Photocatalytic ozonation of monuron over suspended and immobilized TiO$_2$ — study of transformation, mineralization and economic feasibility

Gergő Simon$^{a,b,c}$, Tamás Gyulavári$^{b,d}$, Klára Hernadi$^{b,d}$, Milán Molnár$^{a,c}$, Zsolt Pap$^{b,e,f,g}$, Gábor Veréb$^{b,h}$, Krisztina Schrantz$^{a,c}$, Máté Náfrádi$^{a,c}$, Tünde Alapi$^{a,c,*}$

$^a$Research Group of Environmental Analytical Chemistry, Institute of Chemistry, University of Szeged, H-6720, Dóm tér 7, Szeged, Hungary

$^b$Research Group of Environmental Chemistry, Institute of Chemistry, University of Szeged; H-6720, Tisza Lajos krt. 103., Szeged, Hungary

$^c$Department of Inorganic and Analytical Chemistry, Institute of Chemistry, University of Szeged, Dóm tér 7, H-6720 Szeged, Hungary

$^d$Department of Applied and Environmental Chemistry, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, H-6720 Szeged, Hungary

$^e$Faculty of Physics, Babeş–Bolyai University M. Kogălniceanu 1, RO–400084 Cluj–Napoca, Romania

$^f$Institute for Interdisciplinary Research on Bio-Nano-Sciences, Treboniu Laurian 42, RO–400271 Cluj-Napoca, Romania

$^g$Institute of Environmental Science and Technology, University of Szeged, Tisza Lajos krt. 103, Szeged HU-6720, Hungary

$^h$Department of Process Engineering, Faculty of Engineering, University of Szeged Moszkvai krt. 9., H-6725 Szeged, Hungary

$^*$Corresponding author: tel.: +36-62-54-4719, e-mail: alapi@chem.u-szeged.hu
Address: H-6720 Szeged, Dóm tér 7, Hungary

Graphical abstract
Highlights

- addition of O₃ increased the transformation and mineralization rate of monuron
- TiO₂ decreased the concentration of dissolved O₃
- synergism was not observed in the transformation or mineralization rate of monuron
- synergism manifested in the energy requirement of mineralization using susp-TiO₂/O₃

Abstract

The transformation and mineralization of monuron herbicide were investigated by heterogeneous photocatalysis, ozonation, and their combination (photocatalytic ozonation) at various ozone (O₃) concentrations (0–20 mg·dm⁻³ in gas phase), using TiO₂ in suspensions and in immobilized form.

The applied AOPs were characterized by the transformation and mineralization rate of monuron, the concentration of dissolved O₃, and the economic feasibility based on the values of Electrical Energy per Order related to the rate of decrease of monuron concentration and of the total organic carbon content. In the case of photocatalytic ozonation, the transformation and mineralization rate of monuron increased with the increase of O₃ concentration. However, there was no significant synergistic effect. Electrical Energy per Order decreased with the increase of O₃ concentration, and economical efficiency of the photocatalytic ozonation using TiO₂ in suspensions highly exceed that of both ozonation and heterogeneous photocatalysis regarding the value determined for the decrease of total organic carbon content.

Keywords: TiO₂ immobilization, monuron, photocatalysis, photocatalytic ozonation, ozone, Electric Energy per Order
1. Introduction

Although necessary, the application of pesticides can have severe negative effects for environmental systems, resulting in their accumulation in soil and appearance in waters, including drinking waters. Moreover, a number of these compounds are supposed or proven carcinogens, mutagens or endocrine disruptors (Bonnemoy et al., 2004; Benitez et al., 2009; Mestankova et al., 2011; Kottuparambil et al., 2013). Their removal from waters therefore is an important task, which can be achieved through the application of advanced oxidation processes (AOPs). The degradation of monuron (3-(p-chlorophenyl)-1,1-dimethylurea) and phenylurea pesticides in general has been studied using several methods, such as photolysis (Kovács et al., 2016a), gamma-radiolysis (Kovács et al., 2014b; Kovács et al., 2016b), electro- and photo–Fenton processes (Bobu et al., 2006; Oturan et al., 2010), ozonation (Tahmasseb et al., 2002; Kovács et al., 2016a), heterogeneous photocatalysis (Rao et al., 2010; Chu et al., 2012; Solís et al., 2016) or their combinations including photocatalytic ozonation (Bobu et al., 2006; Oturan et al., 2010).

