostat; 10: air bottle; 11: flow meter.

(Table 1 and Fig. 2). Thus, ozonation was performed with a UV/VUV lamp and a perforated glass envelope. $O_2$ was flowed through the Teflon packing ring between the wall of the lamp and the envelope, which separates the gas phase and the aqueous solution as shown in Figure 2 $O_3$ generated from pure $O_2$ was bubbled through the solution, which requires a perforated envelope. Through use of a UV lamp and a non-perforated quartz envelope, UV photolysis at 254 nm and its combination with heterogeneous photocatalysis could be investigated. When heterogeneous photocatalysis was applied, the specific fluorescent lamp and non-perforated glass envelope were used.

The combinations of ozonation and UV photolysis and with heterogeneous photocatalysis were carried out with an UV/VUV lamp and a perforated quartz envelope. The combination of ozonation and heterogeneous photocatalysis was achieved through the use of two reactors. The $O_3$ was generated from pure $O_2$ in the first reactor by means of a UV/VUV lamp. The generated $O_3$ was bubbled between the fluorescent lamp and the perforated glass envelope, and hence through the suspension, which was irradiated with the light of a specific fluorescent lamp.

### *Analytical methods*

The concentrations of phenylurea herbicides were determined with an HPLC system (Merck Hitachi, Japan, L-7100 pump, L-4250 UV-Vis detector and Agilent 1100 HPLC, UV-Vis detector). Aromatic compounds were separated on an RP-18 column (Lichrospher 100, Agilent Technologies, Wilmington, DE, USA), with 60% methanol + 40% water as eluent at a flow rate of 0.8 mL $\text{min}^{-1}$. The quantification wavelength for UV detection was 210 nm.

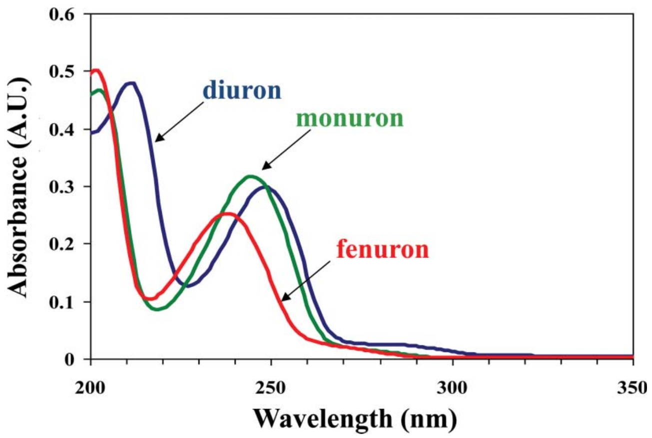

**Figure 3.** Spectra of the investigated compounds.

Spectra (200 to 450 nm, Fig. 3) of the samples were acquired during each degradation measurement on an Agilent 8453 spectrophotometer in 2 mm cells. The concentration of $O_3$ in the gas phase was measured in a flow cell using the same spectrophotometer at 254 nm ($\varepsilon_{254\text{ nm}} = 2952\ \text{mol}^{-1}\ \text{L}\ \text{s}^{-1}$, Atkinson et al.[24]), and was found to be $1.37 \times 10^{-5}$ mol $\text{L}^{-1}$ when oxygen was used.

The adsorbable organically bound halogen (AOX) content was followed through use of an analyzer, consisting of an Analytik Jena multiX 2500 AOX sample unit and an APU2 sample preparation unit. Samples were adsorbed on active carbon, then transferred into the AOX furnace and burnt at 950°C under an $O_2$ flow. Chlorine was quantified by a microcoulometric method.

The total organic carbon (TOC) content was determined with a multi N/C 3100 analyzer (Analytik Jena, Germany). This method is based on thermocatalytic oxidation in the presence of a specific catalyst. The TOC content of a sample is calculated from the amount of $CO_2$ formed.

The decompositions of diuron, monuron and fenuron were characterized by the initial rate of transformation, obtained from linear regression fits to the actual concentration of pesticide versus the duration of irradiation, up to 30% of the concentration of the transformed target compound.

**Table 1.** The light source and envelope applied in the various methods.

| Method | Light source | Envelope |
|---|---|---|
| Ozonation ($O_3$) | UV/VUV lamp | Glass, perforated |
| UV photolysis (254 nm) | UV lamp | quartz, non-perforated |
| heterogeneous photocatalysis ($TiO_2$ 365 nm) | specific fluorescent lamp | glass, non-perforated |
| UV photolysis and ozonation (254 nm / $O_3$) | UV/VUV lamp | quartz, perforated |
| heterogeneous photocatalysis and ozonation ($TiO_2$ 365 nm / $O_3$) | specific fluorescent lamp (UV/VUV for $O_3$ generation) | glass, perforated |
| UV photolysis and heterogeneous photocatalysis($TiO_2$ 254 nm) | UV lamp | quartz, non-perforated |
| UV photolysis and heterogeneous photocatalysis and ozonation ($TiO_2$ 254 nm / $O_3$) | UV/VUV lamp | quartz, perforated |

