Theses of doctoral (PhD) dissertation

Removal of nitrogen-containing organic pollutants and the effect of reaction parameters during heterogeneous photocatalysis

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1. Introduction and short literary review

Water pollution is one of the serious environmental problems caused by human activities. Several non- or hardly biodegradable organic pollutants are released into the environment via effluent of treated wastewaters because traditional water-treatment methods are inefficient in completely removing them. In natural waters and drinking water bases, the pollutants having biological activity can cause serious environmental damage and can be the origin of severe public health problems [1]. Advanced oxidation processes are additional water treatment methods for removing these trace amounts of contaminants from treated wastewaters. Heterogeneous photocatalysis, one of these processes, is based on the oxidation and reduction reactions on the surface of semiconductor photocatalysts illuminated at appropriate wavelengths. [2] However, even with the widely studied TiO_2 and ZnO photocatalysts, the exact mechanism for the conversion of contaminants is often uncertain. To further develop heterogeneous photocatalysis, it is necessary to have a detailed knowledge of the processes taking place and to study the transformation of organic compounds.

Besides the chemical structure of the target pollutant, the reaction mechanisms depend on their adsorption on the surface and the properties of the photocatalyst [3,4]. In photocatalysis, the significance of adsorption is widely accepted, but even for the well-known TiO_2, the different crystal phases (anatase, rutile) cause significant differences [4]. The highly reactive hydroxyl radicals (•OH) play a crucial role. The •OH form on the surface of the catalysts but may diffuse to the bulk phase and react with non-adsorbed compounds in the solution [4,5]. The formation and diffusion of •OH and its contribution along direct charge transfer and other reactive species to transforming organic pollutants is still a matter of debate [6]. Several parameters influence the efficiency of heterogeneous photocatalysis and the reaction mechanism; the most important ones are the intensity of the irradiation, the concentration of the photocatalyst and the organic compound, and the physicochemical properties of the catalyst [3], which can significantly influence the processes taking place on the semiconductor surface and in the solution phase.

The efficiency of the method in treating real wastewaters is fluctuating, but the reasons for the different results are still debated. The organic and inorganic components of the matrix can act as radical scavengers but also affect the surface properties of the photocatalyst particles. Inorganic radicals formed from inorganic ions can also significantly affect the mechanism and efficiency of heterogeneous photocatalysis [3,7].

The investigation of •OH formation is often based on the fluorescent products forming during the reaction of •OH and aromatic model compounds. In this work, coumarin (COU) and coumarin-3-carboxylic acid (3CCA) were used as model compounds; they form highly fluorescent 7-hydroxy-coumarin (7HO-COU) and 7-hydroxy-coumarin-3-carboxylic acid (7HO-3CCA) due to their reactions with •OH. Since COU is not adsorbed, while 3CCA is adsorbed on the surface of TiO_2, their comparison helps understand the role of adsorption [8] during their transformation, their reactions with •OH, and the competition with other compounds. Another way to investigate the role of adsorption in the case of TiO_2 is the use of fluoride ions, as they exchange the surface –OH groups and change the surface properties. From fluorinated TiO_2 (TiO_2^F),

the diffusion of •OH is favoured, while the reaction on the surface with •OH and photogenerated charges is hindered [9].

Besides TiO_2, another widespread and commercially available photocatalyst is ZnO. Although both photocatalysts transform organic compounds primarily via •OH-based reactions, they have several differences. Comparing these photocatalysts based on •OH-formation efficiency, the effects of various matrices and inorganic ions on their activity, and the direct comparison of the transformation of various organic pollutants using these photocatalysts are still lacking.

A crucial point for reactor design is the light source. LED light sources emitting in the UV-A region are becoming more and more popular for the excitation of photocatalysts due to their relatively high electric efficiency, low price, and several favourable properties; therefore, they have become an alternative light source instead of the traditional mercury vapour lamps (MVL) [10]. During our work, two LED light sources were chosen and used for the transformation of organic pollutants; a "High-Power" LED emitting at 365 nm (LED_{365nm}) and a commercially available, cheap one emitting at 398 nm (generally called "UV-LED").

