PhD Theses

The role of reactive oxygen species in the vacuum ultraviolet photolysis of four nonsteroidal anti-inflammatory drugs

Eszter Arany

Doctoral School of Environmental Sciences

University of Szeged, Faculty of Science and Informatics, Institute of Chemistry, Research Group of Environmental Chemistry

Thesis supervisors:

Dr. Tünde Alapi, professor's assistant

Dr. Krisztina Schrantz, assistant professor

Szeged

2014

1. Introduction and objectives

Since the traditional wastewater treatment techniques are based on biological methods, and there are several pollutants which can not be eliminated by the used microorganisms, the decontamination of these waters is of upmost interest nowadays. Nonsteroidal anti-inflammatory drugs (NSAIDs) are usually reported to be recalcitrant water contaminants and therefore ibuprofen (IBU), ketoprofen (KETO), naproxen (NAP) and diclofenac (DICL) were chosen as target molecules and phenol (PhOH) as a model compound.

The application of advanced oxidation processes (AOPs) may solve the above mentioned problem. AOPs are based on the generation of reactive radicals, which can induce the transformation of the contaminants. Although there is plenty of information about the reactions of the most reactive radical, the hydroxyl radical ($HO^{\bullet}$), only a few data is given concerning the less reactive radicals, which might also contribute to the degradation of the pollutant molecules if their concentration is increased.

Vacuum ultraviolet (VUV) photolysis is a suitable method among the AOPs to study the direct reactions and the effects of different parameters (*e.g.* the presence of dissolved O_2 or radical transfer molecules) on the radical set and on the degradation of organic contaminants, since the generated radical set is known, using this technique.

Hydroperoxyl radicals/superoxide radical ions ($HO_2^{\bullet}/O_2^{\bullet-}$) are the most important oxygen containing species along $HO^{\bullet}$. The concentration of H_2O_2 ($c_{H_2O_2}$) refers to their concentration ($c_{HO_2^{\bullet}/O_2^{\bullet-}}$) and therefore, the $c_{H_2O_2}$ was planned to be measured during the VUV photolysis of the target molecules.
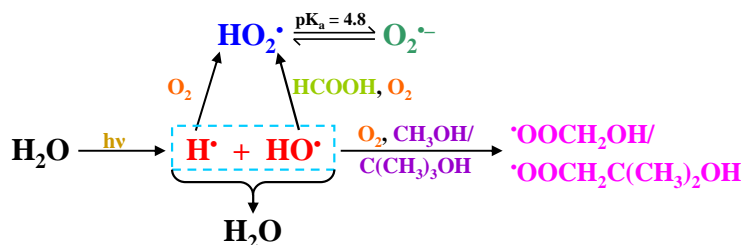

Fig. 1. The effect of different radical transfers on the radical set generated during the VUV photolysis of water.

As it can be seen from Fig. 1, dissolved O_2 affects the radical set from several routes. Therefore, the aim of this study was to investigate the effect of the presence of O_2 on the initial transformation of the pollutants, on the formation and transformation of their main

aromatic by-products and on their mineralization. To study the relatively increasing effect of dissolved O_2, experiments were planned in solutions containing the contaminant molecules in two different initial concentrations.

In the presence of both dissolved O_2 and formate ions, all of primary reactive species of VUV photolysis ($HO^\bullet$ and hydrogen atoms/hydrated electrons ($H^\bullet/e_{aq}^-$)) transform to $HO_2^\bullet/O_2^{\bullet-}$ (Fig. 1). Additionally, altering the pH of the solution the ratio of $HO_2^\bullet$ and $O_2^{\bullet-}$ might also be influenced. Thus, the experiments aimed also the investigation of the effects of $HO_2^\bullet$ and $O_2^{\bullet-}$ on the initial transformation rates of the target compounds.

In the presence of both dissolved O_2 and radical scavengers (methanol or *tert*-butanol), peroxyl radicals ($^\bullet OOCH_2OH$ or $^\bullet OOCH_2C(CH_3)_2OH$) are present in the solution along with $HO_2^\bullet/O_2^{\bullet-}$ (Fig. 1). The aim of this study was to make comparison between the initial transformation of the pollutant molecules in the presence of formate ions and in the presence of radical scavengers, to compare the reactivity of these reactive oxygen species (ROS) with each other.

The radical set is affected also by the contaminants themselves, and therefore the VUV photolysis of the target molecules was planned in four different initial concentrations (c_0).

Since no information was found in the literature concerning the VUV degradation of IBU, KETO, NAP or DICL, the aim of this work was also to give suggestions for the chemical structures of the formed aromatic by-products and to give a tentative mechanism of their formation.

The realization of the aims above could contribute to improve the efficiency of AOPs.

Methods

Two types of experimental setups were used for the VUV investigations. The treated solution was circulated between a thermostated reactor and a reservoir in both cases. The 250 cm^3 or 2 dm^3 solution was irradiated with either a 20 W or with a 100 W xenon excimer lamp, respectively, emitting at 172±14 nm. N$_2$, O$_2$ or air was injected in the irradiated solution to achieve deoxygenated, O$_2$- or air-saturated conditions, respectively.

Samples containing the pollutant molecules were analyzed on an Agilent 1100 series LCMSD VL system. For determination of the total organic carbon content of the solutions, a multi N/C 3100 instrument (Analytik Jena AG) was used.

The apparent reaction rate constants (*k'*) of the degradation of the investigated compounds were determined by performing a nonlinear model fit on the concentrations measured during the HPLC analyses, with the help of Mathematica 8 (Wolfram) software. It should be mentioned that our system is very inhomogeneous. The VUV photons are absorbed in a very thin water layer (< 0.1 mm) and therefore only a thin-walled hollow cylindrical volume of solution is irradiated, near the quartz/water interface. Further, the experimental setup consisted of a partly-irradiated reactor and a reservoir, the determined (apparent) *k'* values therefore referring to the overall transformation rate of the target molecules under the experimental conditions applied.

Novel scientific results

T1. During the initial VUV transformation of the studied contaminants the concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ increases.

The VUV photolysis of oxygenated PhOH, IBU and KETO solutions showed that during the initial transformation of the contaminant molecules the $c_{H_2O_2}$ increases, which could be a proof for the increase of the $c_{HO_2^{\bullet}/O_2^{\bullet-}}$. Although the reactivity of $HO_2^{\bullet}/O_2^{\bullet-}$ is usually reported to be lower than that of $H^{\bullet}$ [1], in an elevated concentration they may also contribute to the degradation of organic contaminants [2].

