The effect of reactive species, radical transfer and radical scavenger materials on the VUV photolysis and γ radiolysis of phenol

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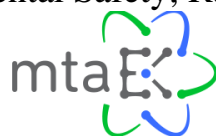
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1. INTRODUCTION AND LITERARY REVIEW

One of the possible auxiliary processes of wastewater treatment methods is the group of **advanced oxidation processes** (**AOP**s), where the degradation of organic materials takes place by reactions with chemically generated reactive species and radicals. The transformation of organic materials is usually traced back to reactions with highly reactive **hyrdoxyl radicals** (**•OH**). However the knowledge of the ongoing chemical processes in the system, roles of the different reactive species, and the effect of reaction conditions is scarce. This knowledge is important in the designing and optimization during the realization of industrial processes. Radicals can be produced without additional reactants by **vacuum ultraviolet photolysis** (**VUV**) and **gamma (γ) radiolysis**, during which •OH is generated directly from water. Therefore, these processes can be used for the investigation of radical reactions, and the discovery of the mechanisms of complex radical processes.

Xenon-excimer lamp emitting at 172 nm wavelength can be used for the VUV photolysis of water. The energy of the 172 nm photons is high enough for the homolytic decomposition of water molecules resulting in •OH and hydrogen radicals (•H) as primary radicals ($\Phi_{172\,nm}$=0,42 [1]), and the ionization of water to a lesser extent ($\Phi_{172\,nm}$≤0,05 [2]). The 172 nm light is absorbed by an extremely thin, 0.035 mm layer of water ($\varepsilon_{172\,nm}$=9,9 mol^{-1} dm^3 cm^{-1}, at 25 °C [3]), producing a quite inhomogeneous system with regards to the concentration of the radicals and the dissolved O_2. During the radiolysis of water, •OH, hydrated electrons (e_{aq}^-) (0,28 µmol J^{-1}), and with a lower yield •H (0,062 µmol J^{-1}) are generated in the first step in a homogeneous distribution [4].

There is a wide spectrum of data and knowledge available in the literature regarding the reactions of **phenol** (PhOH, as a simple model compound) with primary radicals. Based on these, there are several suggestions for the transformation mechanisms of both VUV photolysis and γ radiolysis. Following the addition of •H and •OH onto the aromatic ring hydroxy- (HCD•) and dihydroxy-cyclohexadienyl (DHCD•) radicals are formed, whose recombination and disproportioning results in the partial reformation of PhOH. In parallel, depending on the attack site of the •OH, the formation of substituted 1,2-; 1,3; and 1,4-dihydroxybenzenes is possible. In solutions saturated with O_2, the addition of the O_2 molecules onto the cyclohexadienyl-type radicals can take place, followed by the elimination of HO$_2$• (which in the case of HCD• results in the reformation of PhOH [5]). In further oxidation steps ring-opening and fragmentation occur most probably [6]. In solutions containing O_2, hydroperoxil radical (HO$_2$•) and superoxide radical anion (O_2•$^-$) form in high concentrations, partly due to the reaction of primary species

($^{\bullet}$OH, $^{\bullet}$H and e_{aq}^-) with O_2, and partly due to the transformation of organic materials through peroxyl radicals. So far, only the $HO_2^{\bullet}$ radical's rate constant with PhOH has been determined out of the $HO_2^{\bullet}/O_2^{\bullet-}$ radical pair according to the literature. This rate constant, however, is significantly lower than the rate constants of the primary radicals [7].