2. Objectives

This doctoral dissertation aimed to study heterogeneous photocatalysis, especially the clarification of the role of adsorption in the contribution of •OH-based reactions to the transformation of organic substances. The effect of reaction parameters, radical scavengers, matrix effect, including the effect of inorganic ions, and the removal of four nitrogen-containing organic pollutants using TiO_2 and ZnO photocatalyst were also the objectives of this work. Mercury vapour lamps and two different LED light sources were also used, therefore their applicability during heterogeneous photocatalysis was also compared.

The investigation of the significance of adsorption on the reactions of •OH was planned based on the transformation of poorly adsorbed COU, and 3CCA, a well-adsorbed organic substance, and the formation of their fluorescent hydroxylated products due to their reactions with •OH. In the case of both compounds, the effect of the reaction parameters, radical scavengers, inorganic ions, and fluoride ions, which significantly influenced the surface, and thus adsorption, were studied in detail.

Using COU, the comparison of the •OH formation rate in the case of TiO_2 and ZnO and the contribution of radical-based and direct charge transfer reactions to the transformation was planned using two LED light sources emitting at 365 nm and 398 nm. The heterogeneous photocatalytic transformation of two neonicotinoid pesticides (imidacloprid and thiacloprid) and two sulfonamides (sulfamethazine and sulfamethoxypyridazine) were studied and compared. In addition to examining the effect of reaction conditions, the mineralization rates and the impact of matrices and their typical inorganic components were also studied, as these significantly affect the practical applicability. Using the two types of LEDs also provided an opportunity to study the effect of irradiating wavelength.

A further objective was to test photoreactors equipped with UV-LED light sources to replace mercury-vapour lamps generally used in heterogeneous photocatalysis. The comparison was based on the formation of •OH, electric energy consumption, and quantum efficiency calculated during the transformation of organic pollutants. The main goal was to determine if the efficiency and operating costs could be improved using LED light sources during the TiO_2/UV and ZnO/UV processes.

3. Experimental conditions, chemicals, and analytical methods

Pulse and gamma radiolysis

The reaction rate constants of COU and 3CCA were determined based on transient UV-Vis spectra measured during irradiations with a Tesla Linac LPR-4 electron accelerator [11]. Gamma radiolysis experiments were performed in a panoramic irradiator using ^{60}Co gamma-source. The formation of the required radicals was achieved by controlling dissolved gases, the pH, and adding radical scavengers.

Photocatalytic experiments

Commercial TiO_2 Aeroxid P25 (Acros Organics) and ZnO (Sigma Aldrich) photocatalysts were used during the experiments. A fluorescent MVL emitting between 300 and 400 nm and UV-LEDs emitting at 365 and 398 nm (Table 1.) were used, and their photon flux was determined using iron-oxalate and Reinecke's salt chemical actinometer [12,13]. Experiments were performed in ultrapure (MQ) water, tap water, and biologically treated commercial wastewater from Szeged.

Table 1. *Main parameters of the used UV-sources*

	MVL	**LED$_{365nm}$**	**LED$_{398nm}$**
Emission range	300 - 400 nm	355 - 375 nm	385 - 415 nm
Emission maximum	365 nm	365 nm	398 nm
Photon flux	5.0×10^{-6} mol_{photon} s^{-1}	5.5×10^{-6} mol_{photon} s^{-1}	4.7×10^{-6} mol_{photon} s^{-1}
Electric power	15 W	6.6 W	4.6 W
Electric efficiency	~11%	27%	30 - 37%