T2. The role of reductive ($H^{\bullet}/e_{aq}^-$) and oxidative ($HO_2^{\bullet}/O_2^{\bullet-}$ and $HO^{\bullet}$) reactive species in the transformation of organic pollutants depends strongly on the structure of the contaminant molecules, which influences their reaction rate constants with the mentioned radicals.

The initial VUV transformation rates (r_0) of PhOH were higher in the presence of dissolved O_2, although they were lower in the case of irradiating NAP and 1.0×10^{-5} mol dm^{-3} IBU solutions. In the case of KETO, DICL and 1.0×10^{-4} mol dm^{-3} IBU solutions the r_0 values didn't depend on the c_{O_2} (Table I).

Table I. The initial VUV transformation rates of the investigated compounds in the presence and absence of dissolved O_2.

comp.	gas	$c_0 = 1.0 \times 10^{-5}$ mol dm^{-3}		$c_0 = 1.0 \times 10^{-4}$ mol dm^{-3}	
		r_0 ($\times 10^{-7}$ mol $dm^{-3}\,s^{-1}$)	SD ($\times 10^{-7}$ mol $dm^{-3}\,s^{-1}$)	r_0 ($\times 10^{-7}$ mol $dm^{-3}\,s^{-1}$)	SD ($\times 10^{-7}$ mol $dm^{-3}\,s^{-1}$)
PhOH	O_2	2.4	0.05	4.4	0.10
	N_2	1.9	0.05	1.2	0.03
IBU	O_2	1.2	0.07	5.3	0.20
	N_2	1.6	0.06	5.2	0.30
KETO	O_2	2.8	0.10	10.0	0.30
	N_2	2.7	0.04	10.3	0.40
NAP	O_2	1.4	0.04	6.8	0.20
	N_2	3.2	0.20	8.6	0.40
DICL	O_2	1.9	0.05	5.7	0.30
	N_2	1.8	0.08	5.5	0.08

In the case of PhOH, dissolved O_2 could prevent the recombination of $H^{\bullet}/e_{aq}^{-}$ and $HO^{\bullet}$, it converts reductive $H^{\bullet}/e_{aq}^{-}$ to oxidative $HO_2^{\bullet}/O_2^{\bullet-}$, and at the same time it may hinder the backward reactions of $R^{\bullet}$ and $(RHOH)^{\bullet}$ (generated in the reactions of the pollutant molecules and $HO^{\bullet}$). These effects could result in the increase of the initial transformation rate of PhOH in the presence of O_2.

In contrast, the results of the VUV photolysis of NAP and 1.0×10^{-5} mol dm^{-3} IBU solutions suggested that in this case the contribution of $H^{\bullet}/e_{aq}^{-}$ to the transformation of the target molecules was much more significant than that of $HO_2^{\bullet}/O_2^{\bullet-}$ [3]. In the case of KETO, DICL and 1.0×10^{-4} mol dm^{-3} IBU solutions, where the r_0 values didn't depend on the c_{O_2}, showed, that although the concentration of $H^{\bullet}/e_{aq}^{-}$ is decreased in the presence of O_2, this effect may be compensated by the increased concentration of ROS [4].

T3. The presence of dissolved O_2 was found to be essential during the effective VUV induced decontamination of NSAID-containing solutions.

Since in the absence of dissolved O_2 the rate of mineralization was so low, it seems that in deoxygenated solutions some undetected recalcitrant by-products (maybe the dimers and oligomers of the target molecules) were formed [4].

T4. The reaction rate of $HO_2^{\bullet}/O_2^{\bullet-}$ with organic compounds depends highly on the structure of the target molecules.

Table II. The initial VUV transformation rates of the investigated compounds in case of converting the majority of the radicals to $HO_2^{\bullet}$ or to $O_2^{\bullet-}$.

comp.	$HO_2^{\bullet}$		$O_2^{\bullet-}$	
	r_0 ($\times 10^{-8}$ mol dm^{-3} s^{-1})	SD ($\times 10^{-8}$ mol dm^{-3} s^{-1})	r_0 ($\times 10^{-8}$ mol dm^{-3} s^{-1})	SD ($\times 10^{-8}$ mol dm^{-3} s^{-1})
PhOH	13.0	1.00	1.1	0.10
IBU	2.2	0.20	5.2	0.20
KETO	3.2	0.05	8.8	0.30
NAP	2.2	0.20	1.1	0.03

If both formate ions and O_2 are present in the solution, almost all primary radicals of VUV photolysis can be converted to $HO_2^{\bullet}/O_2^{\bullet-}$. Under acidic conditions most of the radicals appear in form of $HO_2^{\bullet}$, while under basic conditions they are almost completely transformed to $O_2^{\bullet-}$. The results of the VUV photolysis of the studied compounds under

these conditions suggested that during the transformation of PhOH and NAP, the contribution of $HO_2^{\bullet}$ [5], while in the case of IBU and KETO, the contribution of $O_2^{\bullet-}$ was higher among $HO_2^{\bullet}/O_2^{\bullet-}$ (Table II).

Because of the low solubility of DICL below pH = 5.8, the contribution of $HO_2^{\bullet}$ and $O_2^{\bullet-}$ to the transformation of this molecule was studied by performing experiments in the presence and in the absence of phosphates. In solutions prepared in phosphate buffer (PB) $HO_2^{\bullet}/O_2^{\bullet-}$ was present mainly in the form of $O_2^{\bullet-}$ during the whole treatment. In the case of DICL dissolved in Milli-Q water, the majority of $O_2^{\bullet-}$ was converted to $HO_2^{\bullet}$, using longer irradiation times (t > 180 s). After 180 s of irradiation, the decay of DICL was slightly increased in Milli-Q water. Additionally, the concentrations of the aromatic by-products were higher in the presence of PB. These results suggested that the reaction rates of DICL and its by-products with $O_2^{\bullet-}$ are probably lower than those with $HO_2^{\bullet}$ [4].

T5. The contribution of the peroxyl radicals formed from methanol and tert-butanol ($^{\bullet}OOCH_2OH$ and $^{\bullet}OOCH_2C(CH_3)_2OH$, respectively) to the VUV transformation of the studied contaminants may be higher than that of $HO_2^{\bullet}/O_2^{\bullet-}$.