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**Table 2.** Initial rate of transformation ($r_0$ ($\times 10^{-8}$ mol $L^{-1}$ $s^{-1}$)).

| | 254 nm | $O_3$ | $TiO_2$ 365 nm | 254 nm $O_3$ | $TiO_2$ 254 nm | $TiO_2$ 365 nm $O_3$ | $TiO_2$ 254 nm $O_3$ |
|---|---|---|---|---|---|---|---|
| Diuron | 13.6 ± 1.2 | 1.0 ± 0.05 | 7.9 ± 0.3 | 27.3 ± 0.9 | 11.0 ± 0.4 | 26.5 ± 0.8 | 25.0 ± 1.1 |
| monuron | 46.0 ± 2.2 | 0.6 ± 0.02 | 13.1 ± 0.4 | 56.8 ± 1.1 | 18.4 ± 0.5 | 25.8 ± 1.1 | 37.9 ± 1.6 |
| fenuron | 2.7 ± 0.2 | 10.6 ± 0.2 | 16.2 ± 0.3 | 22.5 ± 0.7 | 23.1 ± 1.2 | 37.7 ± 1.1 | 55.7 ± 1.7 |

## Results and discussion

### UV photolysis (254 nm)

The rate of photolytic transformation is determined by the molar absorbance and quantum yield of the compound. The absorption coefficients of the pesticides at 254 nm, determined via the Beer-Lambert law, were found to be 4500, 12500 and 15000 $mol^{-1}$ L $cm^{-1}$ of fenuron, monuron and diuron, respectively. At the applied initial concentration ($c_0 = 1.70 \times 10^{-4}$ mol $L^{-1}$), the diuron and monuron solutions absorbed the emitted photons fully, while the fenuron solution absorbed 80% of them.

Although diuron has a higher molar absorbance than monuron, monuron was transformed approximately 3 times faster than diuron (Table 2), which can be explained by the higher quantum yield. The apparent quantum yields, calculated on the basis of the absorbed photon flow and the initial rate of transformation, were 0.002, 0.03 and 0.008 for fenuron, monuron and diuron, respectively. The quantum yields determined by other authors for the transformation due to UV photolysis were systematically higher: 0.005 and 0.05[32] for fenuron and monuron respectively, and 0.0115[33] for diuron. Djebbar et al.[47] found that the quantum yield of photolysis of diuron at 253.7 nm was 0.0125, and was insensitive to pH in the range 2–8.5.

### Ozonation

In aqueous solutions molecular $O_3$ can decompose to form very reactive species such as $^\bullet$OH which is a stronger oxidizing agent ($E_0 = 2.80$ V) than $O_3$ ($E_0 = 2.07$ V). During the transformations of these chlorine containing compounds, the pH decreased from 6.9 to 3.8 and from 8.3 to 4.1 in the cases of monuron and diuron, respectively. Since the decomposition of $O_3$ in aqueous solution is initiated by $OH^-$, at neutral and/or acidic pH the dominant oxidant species should be molecular $O_3$.

The initial rates of transformation determined in this work (10.6 ± 0.2, 0.6 ± 0.02 and 1.0 ± 0.05 $\times 10^{-8}$ mol $L^{-1}$ $s^{-1}$ for fenuron, monuron and diuron, respectively; Table 2.) reflect the sequence of the rate constants of the reactions of $O_3$ with these substances.[36,37] This is in agreement with the electro-attracting effect of chlorine, which reduces the reactivity of the phenyl ring with regard to electrophilic attacks due to $O_3$. The results prove that a correlation is conceivable between the halogen content and the effectiveness of ozonation of these phenylurea pesticides.

### Heterogeneous photocatalysis ($TiO_2$ 365 nm)

The light emitted by the fluorescent lamp is suitable for the excitation of $TiO_2$, but no direct photolysis of the compounds occurred. The efficiency of heterogeneous photocatalysis and the reaction pathway of the transformation, which can be based on the $^\bullet$OH and/or direct electron transfer between the photogenerated positive hole and absorbed organic substance, depend strongly on the interaction of organic molecules with the $TiO_2$ surface.

The amount of organic substrate adsorbed at the given concentrations ($1.7 \times 10^{-4}$ mol $L^{-1}$ pesticide and 1.00 g $L^{-1}$ $TiO_2$) was <6% of the initial concentration in all cases. In the case of heterogeneous photocatalysis the adsorption kinetic is accepted.[25,40] The rate of transformation of the substrate exhibits a saturation curve as a function of amount of photocatalyst. Most of the studies involving heterogeneous photocatalysis are carried out with a 1.00 g $L^{-1}$ suspension of powdered photocatalyst in aqueous solutions.