Analytical methods

The concentration of COU and 3CCA were determined using UV-Vis spectrophotometry (Agilent 8453). The concentration of formed 7HO-COU and 7HO-3CCA were measured by fluorescent spectroscopy (Hitachi F−4500). The concentration of organic pollutants was determined using UV (DAD) detection after HPLC separation (Agilent 1100 HPLC, Lichrosphere 100 RP−18, 5 µm column). The formed organic degradation products were identified using a mass spectrometer (Agilent LC/MSD VL) connected to the mentioned HPLC device. Depending on the analytes, atmospheric pressure chemical (APCI) or electrospray (ESI) ionization was used. Samples were prepared using solid-phase extraction (SPE). For the TOC measurements, an Analytik Jena N/C 3100 analyzer was used. The measurement of adsorbable organic halogens (AOX) was performed using Analytik Jena multi X2500. Activated carbon sorbents were used for sample preparation (APU-2). Chemical oxygen demand (COD), H_2O_2 concentration, and the formation of inorganic ions (NO_2^-, NO_3^-, NH_4^+, CN^-) were determined using colorimetric cuvette tests, measured in Spectroquant® Multy and Hach DR2800 Vis−spectrophotometers. The concentration of inorganic degradation products was measured

using an ion chromatograph (Shimadzu Prominence LC-20AD, Shodex 5U-YS-50 és Shodex NI-424 5U columns).

Ecotoxicity measurements

The determination of ecotoxicity changes is important for the transformation of toxic organic compounds. Ecotoxicity was measured based on the bioluminescence inhibition of marine bacteria *Vibrio Fischeri* (LCK480, Hach Lange).

Methods used for the characterization of the photocatalysts

Zeta potential and particle size were determined during dynamic light scattering (DLS) measurements (Nano ZS, Malvern). The determination of the absorbance of the photocatalysts was done based on diffuse reflectance spectroscopy (DRS, Ocean Optics USB4000), and the calculation of bandgap energies was performed using Tauc plot and the Kubelka-Munk approach. The crystal phase and composition of the photocatalysts were verified using X-ray diffraction (XRD, Rigaku Miniflex II, Cu Kα X-ray source). The specific surface area was determined using N_2–adsorption/desorption isotherms (BET) using a Quantachrome NOVA 2200. The pore size distribution was calculated using the BJH-method.

5. Theses of doctoral (PhD) dissertation

1) ***The addition of NaF to TiO_2 suspensions initiates the desorption of adsorbed substrates and helps with the precise determination of initial reaction rates. The method is not usable when compounds forming strong surface complexes are present.***

After the addition of NaF, the surface hydroxyl groups of TiO_2 change to fluoride groups (TiO_2^F). This influences the surface and adsorption properties. At 1.0×10^{-4} M initial concentration and 1.0 g dm^{-3} suspension concentration, the adsorption of COU and 7HO-COU was negligible, while 30% of 3CCA adsorbed on TiO_2, on TiO_2^F neither compound adsorbed. After adding 5.0×10^{-3} M NaF to TiO_2, close to 100% of adsorbed 3CCA and 7HO−3CCA can be desorbed. After the addition of NaF, the measured initial reaction rate of 3CCA was nearly five times, and the formation rate of 7HO-3CCA was three times higher compared to measurements without desorption (NaF-addition). By adding NaF to the samples the determination of initial reaction rates can be clarified for well-adsorbed compounds, as the adsorbed part is not treated as transformed. In the case of weakly adsorbed (<1%) COU no change was observed when using the desorption method. The addition of F^- does not affect the adsorption of strong chelating agents (e.g. EDTA, oxalic acid), fluorination of the surface is hindered in their presence.

Related Publication:

M. Náfrádi, L. Farkas, T. Alapi, K. Hernádi, K. Kovács, L. Wojnárovits, E. Takács: *Application of coumarin and coumarin−3−carboxylic acid for the determination of hydroxyl radicals during different advanced oxidation processes*, Radiation Physics and Chemistry, 2020, 170, 108610 *https://doi.org/10.1016/j.radphyschem.2019.108610*.