Table III. The ratio of the initial VUV transformation rates of the investigated compounds in the presence of different radical transfers.

comp.	r_0 (O_2)/ r_0 $(HO_2^{\bullet})$	r_0 (O_2)/ r_0 $(O_2^{\bullet-})$	r_0 (O_2)/ r_0 (lower $c_{rad.\ scav.}$)	r_0 (O_2)/ r_0 (higher $c_{rad.\ scav.}$)
PhOH	3.4	40.0	5.3	8.0
IBU	24.1	10.2	1.8	n.m.[*]
KETO	31.3	11.4	1.1	1.9
NAP	30.9	60.2	3.3	5.0
DICL	n.m.	n.m.	1.5	2.6

[*]not measured

The ratios of the initial VUV transformation rates of the studied molecules in the presence of dissolved O_2 and in the presence of both O_2 and formate ions (to convert the radicals to $HO_2^{\bullet}/O_2^{\bullet-}$) ($r_0$ $(O_2)/r_0$ $(HO_2^{\bullet})$ or r_0 $(O_2)/r_0$ $(O_2^{\bullet-})$) with the ratios of the transformation rates in the presence of dissolved O_2 and in the presence of both O_2 and radical scavengers (CH_3OH or *tert*-butanol) (r_0 $(O_2)/r_0$ (lower $c_{rad.\ scav.}$) or r_0 $(O_2)/r_0$ (higher $c_{rad.\ scav.}$)) were compared. From Table X it can be seen that the former values are significantly (in almost all cases with one order of magnitude) higher than the latter ones.

The only exception is the case of irradiating PhOH in the presence of both O_2 and formate ions at acidic pH.

The reason of the former surprizing observation might be that the contribution of the peroxyl radicals (formed in the presence of both O_2 and the radical scavengers: $^\bullet OOCH_2OH$ and $^\bullet OOCH_2C(CH_3)_2OH$, respectively) to the transformation of the contaminants may be higher than that of $HO_2^\bullet/O_2^{\bullet-}$ (formed in the presence of both O_2 and formate ions). The contribution of these peroxyl radicals to the degradation of organic pollutants should therefore not be neglected. Thus, methanol and *tert*-butanol should also be considered as radical transfers instead of radical scavengers.

The relatively low value of r_0 $(O_2)/r_0$ $(HO_2^\bullet)$ in case of irradiating PhOH suggests that the reaction rate constants of $HO_2^\bullet$ are lower in case of the NSAIDs than that of PhOH $(2.7 \times 10^3$ dm^3 mol^{-1} s^{-1} [5]). Therefore, the contribution of $HO_2^\bullet$ to the degradation of the contaminants seems to be negligible in case of the studied drugs and it seems to have a minor significance in case of PhOH.

T6. In oxygenated solutions, the steady-state concentration of $HO^\bullet$ ($[HO^\bullet]_{SS}$) decreases with the increase of c_0, which results in the decrease of the apparent first-order VUV degradation rate constants ($k' = k \times [HO^\bullet]_{SS}$).

If the c_0 is fixed, the pseudo-first-order approach is suitable for a description of the degradation kinetics of the VUV photolysis of the investigated contaminants. However, in oxygenated solutions, the apparent first-order rate constants ($k' = k \times [HO^\bullet]_{SS}$) decreased in almost all cases with the increase of the c_0. The reason of these observations might be that at higher c_0, more $HO^\bullet$ are involved in reactions with the NSAIDs and the steady-state concentration of $HO^\bullet$ ($[HO^\bullet]_{SS}$) therefore decreases, along the constant value of k [3, 4]. In case of PhOH, the results correlate well with the work of *Sato et al.* [6].

T7. H-abstraction, $HO^\bullet/H^\bullet$-addition and decarboxylation reactions, as well as the reactions of the peroxyl radicals (formed from the target molecules) are the key steps during the VUV degradation of the studied NSAIDs. Some of these reactions take place only in oxygenated solutions, while others both in the presence and absence of dissolved O_2.

During the VUV photolysis of the investigated NSAIDs four aromatic by-products of IBU and KETO and three by-products of NAP and DICL were detected. With the help of

8

the HPLC-MS analysis, suggestions could be given for the chemical structures of these compounds. At the same time, a tentatively determined mechanism of the VUV photolysis of the studied drugs could be given (Figs. 2–5). The formation of the by-products of KETO and NAP could be interpreted with the reactions of the aliphatic chains, the formation of the by-products of DICL with the reactions of the aromatic rings [4], while the formation of the by-products of IBU with the reactions of both the aromatic ring and the aliphatic chains.
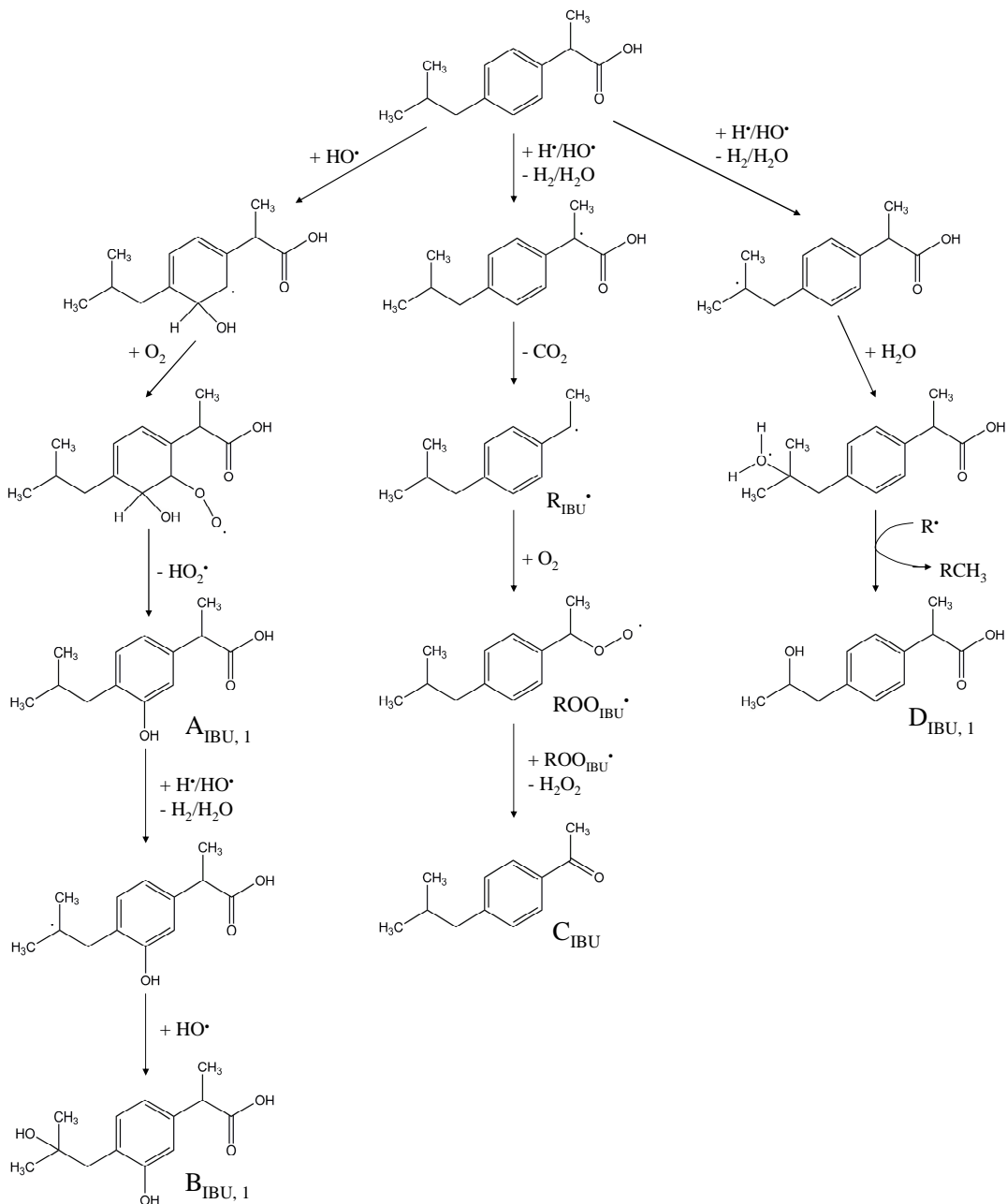