Previously we have determined the absorbance of the $TiO_2$ suspension in the range of 0.02–1.00 g $L^{-1}$ $TiO_2$ using the same light sources. In our photoreactor applied, a 0.25 g $L^{-1}$ $TiO_2$ suspension fully absorbed the emitted light of both the low pressure mercury vapor lamp and the fluorescent lamp. $TiO_2$ concentrations in the interval of 0.25–1.00 g $L^{-1}$ did not exert a significant effect on the initial rate of transformation, probably because these values are close to the saturation point. On change of the $TiO_2$ concentration from 0.25 to 0.50 g $L^{-1}$, the rate of the transformation increased slightly, whereas on further to 1.00 g $L^{-1}$, the rate decreased slightly (Table 3), most probably because of the higher importance of the dispersion of light. Consequently, we used 0.50 g $L^{-1}$ of $TiO_2$ in the subsequent experiments.

With heterogeneous photocatalysis, a correlation was observed between the number of chlorine atoms in the pesticide molecules and their degradation rates (7.9, 13.1 and 16.2 $\times 10^{-8}$ mol $L^{-1}$ $s^{-1}$ for diuron, monuron and fenuron, respectively, (Table 2). A lower number of chlorine atoms on the aromatic ring were associated with a higher rate of transformation. A comparison of the heterogeneous photocatalysis of various well-adsorbed and non-adsorbed compounds, including diuron, led to the conclusion that the transformation of the non-adsorbed compounds, e.g. phenylurea pesticides, is initiated mainly by $^\bullet$OH-based reactions.[40] Oturan et al.[46] determined the rate constants of reactions of $^\bullet$OH with pesticides and

**Table 3.** Effects of the concentration of the $TiO_2$ suspension on the initial rate of transformation.

| | Concentration of $TiO_2$ suspension | | |
|---|---|---|---|
| | 0.25 g $L^{-1}$ | 0.50 g $L^{-1}$ | 1.00 g $L^{-1}$ |
| Diuron | 6.6 ± 0.7 | 7.9 ± 0.3 | 5.6 ± 0.6 |
| Monuron | 11.0 ± 1.3 | 13.1 ± 0.4 | 10.5 ± 0.8 |
| Fenuron | 15.0 ± 0.6 | 16.2 ± 0.6 | 12.0 ± 0.9 |

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reported $1.2 \times 10^{10}$, $7.3 \times 10^9$ and $4.8 \times 10^9$ $mol^{-1}$ L $s^{-1}$ for fenuron, monuron and diuron, respectively. Our results are of the same order for the rates of transformation, suggesting that the transformations of these compounds are probably initiated by $^\bullet$OH-based reactions.

## Combinations of methods

### Combination of UV photolysis and ozonation (254 nm / $O_3$)

The initial rates of degradation (Table 2) indicate that, the combination of UV photolysis and ozonation (254 nm/$O_3$) led to a synergistic effect since the degradation rates were higher than the sums of the separate rates, which can be explained mainly by the formation of $^\bullet$OH from $O_3$. Both UV photolysis and ozonation are quite selective methods for the oxidative transformation of organic substances. Their combination can produce reactive species through the UV photolysis of $O_3$, mainly $^\bullet$OH formed. 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.

The degree of this synergistic effect proved to be higher for diuron than for monuron $r_0$ (254 nm/$O_3$) / $r_0$ (254 nm) = 2.0 and $r_0$ (254 nm/$O_3$) / $r_0$ (254 nm) = 1.2, respectively. It should be mentioned that, in the cases of the chlorine-containing pesticides the relative contribution of the direct photolysis to the transformation probably remained high, because of their high molar absorbance and the relatively low concentration of $O_3$. Under the experimental conditions applied, the light absorption of $O_3$ was negligible compared to that of diuron or monuron. In the case of fenuron, the relative contribution of direct photolysis was probably lower and the radical-based reactions predominated when ozonation and UV irradiation were applied simultaneously. Addition of $O_3$ in relatively low concentration, led to an almost one magnitude higher rate of decomposition in this case ($r_0$ (254 nm/$O_3$) / $r_0$ (254 nm) = 8.1).