2) ***When using TiO_2 Aeroxide P25, the importance of adsorption on the transformation rate of organic compounds is negligible when $^{\bullet}OH$ is the dominant reactant. If several different organic compounds are present, the extent of their adsorption is important when competing for the $^{\bullet}OH$.***

Increasing the pH of the suspensions (above pH 6) and the addition of 5.0×10^{-3} M NaF hinders the adsorption of 3CCA, but their effect on the transformation rate and the formation of hydroxylated product is negligible. Comparing the ratio of the transformation rates ($r_0^{COU} / r_0^{3CCA} = 1.39$) and the ratio of reaction rate constants with $^{\bullet}OH$ ($k^{COU} / k^{3CCA} = 1.40$) similar values were calculated, therefore when adsorption is negligible, the main reactant is $^{\bullet}OH_{aq}$. When the extent of adsorption increases (pH<4), the contribution of $^{\bullet}OH_{ads}$ and direct charge transfer may increase. Using different radical scavengers (methanol, *t*-butanol, *p*-benzoquinone, $ETDA^{2-}$, oxalic acid) in the case of TiO_2 and TiO_2^F, the role of adsorption was found to be crucial when different organic compounds are competing for $^{\bullet}OH$ in multi-component systems. The scavengers could not compete for $^{\bullet}OH$ with the well−adsorbed 3CCA even in large excess. In TiO_2^F suspension, the effect of the scavengers is similar for both COU and 3CCA.

Related Publication:

M. Náfrádi, L. Farkas, T. Alapi, K. Hernádi, K. Kovács, L. Wojnárovits, E. Takács: *Application of coumarin and coumarin−3−carboxylic acid for the determination of hydroxyl radicals during different*

advanced oxidation processes, Radiation Physics and Chemistry, 2020, 170, 108610 *https://doi.org/10.1016/j.radphyschem.2019.108610*.

3) ***The photocatalytic transformation of imidacloprid and thiacloprid occurs mainly in the bulk phase via $^{\bullet}OH$, but direct charge transfer may contribute in the case of imidacloprid. In the case of TiO_2^F, the reaction rates do not change significantly, but the product distribution changes, and the mineralization rate is significantly reduced.***

Based on its transformation in deoxygenated suspensions, IMIDA may react to an extent via direct charge transfer despite its negligible adsorption. This is further reinforced by the different ratios of degradation products in the case of TiO_2^F. For THIA, no change was observed. Based on the effect of radical scavengers (methanol, *t*-butanol, *p*-benzoquinone, $ETDA^{2-}$, oxalic acid, I^-), the main reactant is bulk phase $^{\bullet}OH_{aq}$ for both neonicotinoids, direct charge transfer is not the dominant pathway, even for IMIDA. At 1.0×10^{-4} M concentration, the total organic carbon content could not be reduced below 20% using TiO_2, and below 40% using TiO_2^F, therefore the formed products are resistant to further photocatalytic degradation. These results suggest that the increased $^{\bullet}OH_{aq}$ due to surface fluorination is not necessarily favourable for the mineralization rate, presumably due to the hindered direct charge transfer, which could play an important role during the further transformation of intermediates.

Related Publications**:**

G. Rózsa, **M. Náfrádi**, T. Alapi, K. Schrantz, L. Szabó, L. Wojnárovits, E. Takács, A. Tungler: *Photocatalytic, photolytic and radiolytic elimination of imidacloprid from aqueous solution: reaction mechanism, efficiency, and economic considerations;* Applied Catalysis B: Environmental, 2019, 250, 429−439 https://doi.org/10.1016/j.apcatb.2019.01.065

M Náfrádi, T. Hlogyik, L. Farkas, T. Alapi: *Comparison of the heterogeneous photocatalysis of imidacloprid and thiacloprid – reaction mechanism, ecotoxicity, and the effect of matrices;* Journal of Environmental Chemical Engineering, 2021, 9, 106684 https://doi.org/10.1016/j.jece.2021.106684

4) ***The photocatalytic transformation of imidacloprid leads to increased ecotoxicity, presumably caused by the formed NO_2^-/NO_3^- ions.***

The toxicity of the two neonicotinoids changes differently during photocatalytic treatment. The inhibition of bioluminescence of the *Vibrio Fischeri* test bacteria was decreased in the case of THIA (from 50% to 20%), while for IMDA it was increased (from 38% to 65%). It may be indirectly caused by NO_2^- / NO_3^- formation (which is negligible for THIA), leading to the formation and reactions of reactive nitrogen species.