The majority of AOPs is based on the role of $^{\bullet}$OH, and the literature is also mostly focused on the reactions of $^{\bullet}$OH. At the same time, during the oxidative treatment of aqueous solutions, besides $^{\bullet}$OH, there are a large number of reactive species whose concentration, role and significance can change with the reaction conditions. For the purposeful influence of the concentration of each of the radicals, for the transformation of species, and as a result, for the investigation of the roles of the individual radical reactions, **radical transfer** and **radical scavenger materials** can be used [8]. During the experiments O_2 and N_2O gases were used as radical scavenger/transfer materials. Furthermore, tert-butanol (t-BuOH, $(CH_3)_3COH$), methanol (MeOH, CH_3OH), formic acid (HCOOH), sodium formate (HCOONa) (and partially isopropanol (i-PrOH)) were used. The specific reactions of these compounds are summarized on Figure 1, and their rate constants with primary radicals in Table 1.
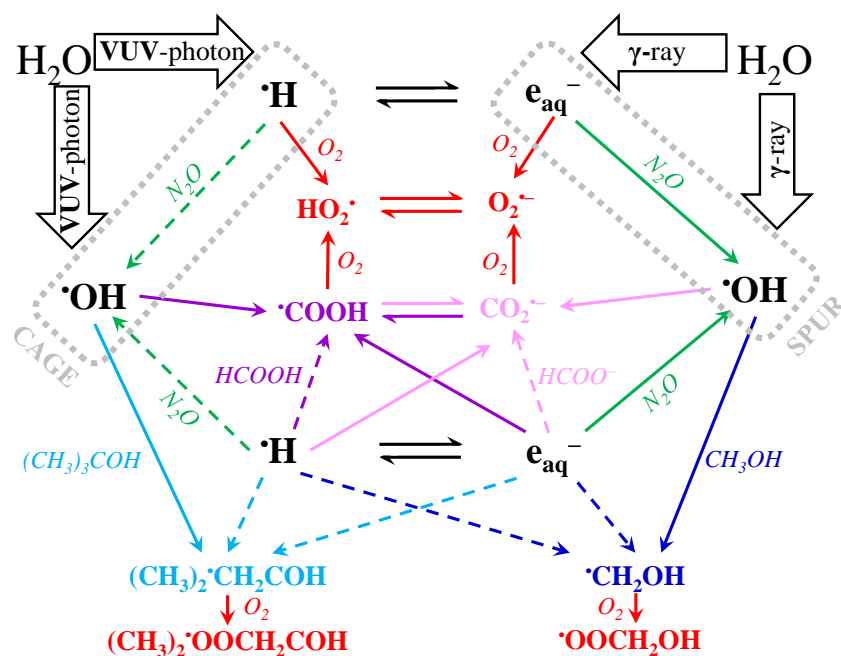

Figure 1: *The primary and secondary radicals formed during the VUV photolysis and γ radiolysis of water in the presence of various radical transfer and scavenger materials and their conversions (the dashed lines signify the lower rate processes)*

Table 1: *The materials applied during the experiments and the rate constans of primary species' reatcions (mol^{-1} dm^3 s^{-1})*

X	k(X+$^{\bullet}$OH)	k(X+$^{\bullet}$H)	k(X+e_{aq}^-)
PhOH	8.4×10^9 [9]	1.7×10^9 [10]	3.0×10^7 [11]
COU	2.0×10^9 [12]	n.a.*	1.6×10^{10} [13]
O$_2$	–	2.1×10^{10} [10]	1.9×10^{10} [10]
N$_2$O	–	2.1×10^6 [14]	9.1×10^9 [15]
t-BuOH	6.2×10^8 [16]	2.3×10^5 [17]	<4.0×10^5 [18]
MeOH	9.7×10^8 [5]	1.1×10^6 [17]	<1.0×10^4 [19]
i-PrOH	2.0×10^9 [16]	5.3×10^6 [17]	n.a.
HCOOH	1.3×10^8 [10]	4.4×10^5 [10]	1.4×10^8 [20]
HCOO$^-$	3.2×10^9 [10]	2.1×10^8 [10]	8.0×10^3 [21]

*: no available data

For the detection and quantification of $^{\bullet}$OH and the investigation of the effect of the reaction conditions on the concentration of $^{\bullet}$OH during the photo- and radiochemical reactions, a technique was used based on the formation of a fluorescent product (**7-hydroxycoumarin**, umbelliferone, 7HC) in the reaction between **coumarin** (COU) and $^{\bullet}$OH [22, 23]. The efficiency of the individiual processes were compared using a comparison method by Bolton et al. [24], that is independent from the reaction parameters. This is based on the calculation of the input energy required for the transformation of the target compound ('**electric energy per order**', (E_{EO})).

$$E_{EO} = \frac{P \times t}{V \times \lg(c_1/c_2)}$$

Where P is the power requirement of the method [kW], t is the time needed [h] to decrease the c_1 initial concentration of target molecule to the one order of magnitude smaller c_2 concentration [mol dm^{-3}], and V is the solution volume treated [m^3].

2. OBJECTIVES

The goal of this work was the detailed characterization of the radical processes that take place during VUV photolytic and γ radiolytic transformation of a simple model molecule, PhOH, while comparing, and gaining a profound understanding of the processes. For this purpose, different dissolved gases (O_2, N_2O) were used to influence the radical set of the system. The formation of the fluorescent product (7HC) during the transformation of COU, and through this the formation rate of $^{\bullet}OH$ was studied.

One of the objectives was the investigation of the effect of the most frequently used $^{\bullet}OH$ scavengers (such as t-BuOH, MeOH, HCOOH, HCOONa (and partly i-PrOH)) on the transformation of PhOH with different reaction parameters (radical scavenger concentration, presence of O_2 and N_2O). While studying the effect of radical transfers the concentration change of PhOH and H_2O_2, and also the pH change, and its influence on the reactions were investigated. Moreover, the effect of the initial pH on the transformation rate of PhOH was studied.