## Combination of UV photolysis and heterogeneous photocatalysis ($TiO_2$ / 254 nm)

As compared with the effectiveness of direct photolysis, the addition of $TiO_2$ dramatically decreased the rate of degradation of monuron ($r_0$ ($TiO_2$ / 254 nm) / $r_0$ (254 nm) = 0.4), but only slightly in the case of diuron ($r_0$ ($TiO_2$ / 254 nm) / $r_0$ (254 nm) = 0.8). In contrast, the rate of degradation of fenuron, ($r_0$ ($TiO_2$ /254 nm) / $r_0$ (254 nm) = 7.7) increased extremely (Table 2). With the combination of UV photolysis and heterogeneous photocatalysis, a competition for the 254 nm photons occurs between the organic substrates and the $TiO_2$ particles. Since 254 nm light is absorbed fully when the photocatalyst $TiO_2$ is added, direct photolysis is suppressed and heterogeneous photocatalysis is likely to predominate at 0.50 g $L^{-1}$ $TiO_2$. At the same time, the quantum yields of the transformation of organic substrates are quite low, when heterogeneous photocatalysis is applied. This may be one of the reasons why the addition of $TiO_2$ decreased the rates of transformation of chlorinated compounds, with relatively high molar absorbances and quantum yields of the direct photooxidative transformations. However, fenuron has a

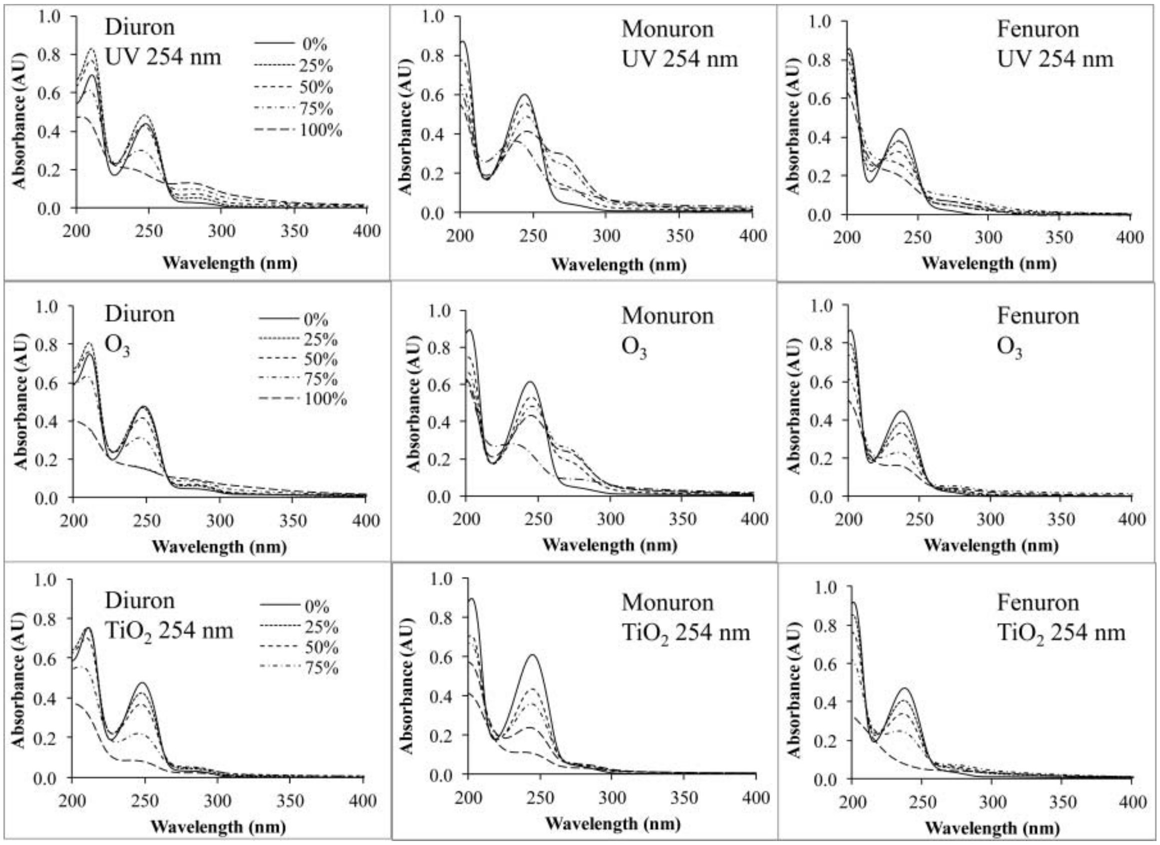

Figure 4. Spectra of the treated solutions individual methods [UV photolysis (254 nm), ozonation ($O_3$) and heterogeneous photocatalysis ($TiO_2$ / 365 nm)].

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relatively low molar absorbance, and the lowest apparent quantum yield of the direct photo-initiated transformation. Consequently, addition of the photocatalyst could enhance its rate of transformation by almost an order of magnitude.

In the cases of the irradiated $TiO_2$ suspensions, the ratio of the rate of transformation when a fluorescent lamp (365 nm) or a low-pressure mercury vapor lamp (254 nm) was utilized was found to be 1.3–1.4 and correlated with the ratio of the photon fluxes of the light sources ($8.10(\pm 0.65)\times 10^{-6}$ $mol_{photon}$ $s^{-1}$ at 254 nm and $1.20(\pm 0.06)\times 10^{-5}$ $mol_{photon}$ $s^{-1}$ at 365 nm, with a ratio of 1.5). This suggests that, the use of 254 nm light and 0.50 g $L^{-1}$ $TiO_2$ simultaneously suppresses the transformations due to the heterogeneous photocatalysis.