Related Publications:

M Náfrádi, T. Hlogyik, L. Farkas, T. Alapi: *Comparison of the heterogeneous photocatalysis of imidacloprid and thiacloprid – reaction mechanism, ecotoxicity, and the effect of matrices;* Journal of Environmental Chemical Engineering, 2021, 9, 106684 https://doi.org/10.1016/j.jece.2021.106684

5) ***In the case of LED_{365nm}, increasing the intensity decreases the photonic efficiency of coumarin transformation and $^{\bullet}OH$ formation, and needlessly increases the electric power consumption. Despite its favourable electric efficiency, LED_{398nm} is less effective for the excitation of TiO_2 and ZnO due to its lower photonic energy.***

The used LEDs have higher electric efficiency (~27-37%) compared to the mercury vapour lamp (~11%). LED_{365nm} could be a favourable alternative UV source to the mercury vapor lamp. When changing the intensity (1.4 - 8.5 × 10^{-5} mol_{photon} s^{-1} dm^{-3}), lowering the power input of LED_{365nm} from 20,8 W to 6,5 W results in ~2.5 times higher quantum efficiency of COU degradation and $^{\bullet}OH$-formation. The electric power consumption of the LEDs is more favourable at lower power. Despite its higher electric efficiency (30-37%), for unmodified TiO_2 and ZnO, the LED_{398nm} is not economically favorable due to the low absorbance of the photocatalysts. For modified or different photocatalyst materials with different absorption properties, it can be a highly efficient light source.

Related Publications

M. Náfrádi, G. Bencsik, Cs. Janáky, T. Alapi: *Impact of reaction parameters and water matrices on the removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation;* Nanomaterials 2022, 12(1), 5; https://doi.org/10.3390/nano12010005

6) ***The transformation of coumarin using TiO_2 and ZnO significantly differed in terms of $^{\bullet}OH$ formation rate and the contribution of direct charge transfer.***

The $r_0^{7HO-COU}/r_0^{COU}$ values in the case of LED_{365nm} are two times higher for TiO_2 (0.02) compared to ZnO (0.01). It indicates the formation and contribution of $^{\bullet}OH$ is favourable using TiO_2, while direct charge transfer is more significant for ZnO. The transformation of COU reflects the low (~20%) absorption of 398 nm photons by TiO_2 and ZnO. Despite the lower transformation rate, the yield of 7HO−COU is higher in the case of LED_{398nm} (TiO_2: 0.045, ZnO: 0.06) compared to LED_{365nm} (TiO_2: 0.02, ZnO: 0.01).

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7) ***Investigating the effect of Cl^-, HCO_3^- and two mild water matrices (tapwater, biologically treated commercial wastewater) TiO_2 was found to be more sensitive to the presence of inorganic ions and matrix components compared to ZnO.***

The effect of Cl^- on the transformation of COU and the formation of 7HO−COU was negligible in the case of TiO_2, while a slightly positive effect was found for ZnO. The significant inhibition of HCO_3^- (50-75%) in the case of TiO_2 was explained by scavenging of both $^{\bullet}OH$ and h_{VB}^+, leading to $CO_3^{\bullet-}$ formation, which contributes less to the transformation of COU compared to $^{\bullet}OH$. The inhibitory effect of HCO_3^- (20-30%) was less significant in the case of ZnO, as h_{VB}^+ scavenging is not favoured. This was further confirmed by studying the mineralization rates. In the case of ZnO the effect of both matrices can be

explained by the combined effect of Cl^- and HCO_3^-, but for TiO_2 the inhibition was greater than expected based on the combined effect of inorganic anions.

Related Publications:

M. Náfrádi, G. Bencsik, Cs. Janáky, T. Alapi: *Impact of reaction parameters and water matrices on the removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation;* Nanomaterials 2022, 12(1), 5; https://doi.org/10.3390/nano12010005

8) ***The transformation and mineralization efficiency of heteroaromatic (nitrogen, sulfur-containing) organic pollutants are different using TiO_2 and ZnO, especially in the presence of HCO_3^-.***

The transformation rates of the sulfonamides were higher in the case of ZnO, most likely due to the higher contribution of charge transfer, while in the case of neonicotinoids no significant difference was found between the two photocatalysts. TiO_2 was more efficient in terms of mineralization rate for all pollutants, as it reduced the total organic carbon content below 20% after 120 minutes. When using ZnO, 40% organic carbon remained in the suspensions. The inhibition effect of HCO_3^- depends on the reaction rate constant of the $CO_3^{\bullet-}$ and the organic pollutants, less significant inhibition was measured in the case of sulfonamides and neonicotinoids compared to COU.