Special emphasis was put onto the clarification of the possible roles of less reactive radicals ($HO_2^{\bullet}/O_2^{\bullet-}$) and the carbon-centred radicals that form from the radical scavenger materials in the transformation of PhOH.

3. EXPERIMENTAL MATERIALS AND METHODS

During the experiments the concentration of the PhOH and COU solutions was 1.0×10^{-4} **mol dm^{-3}** in all cases. Depending on the experiment, the PhOH solutions contained 5.0×10^{-1}; 5.0×10^{-2} or 1.0×10^{-3} **mol dm^{-3}** concentration of **t-BuOH**, **MeOH**, **i-PrOH**, **HCOOH** or **HCOONa** as radical scavengers. For the VUV photolytic experiments a Xe-excimer lamp of 20 W electrical power, emitting at **172±14 nm** wavelength was used, while the γ radiolytic experiments were performed with a **panorama type ^{60}Co-**radiation source (Table 2).

Table 2: *The parameters of VUV photolysis and γ radiolysis and the differences between the two methods*

Viewpoints	VUV photolysis	γ radiolysis
primary species	$^{\bullet}$OH and $^{\bullet}$H	$^{\bullet}$OH and e_{aq}^{-}
photon source	Xe excimer lamp (VUV photon)	^{60}Co isotope (γ-ray)
E_{photon}	7.21 eV	1.33×10^{6} eV
radical formation rate ($^{\bullet}$OH + $^{\bullet}$H + e_{aq}^{-})	1.1×10^{-5} mol dm^{-3} s^{-1}	1.6×10^{-6} mol dm^{-3} s^{-1}
radical formation	only in the photoreactive zone near to the lamp surface	in the whole volume
radical distribution	inhomogeneous	homogeneous
conveyance of solution	circulation and mixing	mixing / no flow[*]
gas inner	continuous	continuous / preliminary saturation[*]

[*]: During experiments performed in ampoules.

The concentration of the forming H_2O_2 was measured by UV-Vis spectroscopy using a Spectroquant® H_2O_2 test traded by Merck. For the separation and quantification of 1,2- and 1,4-dihydroxybenzene (intermediates of PhOH transformation) an HPLC apparatus was used equipped with a diode array UV detector. The concentration of COU was determined by UV spectroscopy (ABS$_{max}$=277 nm), and the concentration of the forming 7HC by fluorimetry ($\lambda^{excitation}$=332 nm, $\lambda^{emission}$=455 nm).

4. RESULTS AND INTERPRETATION

For both VUV photolysis and γ radiolysis, the presence of O_2 and N_2O increased the transformation rate of PhOH significantly, when compared to the O_2 free cases (O_2: during photolysis 2.9, during radiolysis 5.7 times increase, N_2O: during photolysis 2.1, during radiolysis 9.4 times increase) (Figure 2 a and b). The positive effect of O_2 on the degradation rate was explained by the inhibition of reformation of carbon-centred radicals (DHCD˙ and HCD˙) produced from PhOH. During radiolysis, the positive effect of O_2 is twice as large as in case of VUV photolysis. This difference is most likely caused by the significant difference in the homogenity of the distribution of the radicals. During photolysis, in the small irradiated solution volume the ˙OH and ˙H (and therefore DHCD˙ and HCD˙) concentration is very high, and the dissolved O_2 concentration decreases significantly due to the formation of peroxyl radicals. Because of this, the O_2 cannot exert its positive effect, as in case of γ radiolysis, where the concentration of radicals and the dissolved O_2 can be considered homogeneous. The increase in transformation rate in the presence of N_2O can be explained by the increased ˙OH concentration, which in case of photolysis manifests to a significantly lesser extent than in case of radiolysis, due to the low reaction rate of N_2O and ˙H (during photolysis) and the high reaction rate of N_2O and hydrated electron (during radiolysis).
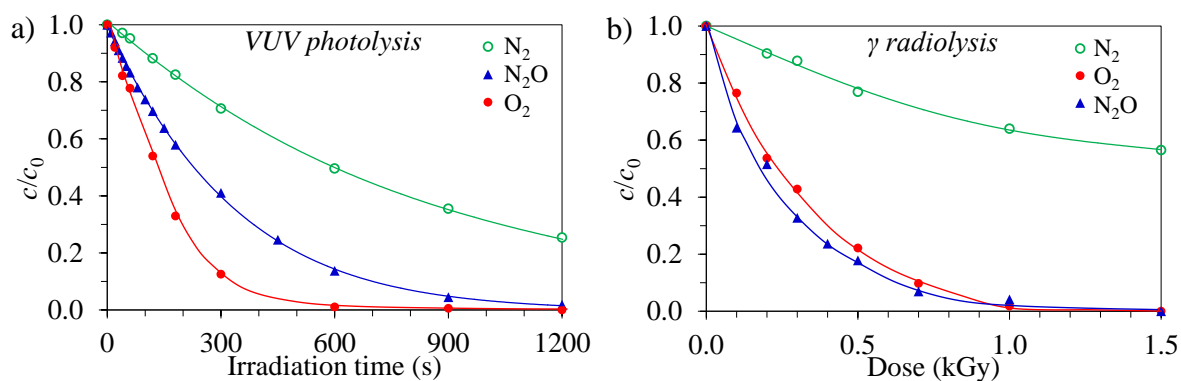