Titanium dioxide (TiO$_2$) is generally considered the most adequate photocatalyst, as it is cheap, inert, and it has prominent photocatalytic activity. After the treatment, it is necessary to separate the TiO$_2$ particles, increasing the operation-cost of heterogeneous photocatalysis as water treatment method. Therefore, numerous attempts have been made to immobilize photocatalysts on various support materials (Krýsa et al., 2006; Behnajady et al., 2008; Tryba, 2008; Zhang et al., 2015). Moreover, immobilization of photocatalyst opens the possibility of heterogeneous photocatalysis application in continuous flow system. The photocatalyst particles can be immobilized onto the surface via several techniques, like dip-coating (Giornelli et al., 2007; Hosseini et al., 2007; Behnajady et al., 2008; Khataee et al., 2013), embedding the photocatalyst particles into polymers (Naskar et al., 1998; Fabiyi et al., 2000; Baudys et al., 2017), and also by electrophoretic deposition (Dunlop et al., 2008). While these methods use pre-made photocatalysts, there are processes, such as the sol-gel process (Balasubramanian et al., 2004; Gelover et al., 2004), or the chemical vapor deposition (Karches et al., 2002; Puma et al., 2008; Zhang et al., 2008), where the catalyst particles are formed in situ, thus their properties are more difficult to control.

While ozonation and heterogeneous photocatalysis are effective processes separately, their combination – photocatalytic ozonation – can have a synergistic effect both in oxidation and mineralization efficiency (Ilisz et al., 2004; Beltrán et al., 2005; Farré et al., 2005). Despite of the additional electrical energy for ozone generation, several publications proved that heterogeneous photocatalytic ozonation may be a cost-effective alternative for wastewater...
treatment primarily because of the shortened treatment time. (Kopf et al., 2000; Mehrjouei et al., 2014b). Synergistic effect was reported in the transformation and mineralization rate of various target substances (Jing et al., 2011; Aguinaco et al., 2012; Xiao et al., 2015; Fathinia et al., 2016) in aqueous solutions. The pH depending synergistic effect was demonstrated in the case of neonicotinoid insecticides (Černigoj et al., 2007). However Farré et al. (2005) reported that, there is no enhanced efficiency in the case of diuron and clofenvinphos, and only the mineralization was enhanced for nitrogen containing compounds (Klare et al., 1999). No enhanced efficiency was observed neither for transformation nor for the degradation rate of dichlorophenol (Melián et al., 2013) and Triton X-100 non-ionic surfactant (Hegedűs et al., 2015) using the combination of ozonation and heterogeneous photocatalysis.

Using UV irradiated TiO$_2$ the transformation of organic substances can occur via direct charge transfer or via \textquotesingle OH based reaction. The enhanced efficiency of photocatalytic ozonation can be explained by the considerably higher electron affinity of ozone (O$_3$) compared to oxygen (O$_2$) (Pichat et al., 2000; Mehrjouei et al., 2015). Thus, the role of O$_3$ as a more effective electron trap, must be considered. O$_3$ adsorbs onto the surface of TiO$_2$ via Lewis acid sites (dissociative adsorption) or by weak hydrogen bonds, resulting in active oxygen radicals (O'), which produce \textquotesingle OH by reacting with water molecules (Mehrjouei et al., 2015). The generation of one \textquotesingle OH consumes only one electron due to the transformation of O$_3$ on the surface of TiO$_2$, while using O$_2$ three electrons are needed (Sánchez et al., 1998; Klare et al., 1999). Consequently, the positive effect of O$_3$ can originated in two reasons: the enhanced separation and lifetime of photogenerated charges and higher formation rate of \textquotesingle OH.

The goal of this study is to investigate the degradation and mineralization of the phenylurea herbicide monuron (3-(p-chlorophenyl)-1,1-dimethylurea) by ozonation, heterogeneous photocatalysis – in TiO$_2$ suspensions and using self-made immobilized TiO$_2$ sheets – and their combination (photocatalytic ozonation) at various O$_3$ concentrations. The possibility of the synergistic effect was investigated through the transformation and mineralization rate of monuron. The quality and quantity of byproducts was also investigated. The economic feasibility of treatments was compared based on the obtained values of Electrical Energy per Order ($E_{EO}$) determined for the decrease of monuron concentration and total organic carbon content.

2. Materials and methods

2.1. Materials
Aeroxide P25® (73-85 % anatase and 14-17 % rutile (Ohtani et al., 2010), $S_{BET} = 35–65 \text{ m}^2\cdot\text{g}^{-1}$, $d_{\text{anatase}} \sim 25 \text{ nm}, d_{\text{rutile}} \sim 40 \text{ nm},$ Evonik Industries) was used either in suspension or immobilized onto a high-purity alumina based ceramic paper (1.6 mm thickness, cat. no.: 300-040-1, COTRONICS Co.). The immobilization process involved titanium ethoxide (Ti(OEt)$_4$, technical grade, Sigma-Aldrich) as fixing agent, and isopropyl alcohol (laboratory grade, VWR). High purity nitrogen gas (99.995 %, Messer) was used to spray the TiO$_2$ suspensions onto the surface.

The model compound was monuron (Fig. 1) (> 99 %, Sigma-Aldrich), the initial concentration was 0.5 mmol·dm$^{-3}$ in all experiments. The initial concentration of MeOH (HPLC pure, VWR) – used as hydroxyl radical scavenger – was 50 times higher, 250 mmol·dm$^{-3}$.