## Combination of heterogeneous photocatalysis and ozonation ($TiO_2$ 365 nm / $O_3$)

This process resulted in significantly higher rates of transformation relative to the single heterogeneous photocatalysis (Table 2) ($r_0$ ($TiO_2$ 365 nm/$O_3$) / $r_0$ ($TiO_2$ 365 nm) = 3.4 for diuron, 2.0 for monuron and 2.3 for fenuron) (Table 2). This could be attributed in part to the better electron-scavenging action of $O_3$ as compared with $O_2$, leading to an enhanced charge separation. On the other hand, the addition of $O_3$ results in more oxygen-containing reactive radicals (mainly $^{\bullet}OH$), which contribute to the degradation of both the target substances and their by-products.

## Combination of UV photolysis, heterogeneous photocatalysis and ozonation ($TiO_2$ / 254 nm / $O_3$)

The addition of $O_3$ to the 254 nm light-irradiated $TiO_2$-containing suspensions further increased the initial rates of transformation ($r_0$ ($TiO_2$/254 nm/$O_3$) / $r_0$ ($TiO_2$/254 nm) = 2.3 for diuron, 2.1 for monuron and 2.4 for fenuron similarly as in the case of the 365 nm irradiated $TiO_2$-containing suspensions. On the other hand, the addition of $TiO_2$ to the $O_3$ containing and 254 nm light-irradiated solutions caused a faster transformation only for fenuron ($r_0$ ($TiO_2$ / 254 nm/$O_3$) / $r_0$ (254 nm/$O_3$) = 0.9 for diuron, 0.7 for monuron and 2.5 for fenuron), which can be explained in that the significant light absorption of the solid catalyst completely suppressed the transformation by direct photolysis.

## Spectrophotometric measurement and HPLC results—intermediates

Spectrophotometric measurements were carried out in each case (Fig. 4). The absorbance of the UV-irradiated and ozonated solutions at ~270 nm increased during the decompositions of diuron and monuron varied according to maximum curves suggesting that aromatic intermediates accumulated and probably decomposed in these cases.

The maximum absorbance at ~277 nm was much higher in the UV-irradiated solutions than in ozonation or with a combination of ozonation and UV photolysis. The aqueous solution of diuron changed from colorless to a strong yellowish-pink, while the aqueous solution of monuron changed from colorless to intense pink when UV photolysis was applied. These color changes were weaker when the combination of UV photolysis and ozonation was applied. Each solution became colorless after decomposition of the parent compounds. On heterogeneous photocatalysis or ozonation, neither color change, nor the increase in absorbance was observed, indicating that the colored aromatic intermediates were most probably mainly formed during the direct UV photolysis.

The Figure 5 presents the chromatograms of the treated solutions at ~ 50% of decomposition. The retention time and the spectra of the peaks relating to the aromatic intermediates reveal that the same intermediates were formed on UV photolysis and on its combination with ozonation, but their quantities (the areas of the peaks) depended strongly on the method applied. Some of the intermediates were completely absent in the case of ozonation or heterogeneous photocatalysis. The relative amounts of the intermediates formed [i.e. Σ(area of peak of intermediate)/(area of peak of residual phenylurea pesticide)] indicate a lower amount of aromatic intermediates on ozonation. These observations again suggest that the amount of