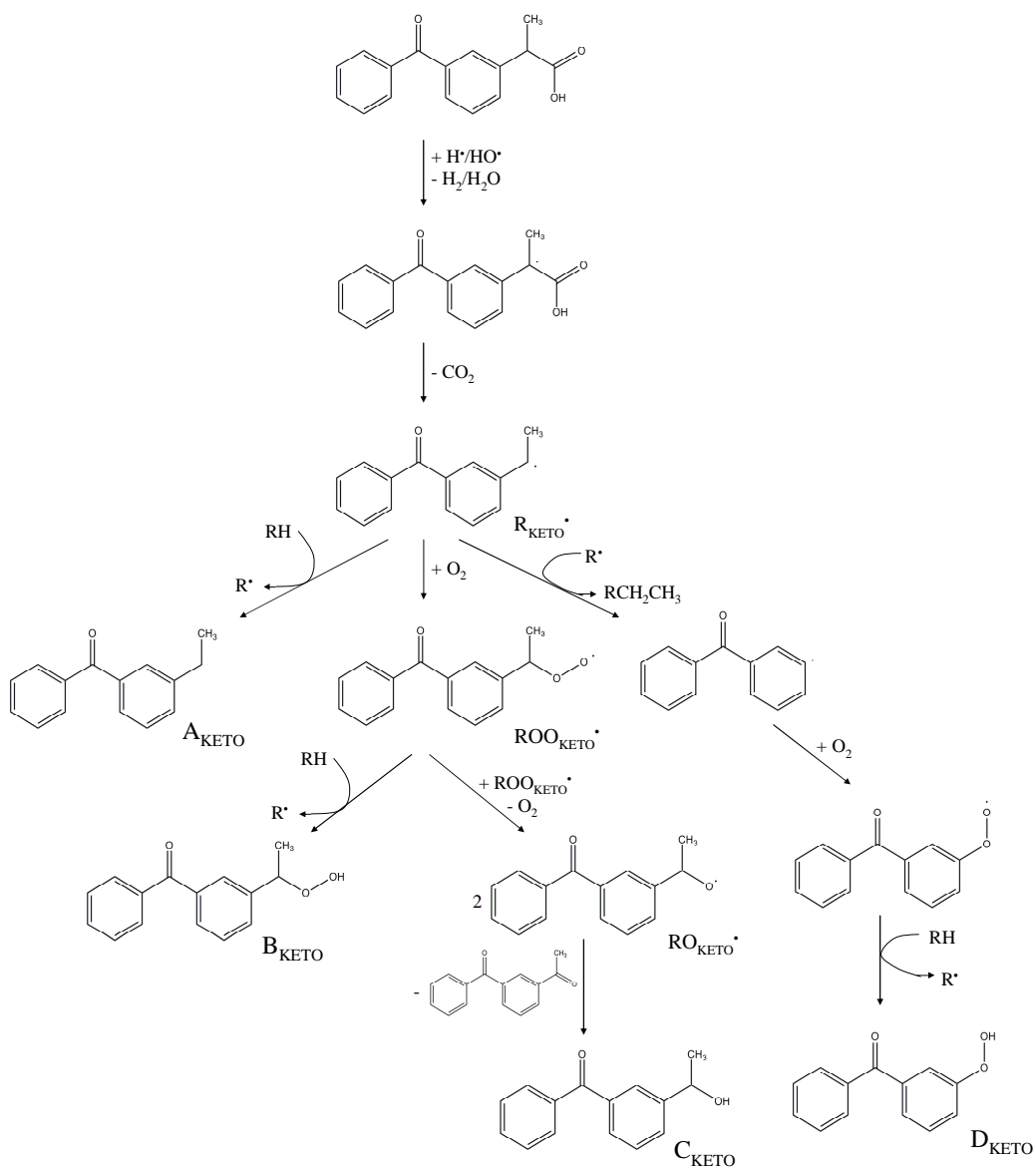Fig. 2. Possible pathway of formation of four VUV degradation by-products of IBU.