Oxygen (99.5 %, Messer) was used to saturate the aqueous solutions and to produce O$_3$. Indigo carmine dye (high purity, Janssen Chimica), NaH$_2$PO$_4$·2H$_2$O (99.0 %, Sigma-Aldrich) and Na$_2$HPO$_4$·2H$_2$O (99.0 %, Sigma-Aldrich) were used for the dissolved O$_3$ determination. For the total organic carbon (TOC) determination orthophosphoric acid (analytical grade, 85 wt. %, VWR) and high purity oxygen (99.9995 %, Messer) were used. Solutions were prepared in ultrapure Milli-Q water.

2.2. Preparation of the immobilized catalysts

The immobilization of TiO$_2$ was carried out following the method described by Veréb et al. (2014). The ceramic paper sheets (34.0×14.0 cm; 476.0 cm$^2$) were immersed in isopropyl alcohol, coated with Ti(OEt)$_4$ and evenly sprayed with isopropanol based TiO$_2$ suspension ($c_{P25} = 76.9 \text{ g} \cdot \text{dm}^{-3}$). Three ceramic papers – named P25-1, P25-2 and P25-3 – were made, having 0.777; 1.555 and 2.332 mg cm$^{-2}$ immobilized Aeroxide P25® on the surface by spraying various volumes (4.8, 9.6 and 14.4 cm$^3$, respectively) of the TiO$_2$ suspension. The prepared sheets were dried for 24 h at room temperature. The amorphous titanium oxide hydroxide formed partly covers and strongly fixes the Aeroxide P25® particles to the surface of the ceramic paper. The prepared sheets were illuminated with 365 nm light for 24 h to evaporate the residual volatile compounds (mainly alcohols) and elimination of organic matter adsorbed on the surface via heterogeneous photocatalysis.

The transformation of monuron was investigated using photocatalyst in suspensions and in immobilized form in the reactor presented in section 2.4. Using 500 cm$^3$ (total volume of the reactor) suspension having 1.0, 2.0 and 3.0 g·dm$^{-3}$ TiO$_2$ concentrations, the amount of TiO$_2$ in
the irradiated volume (370 cm³) were the same than the amount of TiO₂ fixed on the ceramic papers named P25-1, P25-2 and P25-3.

2.3. Analytical methods

Scanning Electron Microscopy (SEM) measurements were made using a Hitachi S-4700 Type II FE-SEM instrument, which operates using a cold field emission gun (5-15 kV). The X-ray diffractograms (XRD) were taken by a Rigaku Miniflex II diffractometer using Cu-Kα radiation (λ = 1.5406 Å), equipped with a graphite monochromator. Data points were taken in the 2θ = 20–40 ° range at a scan speed of 1·min⁻¹. A series of calibration samples were prepared from ceramic sheets milled and mixed with calculated amounts of Aeroxide® P25. From the XRD patterns, the anatase diffraction peak at 25.6 ° was integrated, and calibration was based on the peak area. Ceramic sheets containing the immobilized P25 were treated similarly to the calibration samples.

A JASCO-V650 spectrophotometer with an integration sphere (ILV-724) was used for measuring the diffuse reflectance spectra (DRS) of the samples (λ = 300–800 nm). The possible electron transitions were evaluated by plotting the dR/dλ vs. λ, where R is the reflectance and λ is the wavelength (Pap et al., 2014).

Agilent 8435 UV-Vis spectrophotometer was used to measure the concentration of gaseous O₃ at 254 nm wavelength (ε₂₅₄ nm = 2950 mol⁻¹·dm³·cm⁻¹ (Hart et al., 1983)), using a 1.0 cm quartz flow-through cell at 500 cm³·min⁻¹ gas flow.

The concentration of monuron was determined by high performance liquid chromatography (HPLC), using an Agilent 1100 modular HPLC system with a LiChroCART® C-18 column (250×4 mm, 5 µm particle size) equipped with a diode array detector (DAD) detector. The measurements were made at 25 °C using a mixture of methanol and water mixture (60:40 V/V %) as eluent at 1.0 cm³·min⁻¹ flow rate. The quantification wavelength was 244 nm. The intermediates were separated and detected by the same HPLC system equipped with Agilent G1956A quadrupole mass spectrometric (MS) detector. The MS analysis was carried out in positive and negative ion modes, with an electrospray ionization source (ESI) using 70 and 90 V fragmentor voltages.

The TOC analyses were carried out using an Analytik Jena multi N/C® 3100 apparatus equipped with NDIR detector. The furnace temperature was 800 °C and 1.0 cm³ samples were injected. Three parallel measurements were made in each case.