Figure 2: *The concentration of PhOH versus **a)** the time during VUV photolysis and **b)** the dose absorbed during γ radiolysis in O_2 free (○ and △), O_2 (● and ▲) and N_2O saturated (● and ▲) solutions*

Considering that ˙OH radicals play the primary role in the transformation of PhOH, the transformation of COU and its forming fluorescent intermediate (7HC) under different conditions was studied for the investigation of the ˙OH formation rate. Both of the dissolved gases (O_2 and N_2O) caused an increase in the concentration of the forming 7HC, as compared to the N_2 saturated system. ˙OH was produced at the highest rate and in the highest quantity when the dissolved gas was O_2 (Figure 3 a and b). The results have shown that the two

processes' difference in homogenity regarding the O_2 concentration effected both the degradation of COU and production of $^\bullet$OH. It has been proven that while during radiolysis – due to the homogeneous distribution of O_2 – 7HC forms via peroxyl radical formation, whereas in the case of VUV photolysis, the formation of 7HC by dismutation – that is typical in O_2 free conditions – can also have a role in O_2 saturated solutions. In the presence of dissolved gases the rate of degradation has decreased by 10 to 20%, which was interpreted to be the result of the decreased e_{aq}^- and $^\bullet$H concentrations due to the reactions of O_2 and N_2O. This negative effect cannot be compensated by the increased $^\bullet$OH concentration. Based on these observations, the e_{aq}^- and $^\bullet$H are supposed to have a significant role in the degradation of COU.
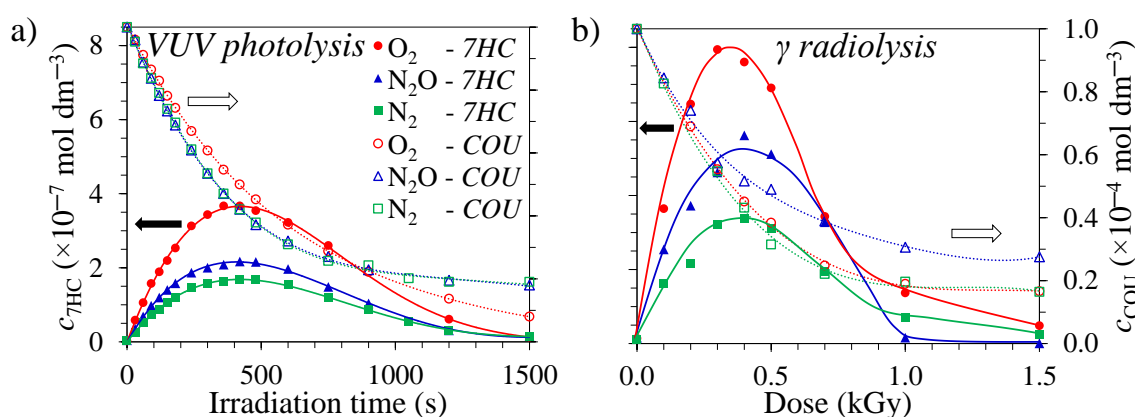

Figure 3: *COU degradation and 7HC formation and tranformation curves versus irradiation time and dose in O_2 free (■ and □), O_2 (● and ○) and N_2O saturated (▲ and △) COU solutions ($c_0 = 1.0 \times 10^{-4}$ mol dm^{-3}) during **a)** VUV photolysis and **b)** γ radiolysis*

The E_{EO} values calculated for the comparison of the efficiency of the two oxidation processes show, that both the O_2 and N_2O considerably decreased (by minimum 60%) the electrical power needed for the decrease of PhOH concentration by one order of magnitude (Table 3). From the point of the specific consumed power, the efficiency of γ radiolysis can surpass the efficiency of VUV photolysis by at least one order of magnitude, irrespective of the applied gas and the properties of the compound to be degraded.