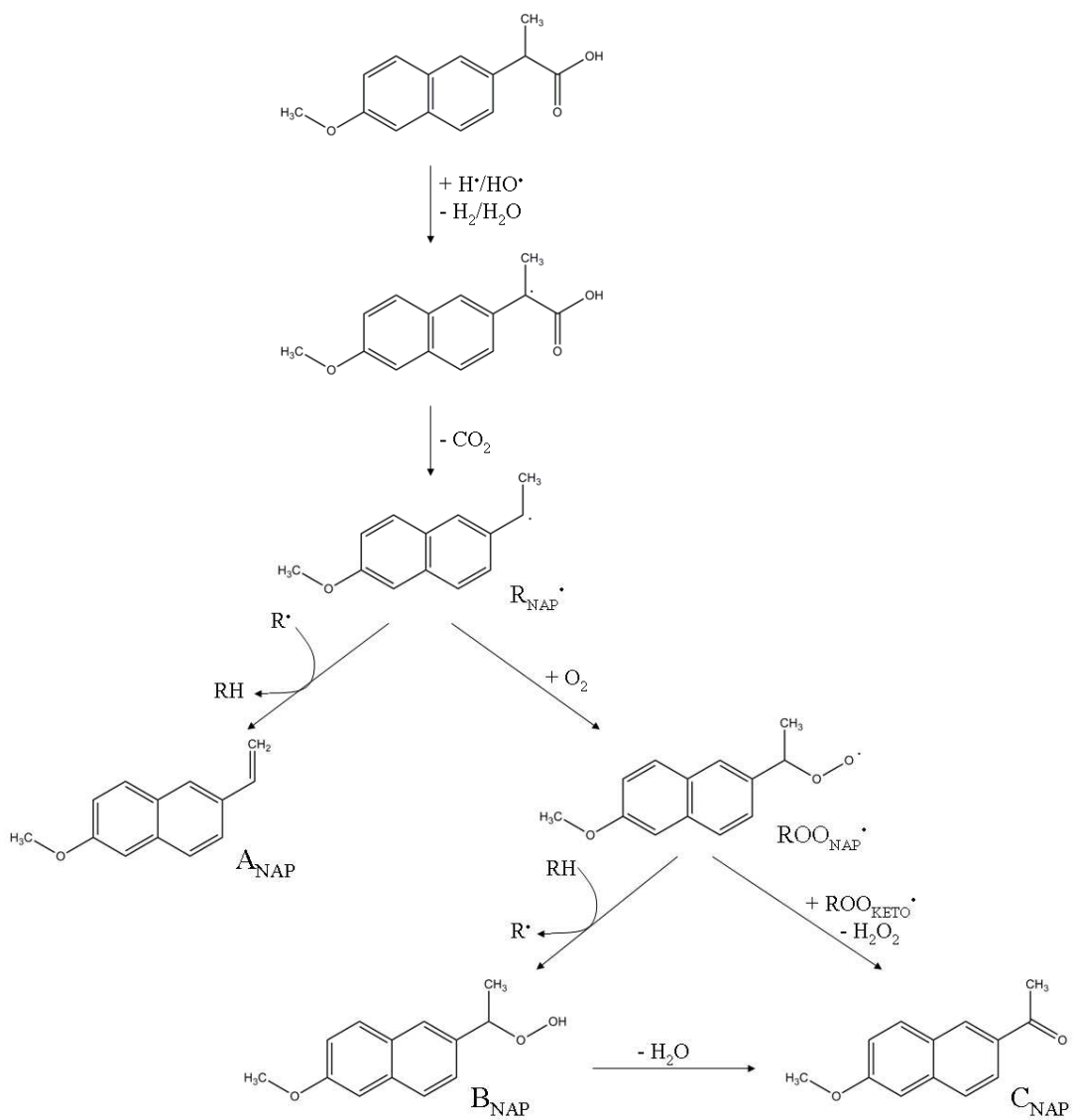Fig. 3. Possible pathway of formation of four VUV degradation by-products of KETO.

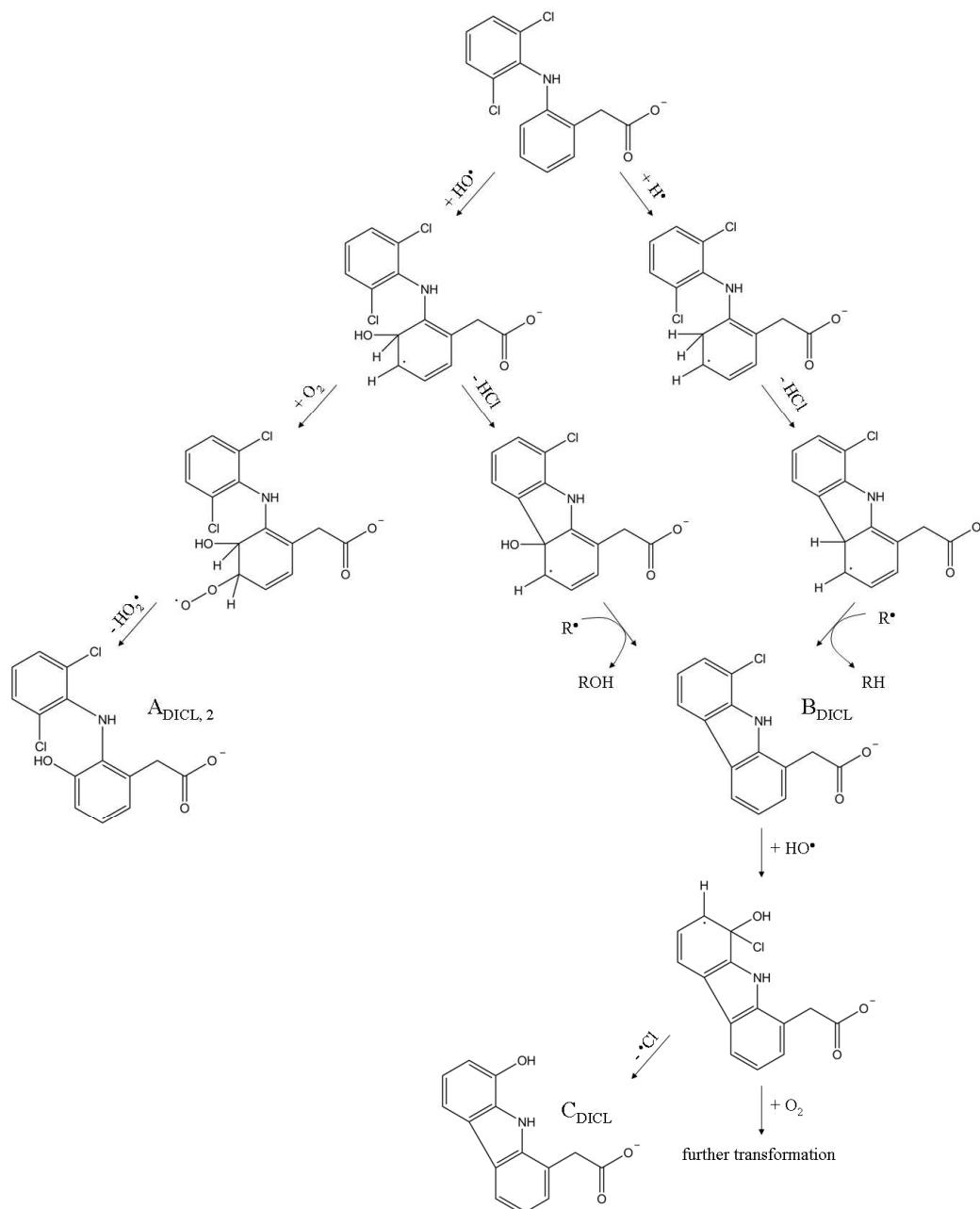Fig. 4. Possible pathway of formation of three VUV degradation by-products of NAP.