The concentration of dissolved O₃ was determined spectrophotometrically by the indigo carmine method (Bader et al., 1981; Chiou et al., 1995).
2.4. Photoreactor
All experiments were performed in the same photoreactor (SUP1). The light source was a fluorescent UV lamp (15 W, GCL303T5/365 nm, LightTech), which emits photons with wavelengths of 300-400 nm with a radiation maximum at 365 nm (SUP2). The photon flux \((1.20(\pm0.06) \times 10^{-5} \text{ mol\_photon s}^{-1})\) was determined by potassium ferrioxalate actinometry (Hatchard et al., 1956). UV lamp with the perforated glass envelope (length 320 mm and internal diameter 28 mm) was centred in the water-cooled, tubular glass reactor (length 340 mm, internal diameter 46 mm, volume 370 cm\(^3\)). The reactor was closed with a screw-off Teflon top fixed to the light source and its envelope. In case of heterogeneous photocatalysis (using suspended TiO\(_2\) (susp-TiO\(_2\)) or immobilized TiO\(_2\) containing ceramic sheet (34.0×14.0 cm) fitted to the inside wall of the reactor (imm-TiO\(_2\)) oxygen (O\(_2\)), while in the case of ozonation and the combined methods (susp-TiO\(_2\)/O\(_3\) and imm-TiO\(_2\)/O\(_3\)) O\(_3\) containing O\(_2\) gas was lead into the reactor through the Teflon packing ring. An ozonizer (Ozomatic Modular 4HC, max. 95 W) was used to produce O\(_3\). Thus, O\(_2\) or O\(_3\) was lead between the wall of the fluorescent lamp and the perforated glass envelope, and bubbled through the irradiated volume of solution/suspension. The solutions were saturated with O\(_2\) for 10 minutes before the kinetic measurements, which were started by switching on the light source and ozonizer. The thermostated (25±0.5 °C) monuron solution (500 cm\(^3\), 5.0·10\(^{-4}\) mol·dm\(^{-3}\)) was circulated (375 cm\(^3\)-min\(^{-1}\)) continuously and stirred in the reservoir. The formal initial transformation rates of monuron were obtained by linear regression fitting to the initial, linear segment of the kinetic curves. Kinetic measurements (heterogeneous photocatalysis (using TiO\(_2\) in both suspended and immobilized form), ozonation and combination of methods were repeated three times, to check their reproducibility.

2.5. Electrical Energy per Order
When choosing the best method for wastewater treatment, some significant factors should be taken under consideration. The economic factor is often seen as the most relevant as AOPs are electric-energy-intensive methods (Bolton et al., 2001). To compare the economic efficiency of the applied AOPs the values of Electrical Energy per Order (\(E_{EO}\)) were calculated for both monuron transformation (\(E_{EO}^{\text{c}}\)) and mineralization (\(E_{EO}^{\text{TOC}}\)). Calculation is based on the standard figures of-merit for the comparison of energy established regardless of the nature of the system, developed by Bolton et al. (2001). The amount of electric energy is 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 [kWh] required to treat 1 m$^3$ of contaminated water (Bolton et al., 2001). $E_{EO}$ values [kWh·m$^{-3}$·order$^{-1}$] are calculated using the following formula in a batch system:

$$E_{EO}^C = \frac{P \times t \times 1000}{V \times \lg(c_i/c_f)}$$  \hspace{1cm} (1)

$$E_{EO}^{TOC} = \frac{P \times t \times 1000}{V \times \lg(TOC_i/TOC_f)}$$  \hspace{1cm} (2)

where $P$ is the rated power [kW] of the AOT the system, $V$ is the volume [dm$^3$] of water treated, $t$ [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. The determination of $t$ necessary for the monuron concentration or TOC decrease from $c_i$ to $c_f$ and TOC$_i$ to TOC$_f$, when necessary, was based on extrapolation of the measured data.

In the present work the power (P) was calculated by the sum of the electric power required for the UV lamp (15 W) and the power needed for ozonizer to generate required O$_3$ concentrations (9.3, 13.8, 18.3, 22.8 W to generate 5.0, 10.0, 15.0, 20.0 mg·dm$^{-3}$ O$_3$ in gas phase, respectively). Similar calculation was presented by Mehrjouei et al. (2014a, b) and Cardoso et al. (2016).

3. Results and discussion
3.1. Characterization of the immobilized TiO$_2$ containing ceramic sheets
The structural and optical analyses were made to verify the success of the immobilization, to determine the possible changes in optical properties and the exact amount of immobilized TiO$_2$ on the ceramic sheets. SEM micrographs provided direct evidence of the successful immobilization of TiO$_2$ nanoparticles on the surface of the ceramic paper. Increasing the amount of the immobilized photocatalyst, larger aggregates of nanoparticles were detected (Fig. 2).

XRD measurements were performed in order to determine the amount of P25 fixed on the ceramic sheets (Table 1. and SUP3.). The amount of TiO$_2$ immobilized was calculated from the volume and concentration of TiO$_2$ suspension sprayed during the process of immobilization (calculated amount). The determination of the immobilized TiO$_2$ amount was
based on XRD data (measured amount) and verified that, the amount of immobilized TiO₂ correspond well to the calculated values (Table 1).