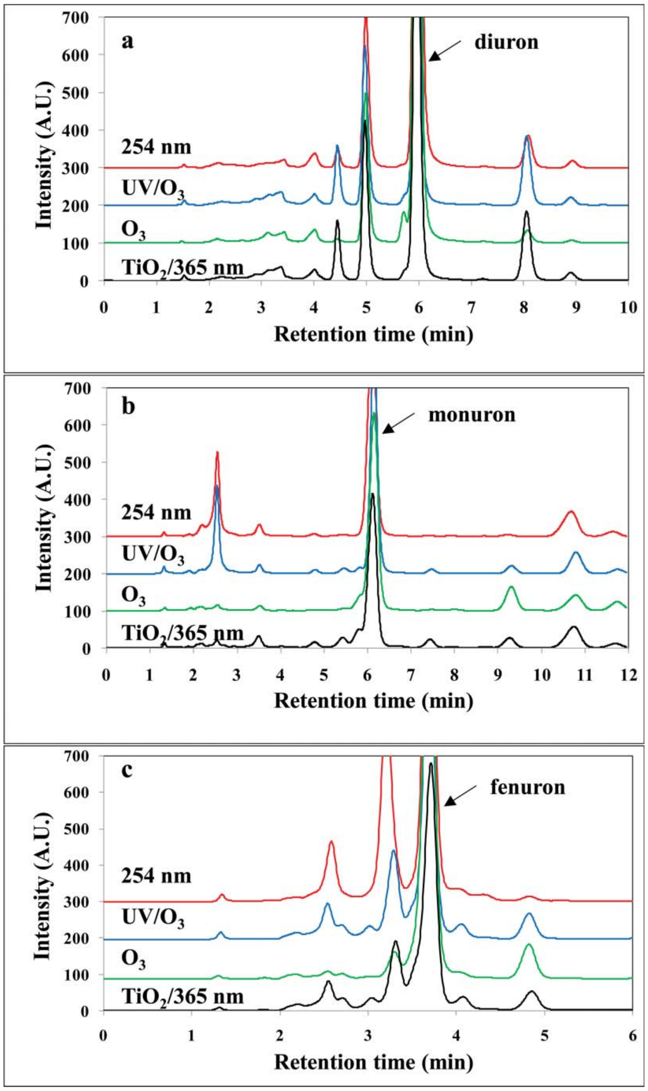

**Figure 5.** Chromatograms of the samples of the treated solutions, at 50% decomposed diuron, monuron and fenuron, individual methods [UV photolysis (254 nm), ozonation ($O_3$) and heterogeneous photocatalysis ($TiO_2$ / 365 nm)].

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the aromatic intermediates depend strongly on the processes applied. The further investigation of the by-products is needed considering the interesting results of spectrophotometric measurement, HPLC results and data obtained from the AOX measurements.

## Mineralization and dehalogenation

The results of the AOX and TOC measurements for each combined method are given in Figures 6 and 7, respectively. In each of the individual methods (UV photolysis, ozonation or heterogeneous photocatalysis), by 100% degradation of the target compounds, virtually no chlorines were present i.e. not only the pesticide itself but also the halogenated by-products were dechlorinated. The rate of dechlorination was higher on UV photolysis than on heterogeneous photocatalysis particularly initially. Direct UV photolysis is quite selective for the transformation of organic substances and can be effective for the transformation of compounds which absorb 254 nm light, such as our target substances and probably their aromatic intermediates, mainly through dissociation of the C-Cl bonds. On the other hand, adsorption has a crucial role in the case of