Table 3: *E_{EO} values of VUV photolysis and γ radiolysis of PhOH and COU $1,0 \times 10^{-4}$ mol dm^{-3} initial concentration in case of O_2 free, O_2 and N_2O saturated COU solutions*

		VUV photolysis			γ radiolysis		
		N_2	O_2	N_2O	N_2	O_2	N_2O
PhOH	E_{EO} (kW m^{-3} order^{-1})	40.0	6.7	16.7	1.67	0.19	0.17
	Relative E_{EO} (%)	100	17	42	100	12	10
	E_{EO} ratios (VUV:γ)	**24 (N_2)**		**34 (O_2)**		**100 (N_2O)**	
COU	E_{EO} (kW m^{-3} order^{-1})	33.0			0.50		
	E_{EO} ratios (VUV:γ)	**66 (N_2, O_2, N_2O)**					

Hereinafter the effect of radical scavengers (t-BuOH, MeOH, HCOOH, HCOO⁻ and partly i-PrOH) (in a 10, 500, and 5000-fold excess compared to PhOH) was investigated on the transformation rate of PhOH in solutions bubbled with N_2, O_2, and N_2O. It was a surprising observation that under O_2 free conditions, in 10-fold excess all scavengers increased the transformation rate of the PhOH compared to the case without scavengers, in case of both processes (during radiolysis the addition of MeOH or HCOOH resulted in a 3 times increase in the transformation rate, while during photolysis t-BuOH increased it by approximately 2 times) (Figure 4). In these cases the large majority of the ˙OH (which plays a major role in the transformation of PhOH) react with the scavengers, while the ˙H still contributes to the transformation of PhOH significantly. The carbon-centred radicals that are produced from the (t-˙BuOH, ˙CH_2OH, ˙COOH, CO_2˙⁻) do not contribute directly to the transformation of PhOH, yet their reactions with HCD˙ and DHCD˙ strongly suppress their recombination and disproportionation, which would result in a partial reformation to PhOH. Finally, the scavengers under certain concentration ratios increase the transformation rate of PhOH, despite the decrease of the concentration of primary radicals. As far as the concentration of all primary radicals is decreased considerably due to a scavenger, then this negative effect cannot counteract the positive effect manifested in the inhibition of the reformation of PhOH. Increasing the PhOH:scavenger ratio to 1:500 and 1:5000, the role of ˙OH and ˙H in the transformation of PhOH is suppressed significantly, and consequently the initial reaction rate decreases.
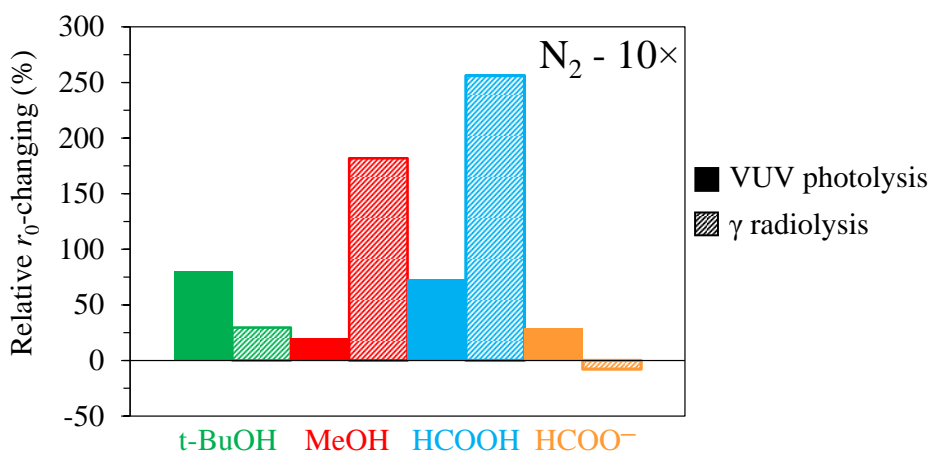

Figure 4: *The relative initial rate shift of PhOH degradation ($c_{0,PhOH}$=1.0×10⁻⁴ mol dm⁻³) to the 10 times excess radical scavengers containing ($c_{0,radical\ scavenger}$=1.0×10⁻³ mol dm⁻³) in O_2 free solutions during VUV photolysis (■) and γ radiolysis (□) compared to the case of absence of radical scavenger*

In solutions bubbled with O_2 and N_2O the transformation rate of PhOH decreased significantly (in an increasing manner with the increase of scavenger concentration) compared to the case without scavenger, in both processes. The primary reason for this is that along with the decrease of concentration of $^\bullet OH$, the concentration of $^\bullet H/e_{aq}^-$ is also markedly decreased due to their reactions with the dissolved gases and scavengers. The dissolved O_2 blocks the reformation of $DHCD^\bullet$ to PhOH via the formation of peroxyl radicals. Besides, O_2 transforms the carbon-centred radicals that form from the scavengers into peroxyl radicals, therefore their positive effect cannot prevail. In N_2O bubbled solutions there is a competition for the $^\bullet H$ between the N_2O, the scavenger, and the PhOH, meaning that during VUV photolysis the positive effect of N_2O on the $^\bullet OH$ concentration will be less prominent. As a result, when using N_2O during radiolysis, there was a considerably larger inhibition when using scavengers, than in case of photolysis. In the presence of dissolved O_2 and N_2O the scavengers exert their effect on the transformation rate of PhOH primarily via the competition for $^\bullet OH$.