Related Publications:

M. Náfrádi, G. Bencsik, Cs. Janáky, T. Alapi: *Impact of reaction parameters and water matrices on the removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation;* Nanomaterials 2022, 12(1), 5; https://doi.org/10.3390/nano12010005

M. Náfrádi, L. Farkas, G. Bencsik, G. Kozma, K. Hernádi, T. Alapi: *Wavelength dependence of the transformation mechanism of sulfonamides using different LED light sources and TiO_2 and ZnO photocatalysts*, Materials, 2022, 16(1), 49; https://doi.org/10.3390/ma15010049

9) ***In the case of sulfamethoxypyridazine, it presumably transformed in TiO_2 Aeroxide P25 suspensions irradiated with 398 nm photons via direct energy transfer.***

In the case of SMP, 398 nm LEDs, and TiO_2 Aeroxid P25 the quantum efficiency was 0.0158, while using 365 nm LEDs it was only 0.061 despite the more favourable excitation of the catalysts. Instead of hydroxylation characteristic to 365 nm irradiation, SMP is mainly transformed via SO_2-extrusion. In the case of ZnO, similar behaviour was not observed, in the case of 398 nm photons the quantum efficiency (0.0009) was an order of magnitude smaller compared to 365 nm LEDs (0.0085). The reaction was very sensitive to the presence of methanol and HCO_3^- (more than 90% inhibition), and a similar transformation occurred in the absence of dissolved O_2, therefore the results can not be interpreted by the reactions of $^{\bullet}OH$ and h_{VB}^+. Compared to data in the literature, the reaction is suspected to happen via direct energy transfer from the excited photocatalyst.

Related Publications:

M. Náfrádi, L. Farkas, G. Bencsik, G. Kozma, K. Hernádi, T. Alapi: *Wavelength dependence of the transformation mechanism of sulfonamides using different LED light sources and TiO_2 and ZnO photocatalysts*, Materials, 2022, 16(1), 49; https://doi.org/10.3390/ma15010049

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7. List of publications

MTMT−identifier: 10061642

Publications in international journals, related to the topic of the dissertation:

1. **M. Náfrádi,** L. Farkas, G. Bencsik, G. Kozma, K. Hernádi, T. Alapi: *Wavelength dependence of the transformation mechanism of sulfonamides using different LED light sources and TiO_2 and ZnO photocatalysts,* Materials, 2022, 16(1), 49; https://doi.org/10.3390/ma15010049
   IF = 3.623 Q2

2. **M. Náfrádi**, G. Bencsik, Cs. Janáky, T. Alapi: *Impact of reaction parameters and water matrices on the removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation,* Nanomaterials 2022, 12(1), 5; https://doi.org/10.3390/nano12010005
   IF = 5,076 Q1

3. **M Náfrádi,** T. Hlogyik, L. Farkas, T. Alapi: *Comparison of the heterogeneous photocatalysis of imidacloprid and thiacloprid – reaction mechanism, ecotoxicity, and the effect of matrices,* Journal of Environmental Chemical Engineering, 2021, 9, 106684 https://doi.org/10.1016/j.jece.2021.106684
   IF=5,909 Q1

4. **M. Náfrádi**, L. Farkas, T. Alapi, K. Hernádi, K. Kovács, L. Wojnárovits, E. Takács: *Application of coumarin and coumarin−3−carboxylic acid for the determination of hydroxyl radicals during different advanced oxidation processes,* Radiation Physics and Chemistry, 2020, 170, 108610 *https://doi.org/10.1016/j.radphyschem.2019.108610.*
   IF=2,226 Q2