Fig. 5. Possible pathway of formation of three VUV degradation by-products of DICL.

References

[1] Gonzalez, M.G.; Oliveros, E.; Wörner, M.; Braun, A.M., *Vacuum-ultraviolet photolysis of aqueous reaction systems*, Journal of Photochemistry and Photobiology, C: Photochemistry Reviews, 5, 225–246, 2004.

[2] Arany, E.; Oppenländer, T.; Gajda-Schrantz, K.; Dombi, A., *Influence of H_2O_2 formed in situ on the photodegradation of ibuprofen and ketoprofen*, Current Physical Chemistry, 2 (3), 286–293, 2012.

[3] Arany, E.; Szabó, R.K.; Apáti, L.; Alapi, T.; Ilisz, I.; Mazellier, P.; Dombi, A.; Gajda-Schrantz, K., *Degradation of naproxen by UV, VUV photolysis and their combination*, Journal of Hazardous Materials, 262, 151–157, 2013.

[4] Arany, E.; Láng, J.; Somogyvári, D.; Láng, O.; Alapi, T.; Ilisz, I.; Gajda-Schrantz, K.; Dombi, A.; Kőhidai, L.; Hernádi, K., *Vacuum ultraviolet photolysis of diclofenac and the effect of the treated aqueous solutions on the proliferation and migratory responses of Tetrahymena pyriformis*, Science of the Total Environment, 468–469, 996–1006, 2014.

[5] Kozmér, Z.; Arany, E.; Alapi, T.; Takács, E.; Wojnárovits, L.; Dombi, A., *Determination of the rate constant of hydroperoxyl radical reaction with phenol*, Radiation Physics and Chemistry, 102, 135-138, 2014.

[6] Sato, K.; Takimoto, K.; Tsuda, S., *Degradation of aqueous phenol solution by gamma-irradiation*, Environmental Science & Technology, 12 (9), 1043-1046, 1978.

Scientific activity

Papers

Papers related to the PhD Thesis

1) Arany, E.; Oppenländer, T.; Gajda-Schrantz, K.; Dombi, A., *Influence of H_2O_2 Formed in Situ on the Photodegradation of Ibuprofen and Ketoprofen*, Current Physical Chemistry, 2 (3), 286-293, 2012.

IF: 1.23; independent citation: 1

2) Arany, E.; Szabó, R.K.; Apáti, L.; Alapi, T.; Ilisz, I.; Mazellier, P.; Dombi, A.; Gajda-Schrantz, K., *Degradation of naproxen by UV, VUV photolysis and their combination*, Journal of Hazardous Materials, 262, 151-157, 2013.

IF: 3.925; independent citations: 2

3) Arany, E.; Láng, J.; Somogyvári, D.; Láng, O.; Alapi, T.; Ilisz, I.; Gajda-Schrantz, K.; Dombi, A.; Kőhidai, L.; Hernádi, K., *Vacuum ultraviolet photolysis of diclofenac and the effects of its treated aqueous solutions on the proliferation and migratory responses of Tetrahymena pyriformis*, Science of the Total Environment 468-469, 996-1006, 2014.

IF: 3.258; independent citation: –

Papers not directly related to the PhD Thesis

4) Bartalis, I.; Siminiceanu, I.; **Arany, E.**: *Enhanced ozonation of phenol in water*, Revista de Chimie, 62 (11) 1047-1051, 2011.

IF: 0.599; independent citation: 1

5) Siminiceanu, I.; Bartalis, I.; **Arany, E.**: *Enhancement of phenol oxidation by ozone in wastewater. II: Kinetic modeling*, Environmental Engineering and Management Journal, 11 (2) 449-455, 2012.

IF: 1.004; independent citations: 5

6) Šojic´, D.; Despotovic´, V.; Orcˇic´, D.; Szabó, E.; **Arany, E.**; Armakovic´, S.; Illés, E.; Gajda-Schrantz, K.; Dombi, A.; Alapi, T.; Sajben-Nagy, E.; Palágyi, A.;

Vágvölgyi, Cs.; Manczinger, L.; Bjelica, L.; Abramovic, B., *Degradation of thiamethoxam and metoprolol by UV, O₃ and UV/O₃ hybrid processes: Kinetics, degradation intermediates and toxicity*, Journal of Hydrology, *47-473*, 314-327., 2012.

IF: 2.656; independent citations: 4

7) Alapi, T.; Berecz, L.; **Arany, E.**; Dombi, A., *Comparison of the UV-Induced Photolysis, Ozonation and their Combination at the Same Energy Input Using a Self-Devised Experimental Apparatus*, Ozone Science & Engineering, 35 (5), 350-358, 2013.

IF: 0.806; independent citation: –

8) Kozmér, Zs.; **Arany, E.**; Alapi, T.; Takács, E.; Wojnárovits L.; Dombi, A., *Determination of the rate constant of hydroperoxyl radical reaction with phenol*, Radiation Physics and Chemistry 102, 135-138, 2014.

IF: 1.189; independent citation: –

Cumulative impact factor: 14.667
Total number of independent citations: 10

Book chapters
Book chapters related to the PhD Thesis

1) Arany, E.; Szabó, R.; Gajda-Schrantz, K.; Mazellier, P.; Dombi, A., *Degradation of naproxen by advanced oxidation processes,* In: A geotermikus energia fenntartható hasznosítása, Eds. Szanyi, J.; Medgyes, T.; Kóbor, B.; Kurunczi, M.; Egyed, E., InnoGeo Kft., Szeged, 2012., ISBN: 978-963-89689-0-6, pp. 209-220.