To verify the optical properties of the ceramic papers, DRS spectra were recorded (Fig. 3). In case of the Ti(OEt)₄ impregnated sheet the band-gap value calculated according to (Flak et al., 2013; Baia et al., 2014; Kovács et al., 2014a) was 3.9 eV (320 nm), which is close to the value registered for amorphous titanium oxide hydroxide (Cheng et al., 2014). Al₂O₃ having band-gap value (7.0 eV (Filatova et al., 2015)) cannot be detected in this range. After the addition of P25, the registered dR/dλ curves and the evaluated band-gap values corresponded to P25. With the increase of the amount of immobilized P25 no significant optical changes were registered.

Heterogeneous photocatalytic measurements were carried out using ceramic sheets containing various amount of P25, such as P25-1, P25-2 and P25-3. There was no significant difference found on the transformation rate of monuron (max. 8 %), using P25-1, P25-2 and P25-3 samples. These results showed that, the ‘active’ surface of immobilized photocatalyst, which can be reached by the monuron, O₃ and UV light, could not be increased by this way. Due to these results, all further experiments were done using 0.777 mg·cm⁻² catalyst surface loading when TiO₂ was applied in immobilized form. In this way, the amount of photocatalyst immobilized was the same as using TiO₂ in suspension, 1.0 g·dm⁻³ concentration, and 500 cm³ total volume (Table 1, first row).

3.2. Reproducibility of the immobilization and the reusability of catalyst sheets
The reproducibility of the preparation of immobilized TiO₂ containing sheets was investigated by the photocatalytic transformation of monuron. Three P25-1, immobilized P25 containing ceramic sheets were made and tested by the same way. There was no significant difference among the measured transformation rates (less than 9%).

The reusability of this ceramic paper with immobilized TiO₂ in the case of simple photocatalysis was verified in the publication of Veréb et al. (2014). In our work the reusability of a TiO₂ containing sheet was tested by photocatalytic ozonation of monuron, using 10 mg·dm⁻³ gaseous O₃. The photocatalytic ozonation (imm-TiO₂/O₃, 10 mg·dm⁻³ O₃) was repeated three times, using the same P25-1 sheet. The transformation rate did not change significantly (max. 4%), confirming that the ceramic sheet can be reused even in the presence of O₃.
3.3. Transformation and mineralization rate of monuron

The comparison of the efficiency of ozonation, photocatalysis and photocatalytic ozonation using photocatalyst in both suspended and immobilized form was based on the initial transformation rates of monuron (Table 2).

The contribution of direct photolysis to the transformation of monuron was determined. The aqueous solution of monuron was irradiated for 60 min using the fluorescent light source. The results showed neither significant decrease in the concentration of monuron, nor change in the spectra of the treated samples. Consequently, the contribution of the direct photolysis to the transformation of monuron in UV irradiated suspension was negligible.

Reactivity of phenyl-urea pesticides toward O$_3$ decreases when Cl is attached to the aromatic ring due to the electro-attracting effect of chlorine, as presented by Benitez et al. (2007) and (Kovács et al., 2016a). In the case of the heterogeneous photocatalysis, the transformation of monuron was suggested to take place mainly through hydroxyl radicals (Krýsa et al., 2006) due to the negligible adsorption monuron and the high value of the rate constant of the reaction of monuron with hydroxyl radical ($7.3 \cdot 10^9$ mol$^{-1}$·dm$^3$·s$^{-1}$ (Oturan et al., 2010)).

The immobilized form (imm-TiO$_2$/O$_3$) proved to be less effective compared to the suspended catalyst (susp-TiO$_2$/O$_3$) (Fig. 4 and Table 2). Suspended TiO$_2$ performs a high total surface area of TiO$_2$ per unit volume, while its immobilized form is often associated with mass transfer limitation over the TiO$_2$ layer. In our case the negative effect of immobilization is most likely because of the strongly decreased surface of P25 particles which can be reached by the monuron, O$_3$ and UV light.

In the present work the increasing amount of O$_3$ improved the transformation rate of monuron in each case (Table 2 and Fig. 4a-c.) and the initial rate of transformation depended linearly on the concentration of O$_3$ in gas phase (SUP4). Increasing the O$_3$ concentration improved the efficiency of the imm-TiO$_2$ process to a larger extent, as the addition of 20 mg·dm$^{-3}$ O$_3$ increased the rate of transformation by up to ~6 times (from $8.1 \cdot 10^{-8}$ to $4.98 \cdot 10^{-7}$ mol·dm$^{-3}$·s$^{-1}$), whereas in the case of susp-TiO$_2$/O$_3$ this increase was only ~3 times (from $2.44 \cdot 10^{-7}$ to $6.86 \cdot 10^{-7}$ mol·dm$^{-3}$·s$^{-1}$). The increase of O$_3$ concentration from 5 mg·dm$^{-3}$ to 20 mg·dm$^{-3}$ itself also increased the reaction rate by up to ~5 times in the case of simple ozonation (from $7.8 \cdot 10^{-8}$ to $4.17 \cdot 10^{-7}$ mol·dm$^{-3}$·s$^{-1}$). In the case of TiO$_2$/O$_3$ method, the positive effect of added O$_3$ is most likely due to both the enhanced transformation rate of monuron via its direct reaction with molecular O$_3$. At the same time, using TiO$_2$/O$_3$ method, the relative contribution of the hydroxyl radicals formed via decomposition of dissolved O$_3$ on the surface of TiO$_2$ can be significant. Consequently, TiO$_2$ decreased the concentration of
dissolved O$_3$. This effect is more significant using TiO$_2$ in suspension because immobilization strongly decreases the surface of TiO$_2$. Moreover, the effect of O$_3$, as a more effective electron trap than O$_2$ must be also considered.