5. G. Rózsa, **M. Náfrádi**, T. Alapi, K. Schrantz, L. Szabó, L. Wojnárovits, E. Takács, A. Tungler: *Photocatalytic, photolytic and radiolytic elimination of imidacloprid from aqueous solution: reaction mechanism, efficiency and economic considerations,* Applied Catalysis B: Environmental, 2019, 250, 429−439 https://doi.org/10.1016/j.apcatb.2019.01.065 IF=16,683

∑IF: 33,517

Full-length publications related to the topic of the dissertation:

1. **M. Náfrádi**, T. Alapi: *Effect of irradiation wavelength on the heterogeneous photocatalytic removal of organic pollutants using TiO_2 and ZnO*; 7th International Symposium on Analytical and Environmental Problems (ISAEP 2021), Szeged, 11. 22−23, 2021 *(ISBN 978−963−306−835−9)*

2. **M. Náfrádi**, T. Hlogyik, L. Farkas, T. Alapi: *Application of high power UV LEDs in heterogeneous photocatalysis* − 26th International Symposium on Analytical and Environmental Problems, Szeged, 2020. 11. 23−24. *(ISBN 978−963−306−771−0, 67−71.)*

3. **M. Náfrádi**, G.t Farkas, B. Vas, T. Alapi: *Heterogeneous photocatalysis of sulfonamides using TiO2 and ZnO photocatalysts with mercury−vapor and led light sources* − 26th International Symposium on Analytical and Environmental Problems, Szeged, 2020. 11.23−24. *(ISBN 978−963−306−771−0, 384−388.)*

4. **M. Náfrádi,** L. Wojnárovits, E. Takács, T. Alapi: *Determination of hydroxyl radicals using coumarin and coumarin−3−carboxylic acid during gamma radiolysis and heterogeneous photocatalysis* − 25th International Symposium on Analytical and Enviromental Problems, Szeged, 2019.10.7−8. *(ISBN 978−963−306−702−4, 23−27.)*

5. T. Hlogyik, **M. Náfrádi,** T. Alapi: *Heterogeneous photocatalysis of imidacloprid – effect of reaction parameters, mineralization and matrices* − 25th International Symposium on Analytical and Enviromental Problems, Szeged, 2019.10.7−8. *(ISBN 978−963−306−702−4, 321−325.)*

6. T. Hlogyik, **M. Náfrádi,** A. Rampal, S. Garg, K. Hernádi, T. Alapi: *Heterogeneous photocatalysis of Imidacloprid – the effect of reaction parameters* − 24th International Symposium on Analytical and Environmental Problems, Szeged, 2018.10. 8−9. *(ISBN 978−963−306−623−2, 290−294.)*

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1. T. Alapi, L. Farkas, **M. Náfrádi**: *Application of Various Advanced Oxidation Processes for Elimination of Sulfonamides from Aqueous Solution: Reaction Mechanism, Efficiency, Toxicity and Economic Considerations* − The 5th International Conference on New Photocatalytic Materials for Environment, Energy and Sustainability, The 6th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces (NPM−5/PAOT−6), Szeged, 05. 24−27, 2021 *(ISBN 978−963−306−789−5)*

2. **M. Náfrádi,** T. Hlogyik, T. Alapi: *Comparison of the Efficiency of Different Light Sources for the Generation of Hydroxyl Radicals using TiO_2 and ZnO Photocatalysts* − The 5th International Conference on New Photocatalytic Materials for Environment, Energy and Sustainability, The 6th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces (NPM−5/PAOT−6), Szeged, 05. 24−27, 2021 *(ISBN 978−963−306−789−5)*

3. **M. Náfrádi**, L. Farkas, G. Farkas, B. Vas, T. Alapi: *Transformation of Sulfamethazine and Sulfamethoxypyridazine using TiO_2 And ZnO Photocatalysts Irradiated with Mercury−Vapor and UV−LED Light Sources* − The 5th International Conference on New Photocatalytic Materials for Environment, Energy and Sustainability, The 6th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces (NPM−5/PAOT−6), Szeged, 05. 24−27, 2021 *(ISBN 978−963−306−789−5, 105.)*

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