2) Arany, E.; Oppenländer, T.; Gajda-Schrantz, K.; Dombi, A., *Influence of H₂O₂ formed in situ on the photodegradation of ibuprofen and ketoprofen,* In: A geotermikus energia fenntartható hasznosítása, Eds. Szanyi, J.; Medgyes, T.; Kóbor, B.; Kurunczi, M.; Egyed, E., InnoGeo Kft., Szeged, 2012., ISBN: 978-963-89689-0-6, pp. 221-241.

3) Gajda-Schrantz, K.; **Arany, E.**; Illés, E.; Szabó, E.; Pap, Zs.; Takács, E.; Wojnárovits, L., *Advanced Oxidation Processes for Ibuprofen ibuprofen removal and ecotoxicological risk assessment of degradation intermediates,* In: Wilton C.C.; Brant R.B.

15

(Eds.) Ibuprofen: Clinical Pharmacology, Medical Uses and Adverse Effects, Nova Science Publishers, Inc., New York, USA, 159-232, 2013, ISBN: 978-1-62618-659-0.

Conference participations

PhD Thesis related participations

1) Szabó, R.; **Szakács, E.**; Gajda-Schrantz, K.; Mazellier, P.; Dombi, A., *Degradation of naproxen (NSAID) by Advanced Oxidation Processes,* XXIII. IUPAC Symposium on Photochemistry, Ferrara, Italy, 2010.07.11-16.

2) Dombi, A.; Gajda-Schrantz, K.; Oppenländer, T.; **Szakács, E.**, *Intrinsic production of hydrogen peroxide by 172 nm photolysis of water and during the photomineralization of ibu- or ketoprofen by 172 nm and/or by 185/254 nm light,* The 36th ISEAC International Symposium on Environmental Analytical Chemistry, Rome, Italy, 2010.10.05-09.

3) Arany, E.; Oppenländer, T.; Gajdáné Schrantz, K.; Dombi, A., *Hidrogén-peroxid képződése a víz 172 nm-es fotolízise, valamint az ibu- és a ketoprofen 172 és/vagy 185/254 nm-es fotomineralizációja során,* XXXIII. Kémiai Előadói Napok, Szeged, Hungary, 2010.10.25-27.

4) Arany, E.; Szabó, R.; Gajda-Schrantz, K.; Mazellier, P.; Dombi, A., *Degradation of naproxen by Advanced Oxidation Processes,* DUF Tudomány Hete, Dunaújváros, Hungary, 2010.11.06-12.

5) Arany, E.; Alapi, T.; Gajdáné Schrantz, K.; Dombi, A., *Diclofenac vákuum-ultraibolya fotolízise,* MKE 1. Nemzeti Konferencia, Sopron, Hungary, 2011.05.22-25.

6) Arany, E.; Alapi, T.; Gajda-Schrantz, K.; Dombi, A., *Vacuum-ultraviolet photolysis of diclofenac,* Photoctalytic and Advanced Oxidation Technologies for Treatment of Water, Air, Soil and Surfaces, Gdańsk, Poland, 2011.07.04.08.

7) Arany, E.; Cerrone, S.; Szabó, R.K.; Alapi, T.; Gajda-Schrantz, K.; Dombi, A., *Vacuum-ultraviolet photolysis of non-steroidal anti-inflammatory drugs,* Proceedings of

the 17th Int. Symp. on Analytical and Environmental Problems, Szeged, Hungary, 2011.09.19., Ed.: Galbács Z., SZAB, Szeged, ISBN: 978-963-306-146-6, pp. 64-67.

8) <u>Arany, E.</u>; Szabó, E.; Illés, E.; Alapi, T.; Gajda-Schrantz, K.; Dombi, A., *The degradation of ibuprofen by different AOPs in pure and natural waters,* Optimization of Cost Effective and Environmentally Friendly Procedures for Treatment of Regional Water Resources – workshop, Szeged, Hungary, 2011.12.01-02.

9) <u>Arany, E.</u>; Szabó, E.; Alapi, T.; Dombi, A.; Gajda-Schrantz, K., *VUV photolysis of pharmaceuticals and pesticides,* Optimization of Cost Effective and Environmentally Friendly Procedures for Treatment of Regional Water Resources – workshop, Szeged, Hungary, 2011.12.01-02.

10) <u>Arany, E.</u>; Kozmér, Zs.; Apáti, L.; Alapi, T.; Gajdáné Schrantz, K.; Dombi, A., *Reakciókörülmények hatása aromás vegyületek vákuum-ultraibolya fotolízisére,* Környezettudományi Doktori Iskolák Konferenciája, Budapest, Hungary, 2012.08.30.-31., Eds. Jurecska, L., Kiss, Á., Pátria Nyomda Zrt., Budapest, 2012, ISBN: 978-963-284-242-4, pp. 211-218.

11) <u>Kozmér, Zs.</u>; **Arany, E.**; Alapi, T.; Dombi, A., *The effect of the reaction conditions on the vacuum ultraviolet photolysis of phenol,* Proceedings of the 18th International Symposium on Analytical and Environmental Problems, Szeged, Hungary, 2012.09.24., Ed. Galbács, Z., SZAB, Szeged, ISBN: 978-963-306-165-7, pp. 177-181.

12) <u>Arany, E.</u>; Illés, E.; Farkas, J.; Szabó, E.; Alapi, T.; Gajdáné Schrantz, K.; Dombi, A.; Takács, E.; Wojnárovits, L., *Szerves mikroszennyezők bontása fotolízissel és radiolízissel,* 1. Környezetkémiai Szimpózium, Mátrafüred, Hungary, 2012.10.11-12.

13) <u>Kozmér, Zs.</u>; Alapi, T.; **Arany, E.**; Dombi, A.; Takács, E.; Wojnárovits, L., *A fenol vákuum-ultraibolya fotolízisének és gamma radiolízisének összehasonlítása különböző gyökátalakító anyagok adagolásával,* XVIII. Nemzetközi Vegyészkonferencia, Cluj-Napoca, Romania, 2012.11.22-25.

14) Kozmér, Zs.; **Arany, E.**; Alapi, T.; Dombi, A.; Takács, E.; Wojnárovits, L.; Hernádi, K., *Similarities and differences between the radicals of reactions produced during vacuum ultraviolet photolysis and gamma radiolysis*, 7th International Conference on Environmental Engineering and Management (Integration Challenges for Sustainability), Wien, Austria, 2013.09.18-21., ISBN 978-973-621-418-9, pp. 115-116.