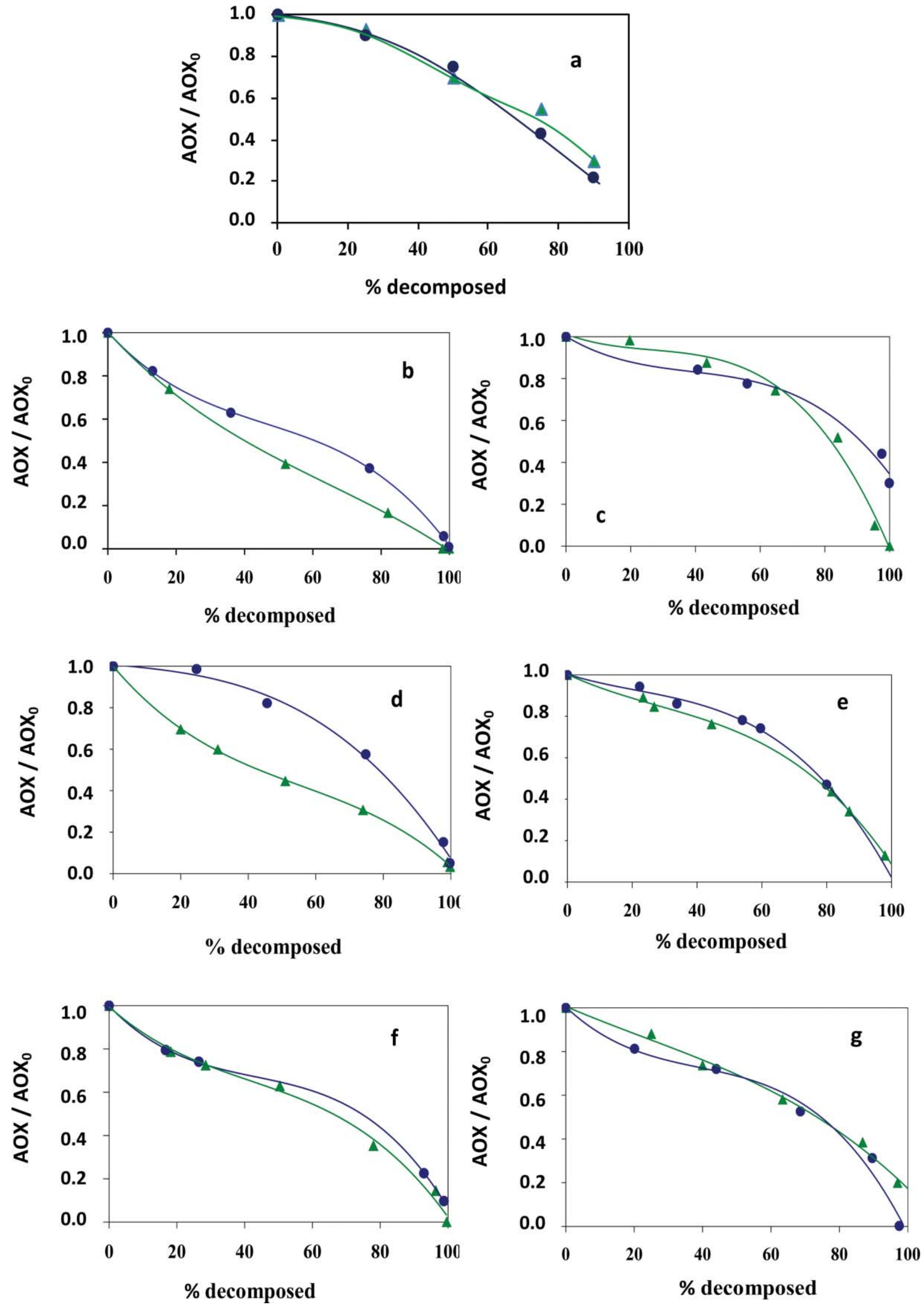

Figure 6. Relative concentration of adsorbable organically bound chlorine versus the percentage of decomposed diuron (•) or monuron (▲) a: Ozonation; b: UV photolysis; c: heterogeneous photocatalysis; d: combination of UV photolysis with ozonation; e: combination of heterogeneous photocatalysis with ozonation; f: combination of heterogeneous photocatalysis with UV photolysis; g: combination of heterogeneous photocatalysis and UV photolysis with ozonation.

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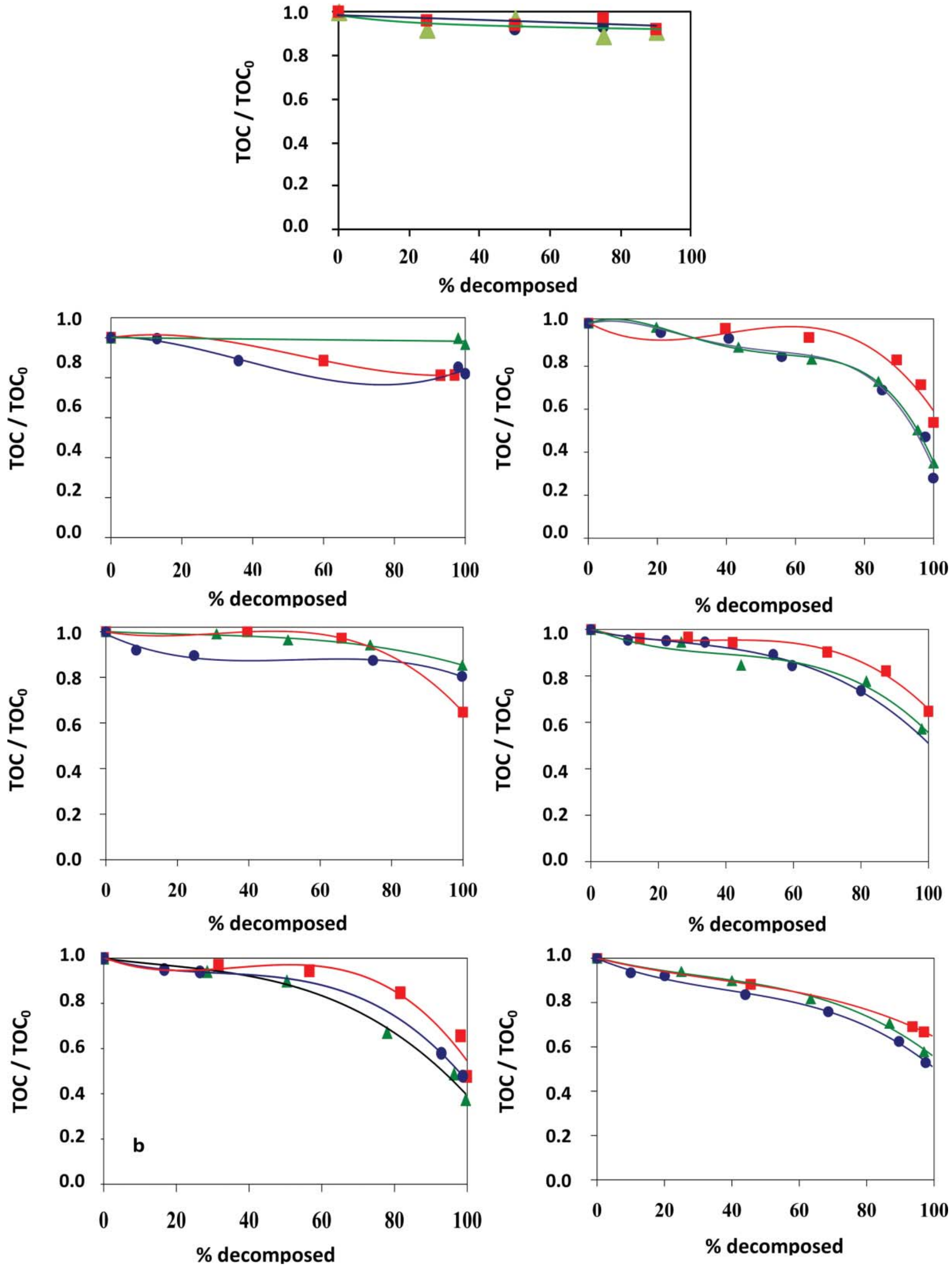