The relative contribution of hydroxyl radical based reactions to the monuron transformation can be determined by the effect of MeOH as hydroxyl radical scavenger on the initial transformation rate of monuron. The addition of MeOH decreased this value from 14.8 to 7.4 mol dm$^{-3}$ s$^{-1}$ using simple ozonation ($c_{O3} = 10$ mg·dm$^{-3}$). Consequently, the amount of monuron transformed via reaction with hydroxyl radical is commensurable with the amount of monuron transformed via reaction with O$_3$ even at pH 5.5. Similar conclusion was reported by Tahmasseb et al. (2001) under analogous conditions. We have also determined the MeOH effect at pH 11, when the decomposition of O$_3$ and the formation of hydroxyl radical are strongly enhanced by the hydroxide ions. In this case the effect of MeOH was more pronounced and decreased the initial rate from 28.3 to 8.3 mol·dm$^{-3}$·s$^{-1}$. Using heterogeneous photocatalysis ($r_0$ decreased from 24.4 to 5.07 mol·dm$^{-3}$·s$^{-1}$) or its combination with ozonation ($r_0$ decreased from 42.5 to 8.4 mol·dm$^{-3}$·s$^{-1}$), the considerable negative effect of MeOH confirmed that, the transformation is mainly due to the hydroxyl radical based reaction in both cases. These obtained values, together with the fact that the suspended TiO$_2$ decreased the dissolved O$_3$ concentration (Table 2), confirm that the addition of O$_3$ to the TiO$_2$ suspension enhances the rate of hydroxyl radical formation and the relative contribution of hydroxyl radical based reaction to the monuron degradation.

One of the main advantages of combining AOPs is the possible synergistic effect. We compared the initial transformation rates of monuron by using the combined processes with the sum of the transformation rates resulted by the corresponding separate methods. Although a minor increase (max. 10 %) in the efficiency of the combined methods could be seen, there was no significant synergism regarding to the transformation rate of monuron under the experimental conditions applied in this work. This could be due to the relative high contribution of the reaction with O$_3$ to the transformation of monuron. (Table 2) Similar conclusion was made by Farré et al. (2005) regarding the transformation rate of diuron. When monuron transformed completely, the decrease of the TOC reached 56% using suspended TiO$_2$ without O$_3$, while ozonation resulted in 31% mineralization at highest O$_3$ concentration (SUP5. and Fig. 4d-e). Byproducts formed mainly during heterogeneous photocatalysis via hydroxylation of aromatic ring (3-(4-chloro-hydroxyphenyl)-urea (Fig. 5a)) and N-demethylation (3-(4-chloro-hydroxyphenyl)-1-methyl urea) (Fig. 5b)). During ozonation the main intermediate was 3-(4-chlorophenyl)-1-methylurea (Fig. 5c), which
formed via N-demethylation. In case of the susp-TiO$_2$/O$_3$ method, O$_3$ strongly enhanced the rate of accumulation and decomposition of intermediates 3-(4-chloro-hydroxyphenyl)-1-methyl urea (Fig 5d) and 3-(hydroxy-4-chlorophenyl)-1,1-methyl urea (Fig. 5e). This observation is agreement with the enhanced TOC removal efficiency due to the increase of O$_3$ concentration. (Table 2. and Fig. 4). Tahmasseb (2002) suggested two main pathways of degradation during ozonation: N-demethylation and OH-substitution of a Cl atom on the phenyl ring. In addition, the transformation mechanism of monuron using heterogeneous photocatalysis includes the hydroxylation of the aromatic ring too (Bobu (2006), Fenoll (2013)). The intermediates identified in our work are in agreement with mechanisms suggested in these works. Considering the evolution of the concentration of detected by-products (Fig. 4 and 5.), their accumulation and decomposition seems to occur in parallel with the transformation of monuron. Similar to the transformation rate of monuron, the efficiency of mineralization using combination of methods (susp-TiO$_2$/O$_3$) only slightly exceeded (with max. 14%) the sum of the mineralization efficiency of the susp-TiO$_2$ and ozonation. (SUP5.) The transformation and mineralization of the monuron can take place due to the reaction with molecular O$_3$, hydroxyl radicals and through the reaction of photogenerated charges with adsorbed monuron. The negative effect caused by the decreased concentration of dissolved O$_3$ due to the presence of TiO$_2$ (Table 2) was probably overcompensated by its positive effect on the concentration of formed hydroxyl radical due to the photocatalytic transformation of O$_3$.