15) Kozmér, Zs.; **Arany, E.**; Alapi, T.; Dombi, A.; Hernádi, K., *Terc-butanol, hidroxilgyökfogó koncentrációjának hatása a fenol vákuum-ultraibolya fotolízisére*, XI. Környezetvédelmi Analitikai és Technológiai Konferencia, Hajdúszoboszló, Hungary, 2013.10.02-04.

16) Kozmér, Zs.; **Arany, E.**; Alapi, T.; Dombi, A.; Takács, E.; Wojnárovits, L., *Hasonlóságok és különbségek a fenol vákuum-ultraibolya fotolízise és γ-radiolízise között, a reakciókörülmények befolyása*, XXXVI. Kémiai Előadói Napok, Szeged, Hungary, 2013.10.28-30.

17) Kozmér, Zs.; **Arany, E.**; Alapi, T.; Takács, E.; Wojnárovits, L.; Dombi, A.; Hernádi, K., *Hangyasav, mint hidroxilgyökfogó koncentrációjának hatása a fenol vákuum-ultraibolya fotolízisére és γ-radiolízisére*, III. Interdiszciplináris Doktorandusz Konferencia 2014, Pécs, Hungary, 2014.04.15-17.

Conference participations not related to the PhD Thesis

18) Alapi, T. ; **Szakács, E.**; Dombi, A., *Fenol vizes oldatának kezelése ózon generálására alkalmas kisnyomású higanygőzlámpával*, VIII. Környezetvédelmi analitikai és technológiai konferencia, Eger, Hungary, 2007.10.10-12.

19) Szakács E.; Alapi T.; Dombi A., *A pH hatása fenol vizes oldatának UV fotolízise, ózonos valamint UV fotolízissel kombinált ózonos kezelése során (Effect of pH on the transformation of phenol in the aqueous solutions treated by UV photolysis, ozonation and their combination)*, XIII. Nemzetközi Vegyészkonferencia, Cluj-Napoca, Romania, 2007.11.08-11, Ed.: Majdik K., ISSN: 1843-6293, pp. 257-261.

20) Alapi, T.; Pallagi, A.; **Szakács, E.**; Dombi, A., *Different effect of the molecular oxygen in the UV-induced transformation of phenol in water and acetonitrile,* Central European Conference on Photochemistry, Bad Hofgastein, Austria, 2008.02.10-14.

21) Dombi, A.; Alapi, T.; Gajdáné Schrantz, K.; Illés, E.; **Szakács, E.**, *Nagyhatékonyságú oxidációs eljárások: fenol bomlásának összehasonlítása különböző eljárásokkal (Advanced oxidation processes; comparison of different methods in case of phenol decomposition),* XIV. Nemzetközi vegyészkonferencia, Cluj-Napoca, Romania 2008.11.13-15, Ed.: Majdik K., ISSN: 1843-6293, pp. 239-242.

22) Batalis, I.; Siminiceanu, I.; **Arany, E.**, *Enhancement of phenol oxidation by ozone in wastewater I. Experimental results,* 6th International Conference Environmental Engineering and Management (ICEEM 06), Balatonalmádi, Hungary, 2011.09.01-04.

23) Siminiceanu, I.; Bartalis, I.; **Arany, E.,** *Enhancement of phenol oxidation by ozone in wastewater II. Kinetic modelling,* 6th International Conference Environmental Engineering and Management (ICEEM 06), Balatonalmádi, Hungary, 2011.09.01-04.

24) Abramović, B.; Alapi, T.; **Arany, E.**; Beszédes, S.; Bjelica, L.; Dalmacija, M.; Despotović, V.; Dombi, A.; Farkas, J.; Gajda-Schrantz, K.; Guzsvany, V.; Illés, E.; Kertész, Sz.; Kler, S.; Kmetykó, Á.; Kredics, L.; László, Zs.; Manczinger, L.; Mazellier, P.; Mogyorósi, K.; Orčić, D.; Pap, Zs.; Rajić, L.; Szabó, E.; Szabó, R.; Šojić, D.; Vágvölgyi, Cs.; Vajda, K.; Veréb, G., *Optimization of Cost Effective and Environmentally Friendly Procedures for Treatment,* Optimization of Cost Effective and Environmentally Friendly Procedures for Treatment of Regional Water Resources – workshop, Szeged, Hungary, 2011.12.01.02.

25) **Arany, E.**; Kovács, K.; Méreg, A.; Alapi, T.; Farkas, J.; Dombi, A., *Nagyhatékonyságú oxidációs eljárások alkalmazása peszticid tartalmú vizek utókezelésére,* Környezettudományi Doktori Iskolák Konferenciája, Budapest, Hungary, 2012.08.30.-31., Eds. Jurecska, L.; Kiss, Á., Pátria Nyomda Zrt., Budapest, 2012, ISBN: 978-963-284-242-4, pp. 184-191.

26) <u>Kozmér, Zs.</u>; Alapi, T.; **Arany, E.**; Dombi, A.; Takács, E.; Wojnárovits, L., *A reaktív intermedierek szerepe fenol vizes oldatának radiolízisében,* Őszi Radiokémiai Napok 2012, Siófok, Hungary, 2012.10.08-10.

27) Šojić, D.; Despotović, V.; Orčić, D.; Szabó, E.; **Arany, E.**; Armaković, S.; Illés, E.; <u>Gajda-Schrantz, K.</u>; Dombi, A.; Alapi, T.; Sajben-Nagy, E.; Palágyi, A.; Vágvölgyi, Cs.; Manczinger, L.; Bjelica, L.; Abramović, B., *Degradation of thiametoxam and metoprolol by UV, O_3 and UV/O_3 hybrid processes: Kinetics, degradation intermediates and toxicity,* The18[th] International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil (AOTs-18), Jacksonwille, Florida, USA, 2012.11.12-15.

28) <u>Kozmér, Zs.</u>; **Arany, E.**; Takács, E.; Wojnárovits, L.; Alapi, T.; Dombi, A., *Effect of the concentration of tert-butanol on the gamma radiolysis of phenol*, International Conference on Photocatalytic and Advanced Oxidation Technologies for Treatment of Water, Air, Surfaces, Gdańsk, Poland, 2013.09.09-12.