While studying the effect of HCOOH and $HCOO^-$ it was observed that in the presence of HCOOH the transformation rate of PhOH was higher during both processes, in all concentration conditions, and in the presence of all three gases, than in the presence of $HCOO^-$. Apart from the larger $^\bullet OH$ and $^\bullet H$ scavenging capacity of $HCOO^-$, this difference can also be explained by the difference in the pH values of the solutions. In the presence of HCOOH the pH strongly decreased (pH=2-3), while in the presence of $HCOO^-$ it increased to a great extent (pH=11-12). It was determined that in both processes the initial reaction rate of PhOH largely depends on the initial pH of the irradiated solution according to a maximum curve, reaching the maximum value at pH=6 (Figure 5). This was understood as the increase of the less reactive $^\bullet O^-$ and PhO^-, and $PhO^\bullet$ (that reform into PhOH during H-abstraction).
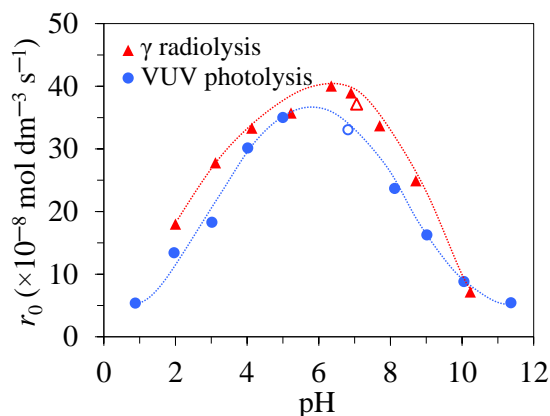

Figure 5: *PhOH initial degradation rate (c_0=1.0×10^{-4} mol dm^{-3}) versus pH in the presence of HClO$_4$ and NaOH in O$_2$ saturated solutions during VUV photolysis (●) and γ radiolysis (▲)*

H_2O_2 was produced in a significant concentration in solutions bubbled with O_2 and N_2O, mainly as a result of the $HO_2^•/O_2^{•-}$ recombination reaction. In O_2 saturated solutions the H_2O_2 concentration increased with the increase of the initial concentration of radical scavengers, which can be explained by the forming peroxyl radicals and the increased $HO_2^•/O_2^{•-}$ concentrations resulting from the transformation of the peroxyl radicals.

In accordance with the objectives the role of the forming low reactivity radicals on the transformation of PhOH was investigated. Using γ radiolysis, in the presence of HCOOH and HCOO$^-$ The rate constant for the reaction between PhOH and $HO_2^•$ ($k_{HO_2^•+PhOH}$ = (2.7 ± 1.2)×10^3 mol^{-1} dm^3 s^{-1}) was determined. It was found that the role of this species is negligible in the transformation of PhOH in the presence of primary radicals. The reactivity of the carbon-centred radicals forming from the scavengers towards PhOH was also studied, by using radical scavengers in suitable concentrations (Figure 6). The reaction rate constants of the latter carbon-centred radicals fall into the range of 10^2-10^4 mol^{-1} dm^3 s^{-1} and the following order of reactivity applies: t-$^•$BuOH > $^•$CH$_2$OH ~ $^•$COOH > $CO_2^{•-}$. It has been demonstrated that the role of the carbon-centred radicals is also negligible when compared to the reactions of primary radicals.

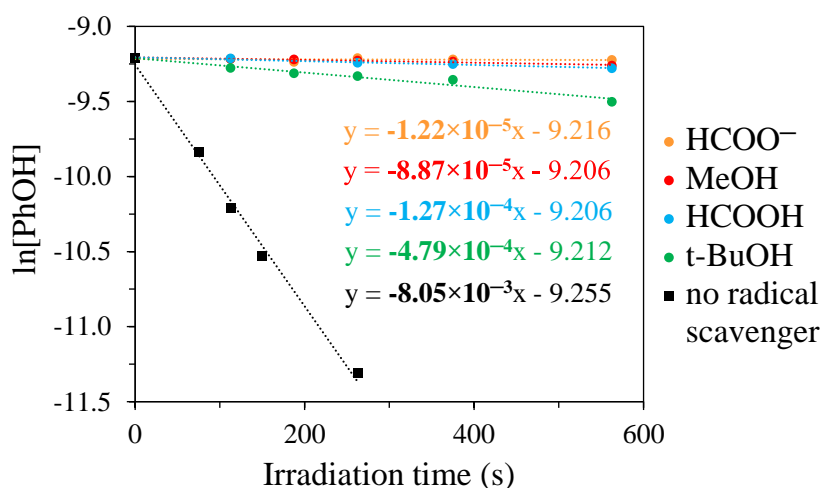***Figure 6:*** *The logarithm of PhOH concentration (c$_0$=1.0×10^{-4} mol dm^{-3}) versus irradiation time in the presence (●) and in the absence (■) of 5.0×10^{-1} mol dm^{-3} radical scavenger in N$_2$O saturated solutions during γ radiolysis*