3.4. Economic aspects of the applied processes

To compare the economic efficiency of the applied AOPs the values of $E_{EO}$ were calculated for both monuron transformation ($E_{EO}^c$) (6a-c) and mineralization ($E_{EO}^{TOC}$) (6d-f). The $E_{EO}$ values decreased with the increase of O$_3$ concentration in each case (Fig. 6). The application of imm-TiO$_2$/O$_3$ resulted in significantly higher $E_{EO}^c$ values than ozonation or susp-TiO$_2$/O$_3$ process (Fig 6c), mainly at lower concentrations of O$_3$. There was no significant difference between the energy requirement of ozonation and susp-TiO$_2$/O$_3$ process regardless of the O$_3$ concentration. However, it should be noted, that the energy requirement of TiO$_2$ separation from suspension was not taken into account. The energy requirement of microfiltration of P25 is about 100 - 300 kWh·m$^{-3}$ and depends strongly on the operation conditions (type of membrane, transmembrane pressure, filtration rate, etc). This value can be decreased with the combination of filtration with vibration (Massé et al., 2011) or coagulation (Judd et al., 2001). In our study, the $E_{EO}^c$ value determined for both susp-TiO$_2$ (30 kWh·m$^{-3}$
and in immobilized form, ozonation, and their combination at various O
of various AOPs, such as heterogeneous photocatalysis, using photocatalyst in suspensions and in immobilized form, ozonation, and their combination at various O₃ concentrations (0–

3·order⁻¹) and imm-TiO₂ processes (85 kWh·m⁻³·order⁻¹) are lower than the estimated energy requirement of microfiltration. Moreover, the difference between the EEOc values of susp-TiO₂/O₃ and imm-TiO₂/O₃ is definitely lower than the minimum energy requirement of microfiltration (100 kWh·m⁻³) of TiO₂. Consequently, the running cost of imm-TiO₂/O₃ method must be lower than the sum of the running cost of microfiltration and susp-TiO₂/O₃ method.

The combination of susp-TiO₂ with ozonation only slightly enhanced the efficiency of both transformation and mineralization rates (Table 2 and Fig. 4), and its economic efficiency corresponded to ozonation, as proved by EEOc values (Fi. 6c). However, the significant positive effect of the O₃ addition to the irradiated susp-TiO₂ is well manifested in EEOc TOC values (Fig. 6f) even at high O₃ concentrations. Using either 15 or 20 mg·dm⁻³ O₃, the EEOc and EEOc TOC values are comparable (Fig. c and f). As Fig. 4 shows the decrease of monuron concentration takes place parallel with decrease of the TOC content, with similar rate in these cases. There was no significant difference between EEOc values for ozonation and the susp-TiO₂/O₃ process (Fig. ), opposed to the EEOc TOC values (Fig. 6f), where the combined process proved to be superior and required only the 30-34% of the EEOc TOC value of the ozonation using either 15 or 20 mg·dm⁻³ O₃.

When immobilized catalyst is used, the EEOc TOC values were the highest. Comparing the EEOc TOC values, the following observations can be made: addition of O₃ at highest concentration (20 mg·dm⁻³) decreased ~50% the EEOc TOC value compared to imm-TiO₂ (from 573 to 306 kWh·dm⁻³·order⁻¹). However, the EEOc TOC of imm-TiO₂/O₃ (306 kWh·dm⁻³·order⁻¹) was more than two times higher than the EEOc TOC of simple ozonation (130 kWh·dm⁻³·order⁻¹), and about seven times higher than the energy requirement of susp-TiO₂/O₃ (44 kWh·dm⁻³·order⁻¹) (Fig. f). Moreover, the value of EEOc TOC of imm-TiO₂/O₃ (285 - 306 kWh·m⁻³·order⁻¹) is commensurable or most probably higher than the sum of the minimum energy requirement of filtration and EEOc TOC related to the application of susp-TiO₂/O₃ (213 - 144 kWh·m⁻³·order⁻¹).

4. Conclusions

In this study the transformation and mineralization of monuron and the economic feasibility of various AOPs, such as heterogeneous photocatalysis, using photocatalyst in suspensions and in immobilized form, ozonation, and their combination at various O₃ concentrations (0–
20 mg·dm⁻³) were investigated. Ceramic sheets containing well fixed P25 were characterized by XRD, DRS and SEM measurements. However significant synergism was not observed, kinetic measurements proved that addition of O₃ increased the rate of both transformation and mineralization. To compare the methods from economic aspect, $E_{EO}$ values related to the decrease of monuron concentration ($E_{EO}^c$) and TOC content ($E_{EO}^{TOC}$) were calculated. Both $E_{EO}^c$ and $E_{EO}^{TOC}$ values decreased with the increase of O₃ concentration. There was no significant difference between $E_{EO}^c$ values for ozonation and the susp-TiO₂/O₃ process, opposed to the $E_{EO}^{TOC}$ values, where the combined process proved to be superior and required only ~30% of the $E_{EO}^{TOC}$ value of the ozonation.