**Figure 7.** Relative concentration of total organic carbon (TOC) versus the percent of decomposed diuron (●), monuron (▲) or fenuron (■) a: Ozonation; b: UV photolysis; c: heterogeneous photocatalysis; d: combination of UV photolysis with ozonation; e: combination of heterogeneous photocatalysis with ozonation; f: combination of heterogeneous photocatalysis with UV photolysis; g: combination of heterogeneous photocatalysis and UV photolysis with ozonation.

heterogeneous photocatalyis. The photocatalytic transformation of acids that adsorb well on $TiO_2$ (formic acid, oxalic acid) was earlier shown to be induced mainly by the direct transfer of photogenerated holes, while compounds that do not adsorb well (4-chlorophenol and monuron) are degraded mainly through the action of photogenerated $^\bullet$OH with lower photoefficiency than for the well-adsorbed compounds.[40] Thus, both competitive adsorption and competition for $^\bullet$OH formed on the surface can occur between the aromatic compounds containing chlorine and the intermediates (mainly acids), which do not contain chlorine and have higher adsorptivity. The formation of intermediates can therefore somewhat decrease of the rate of dechlorination.

Since UV photolysis is quite ineffective for the transformation of aliphatic intermediates formed by opening of the aromatic ring while ozonation is quite selective for the transformation of organic substances, these methods are not effective in mineralization, as that was also observed in the present work. On heterogeneous photocatalysis, the initial rate of mineralization was very low, but the TOC decreased rapidly in the final stages of decomposition of the original compound. As compared with UV photolysis, heterogeneous photocatalysis is less selective method and generally results in the degradation and most often the mineralization of a large variety of organic substances. On the other hand, the transformation of compounds takes place on the surface

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of the $TiO_2$ particles, and adsorption also has a crucial role in this case. The better adsorptivity of aliphatic intermediates (mainly carboxylic acids) is probably the reason for this, as mineralization takes place in parallel with the transformation of the parent compounds. This explanation is in accord with the observation that the rate of change of the concentration of adsorbable organically bound chlorines increases when mineralization predominates.

In the cases of the combination of methods, the changes in AOX values as a function of the extent of decomposition of monuron and diuron exhibited similar tendencies; no organic chlorine-containing substances remained when the original compounds had been fully decomposed, similarly as in the individual methods. Moreover, the addition of ozone to the $TiO_2$-containing suspensions increased the initial rate of dechlorination relative to that of the simple heterogeneous photocatalysis of diuron or monuron, when the dechlorination started very slowly. The rate of mineralization was relatively high when $O_3$ was applied in combination with UV photolysis and/or heterogeneous photocatalysis, when the most important aspect was probably the impact of heterogeneous photocatalysis and/or the formation of $^{\bullet}OH$.

## Conclusions

Each applied AOP is suitable for the decomposition of the examined herbicides, fenuron, monuron and diuron. However, the degradation efficiencies depended considerably on the method used. One of the important aspects of the experimental conditions and results is the energy utilization of these AOPs. Since these light sources require the same electric power and no extra energy was involved (with the exception of the circulation of the solution), the energy utilization was inversely proportional to the measured reaction rate.

UV photolysis was found to be the most effective of the individual processes for chlorine-containing compounds, diuron and monuron. Ozonation was suitable for fenuron, in contrast with the chlorinated herbicides, where its effectiveness was negligible. The efficiency of heterogenous photocatalysis also depended strongly on the chlorine content, decreasing with increase of the number of chlorine atoms.

When process combinations were investigated, competitive light absorption was experienced during simultaneous UV photolysis and heterogeneous photocatalysis. With simultaneous 254 nm light and 0.50 g $L^{-1}$ $TiO_2$, direct photolysis is likely to be suppressed completely by heterogeneous photocatalysis. Consequently, the addition of $TiO_2$ to the 254 nm-irradiated solutions decreased the rates of transformation of diuron and monuron, but greatly increased that of fenuron. Addition of $O_3$ in a relative low concentration caused a further increase of the initial rate of transformation in each case.

Mineralization was found to be significant only during heterogeneous photocatalysis. Though with differing rates, dechlorination was complete in each case.

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