5. THESES OF DOCTORAL (PH.D.) DISSERTATION

1. **The positive (degradation rate improving) effect of O_2 on the VUV photolysis and γ radiolysis of PhOH and COU can mainly be explained by the formation of peroxyl radicals. This effect is less prominent during VUV photolysis than during γ radiolysis that can be interpretted with the inhomogeneity of O_2 concentration in the solutions irradiated by VUV light.**

The O_2 effectively inhibits the reformation of PhOH from cyclohexadienyl radicals by forming peroxyl radicals (via additioning onto carbon-centred radicals at a high rate) and opening up new reaction pathways for their transformation. During photolysis, in the VUV-irradiated thin layer (0.035 mm) the concentration of the primary species and the carbon-centred radicals forming in their reactions is very high. The carbon-centred radicals react with O_2, and thus decrease the O_2 concentration in the system. In the thesis the significance of this inhomogeneity during the photolysis of both PhOH and COU was demonstrated, while this inhomogeneity does not occur in case of γ radiolysis. Due to the difference between the distributions of radicals between the two processes the positive effect of O_2 (that can be traced back to the peroxyl radical formation) is less visible during VUV photolysis, which can be explained with the inhomogeneity of the O_2 concentration.

2. **The rate constant of $HO_2^{\bullet}$ and PhOH reaction was determined: $(2.7 \pm 1.2) \times 10^3$ mol^{-1} dm^3 s^{-1}. The value is about five times higher than the rate constant of $O_2^{\bullet-}$ and PhOH reaction.**

For the determination of the reaction rate constant the γ radiolysis was used, with HCOOH and HCOO$^-$ radical scavengers applied in suitable concentrations. (Publication 1) It was confirmed that $HO_2^{\bullet}/O_2^{\bullet-}$ mainly play role in the H_2O_2 formation and their contribution to the transformation of PhOH is negligible. (Publication 2 and 3)

3. **The reactivity of carbon-centred radicals formed from various radical scavengers were determined. The order of reactivity: $t\text{-}^{\bullet}BuOH > {}^{\bullet}CH_2OH \sim {}^{\bullet}COOH > CO_2^{\bullet-}$. The values of reaction rate constants fall into the range of $10^2\text{-}10^4$ mol^{-1} dm^3 s^{-1}.**

The PhOH degradation rates were measured during γ radiolysis, in N_2O saturated solutions containing radical scavengers in high concentration. Based on these measurements the rate constants of the reactions of carbon-centred radicals formed from radical scavengers with PhOH ($10^2\text{-}10^4$ mol^{-1} dm^3 s^{-1}) are by 5-7 orders of magnitude higher than that of the reaction of primary radicals (${}^{\bullet}OH$, ${}^{\bullet}H$ and e_{aq}^-) and PhOH. Consequently, the contribution of these species to the transformation of PhOH is negligible. The reactivity of the examined carbon-centred radicals varied according to the following order: $t\text{-}^{\bullet}BuOH > {}^{\bullet}CH_2OH \sim {}^{\bullet}COOH > CO_2^{\bullet-}$. (Publication 2 and 3)

4. **Under O_2 free conditions, the radical scavengers in low concentration increased the degradation rate of PhOH. The disproportion of dihydroxy-cyclohexadienyl radicals ($DHCD^{\bullet}$) is inhibited by the reactions of carbon-centred radicals (formed from radical scavengers) and $DHCD^{\bullet}$ (formed from PhOH), diminishing by this the reformation of PhOH.**

Under O_2 free conditions the radical scavengers increased the transformation rate of PhOH, which can be interpreted by the reaction of the radicals that form from the scavengers and the $DHCD^{\bullet}$, which inhibits the reformation of $DHCD^{\bullet}$ to PhOH. This was mainly observable at low scavenger concentration ratios (1:10 = PhOH:scavenger), at higher scavenger concentrations, and in the presence of dissolved gases the degradation rate of PhOH decreased. (Publication 2 and 3)

5. **Comparing the E_{EO} values of VUV photolysis and γ radiolysis of PhOH and COU the observation was made, that E_{EO} values are by one order of magnitude smaller in case of radiolysis, whereas the radical formation rate is higher during VUV photolysis.**

The electrical power needed to decrease the concentration of PhOH by one order of magnitude was decreased by 80% for both processes in the presence of O_2, while it was 80% for radiolysis and 60% for photolysis in the presence of N_2O. At the same time, the dissolved gases had no significant effect in case of COU. This can primarily be traced back to the determining role of e_{aq}^- in the transformation of COU, which is negligible in case of PhOH.