5. Acknowledgement

G. Veréb acknowledges the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The support of the Swiss Contribution (SH7/2/20) and Bilateral Scientific and Technology (S&T) cooperation between Hungary and India (TÉT_15_IN-1-2016-0013) is acknowledged and greatly appreciated.
6. References


10.1016/j.chemosphere.2005.09.034


Ohtani, B., Prieto-Mahaney, O.O., Li, D., Abe, R., 2010. What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and
10.1016/j.jphotochem.2010.07.024


20


Figure captions

Fig. 1 The chemical structure of monuron (3-(p-chlorophenyl)-1,1-dimethylurea)

Fig. 2 SEM images of the bare ceramic paper (a) and the ceramic papers containing various amount of immobilized TiO$_2$ (P25-1 (0.777 mg·cm$^{-2}$) (b); P25-2 (1.555 mg·cm$^{-2}$) (c); and P25-3 (2.332 mg·cm$^{-2}$) (d)
Fig. 3 The DRS spectra (a) and their derivative curves (b) of the ceramic paper impregnated with Ti(OEt)$_4$ and the ceramic papers containing various amount of immobilized P25 (P25-1: 0.755 mg·cm$^{-2}$; P25-2: 1.445 mg·cm$^{-2}$; P25-3: 2.315 mg·cm$^{-2}$ (measured values))

Fig. 4 The relative concentration (c/c$_0$) of monuron (a, b and c) and the relative TOC content (TOC/TOC$_0$) of the treated solutions (d, e and f) versus the time of treatment 
a, d: ozonation; b, e: susp-TiO$_2$/O$_3$; c, f: imm-TiO$_2$/O$_3$
Fig 5 The chromatographic peaks of formed intermediates (A: 3-(4-chloro-hydroxyphenyl)-urea; B: 3-(4-chloro-hydroxyphenyl)-1-methyl urea C: 3-(4-chlorophenyl)-1-methylurea; D: 3-(4-chloro-hydroxyphenyl)-1-methyl urea (stereoisomer of B) E: 3-(hydroxy-4-chlorophenyl)-1,1-methyl urea ) versus time of treatment
Fig. 6 The $E_{EO}^{c}$ values determined for monuron transformation and $E_{EO}^{TOC}$ values determined for monuron mineralization: $E_{EO}^{c}$, imm-TiO$_2$/O$_3$ (a), $E_{EO}^{c}$, susp-TiO$_2$/O$_3$ (b) (white: the part of $E_{EO}^{c}$ required by the UV light source; grey: the part of $E_{EO}^{c}$ required by the ozonizer) and the values of $E_{EO}^{c}$ of each methods (c), $E_{EO}^{TOC}$, imm-TiO$_2$/O$_3$ (d), $E_{EO}^{TOC}$, susp-TiO$_2$/O$_3$ (e) and the values of $E_{EO}^{TOC}$ to compare the methods (f)
Table 1 Calculated and measured amount of TiO$_2$ immobilized on ceramic sheets

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$ immobilized (calculated) (mg·cm$^{-2}$) / (mg)</th>
<th>TiO$_2$ immobilized (measured) (mg·cm$^{-2}$) / (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25-1</td>
<td>0.777 / 370</td>
<td>0.755 / 359</td>
</tr>
<tr>
<td>P25-2</td>
<td>1.555 / 740</td>
<td>1.445 / 688</td>
</tr>
<tr>
<td>P25-3</td>
<td>2.332 / 1110</td>
<td>2.315 / 1102</td>
</tr>
</tbody>
</table>

Table 2 The initial transformation rates of monuron ($r_0$) and the corresponding equilibrium concentrations of dissolved O$_3$ ($c_{O_3}$)

<table>
<thead>
<tr>
<th>$c_{O_3}$ in gas phase (mg·dm$^{-3}$)</th>
<th>Initial rates of transformation ($r_0$ ($\times 10^3$ mol·dm$^{-3}$·s$^{-1}$)) and equilibrium concentrations of dissolved O$<em>3$ ($c</em>{O_3}$ (mg·dm$^{-3}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>ozonation</td>
<td>$r_0$</td>
</tr>
<tr>
<td></td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>$c_{O_3}$</td>
</tr>
<tr>
<td>photocatalytic ozonation using TiO$_2$ in suspension (susp-TiO$_2$/O$_3$)</td>
<td>$r_0$</td>
</tr>
<tr>
<td></td>
<td>24.4±2.2</td>
</tr>
<tr>
<td></td>
<td>$c_{O_3}$</td>
</tr>
<tr>
<td>photocatalytic ozonation using TiO$_2$ in immobilized form (imm-TiO$_2$/O$_3$)</td>
<td>$r_0$</td>
</tr>
<tr>
<td></td>
<td>8.1±1.0</td>
</tr>
<tr>
<td></td>
<td>$c_{O_3}$</td>
</tr>
</tbody>
</table>