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7. LIST OF SCIENTIFIC PUBLICATIONS AND SCIENTIFIC INDICES

Hungarian Scientific Database (MTMT) identifier**: 10038903**

	total	related to the dissertation
Journals:	**4**	**3**
Impact factor (IF):	9.956	5.320
Number of citations (independent):	23 (17)	21 (16)
Book chapter:	**1**	**1**
Full-length publications:	**9**	**6**
Conference participations:	**32**	**15**
As presenter:	14	11
As coauthor:	6	1
Posters:	12	3

Publications related to the scientific topic of the dissertation:

Journals: Σ **IF: 5.320**

1. **Zsuzsanna Kozmér**, Eszter Arany, Tünde Alapi, Erzsébet Takács, László Wojnárovits, András Dombi: Determination of the rate constant of hydroperoxyl radical reaction with phenol, *Radiation Physics and Chemistry,* 102 (**2014**) 135-138
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   Number of citations: 11 (7) **IF: 1.380**

2. **Zsuzsanna Kozmér**, Eszter Arany, Tünde Alapi, Georgina Rózsa, Klára Hernádi, András Dombi: New insights regarding the impact of radical transfer and scavenger materials on the ˙OH-initiated phototransformation of phenol, *Journal of Photochemistry and Photobiology A: Chemistry*, 314 (**2016**) 125-132
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3. **Zsuzsanna Kozmér**, Erzsébet Takács, László Wojnárovits, Tünde Alapi, Klára Hernádi, András Dombi: The influence of radical transfer and scavenger materials in various concentrations on the gamma radiolysis of phenol, *Radiation Physics and Chemistry,* 124 (**2016**) 52-57
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Book chapter:

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Full-length publications:

1. Náfrádi Máté, **Kozmér Zsuzsanna**, Alapi Tünde, Dombi András: Gyöktranszfer anyagok hatása a fenol VUV-fotolízisére N_2O jelenlétében
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2. Máté Náfrádi, **Zsuzsanna Kozmér**, Tünde Alapi, András Dombi: The effect of tert-butanol on vacuum ultraviolet photolysis of phenol in the presence of N_2O
   20th International Symposium on Analytical and Environmental Problems, ISBN 978-963-12-1161-0 (291-295. p.)
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3. **<u>Zsuzsanna Kozmér</u>**, Eszter Arany, Tünde Alapi, András Dombi: The effect of the reaction conditions of the vacuum ultraviolet photolysis of phenol
   18th International Symposium on Analytical and Environmental Problems, ISBN 978-963-306-165-7 (177-181. p.)
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Conference presentations, posters:

International conferences:

1. **<u>Zsuzsanna Kozmér</u>**, Máté Náfrádi, Erzsébet Takács, László Wojnárovits, Tünde Alapi, András Dombi: The influence of alcohols as radical transfer materials on the gamma radiolysis and VUV photolysis of phenol
   13th Tihany Syposium on Radiation Chemistry, (P42)
       BALATONALMÁDI (**HUNGARY**) 2015. 08. 29. - 09. 03.   (English poster)

2. **Zsuzsanna Kozmér**, Liliána Póta, Tünde Alapi, Erzsébet Takács, László Wojnárovits, András Dombi: Tert-butanol as radical scavenger material for investigation of heterogeneous photocatalysis and other advanced oxidation processes

   4th European Young Engineers Conference, ISBN 978-83-936575-1-3 (399. p.)

   WARSAW (**POLAND**) 2015. 04. 27-29.   (English presentation)

3. <u>Máté Náfrádi,</u> **Zsuzsanna Kozmér**, Tünde Alapi, András Dombi: Effects of formic acid and sodium formate on the ˙OH-initiated transformation of phenol

   4th European Young Engineers Conferenc, ISBN 978-83-936575-1-3 (416. p.)

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4. **Zsuzsanna Kozmér**, Eszter Arany, Tünde Alapi, András Dombi, Erzsébet Takács, László Wojnárovits, Klára Hernádi: 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), ISBN 978-973-621-418-9 (115-116. p.)

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5. **Zsuzsanna Kozmér**, Eszter Arany, Erzsébet Takács, László Wojnárovits, Tünde Alapi, András Dombi: Effect of the concentration of tert-butanol on the gamma radiolysis of phenol

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   GDANSK (**POLAND**) 2013. 09. 09-12.   (English presentation)

6. **Kozmér Zsuzsanna**, Alapi Tünde, Arany Eszter, Dombi András, Takács Erzsébet, Wojnárovits László: A fenol vákuum-ultraibolya fotolízisének és gamma radiolízisének összehasonlítása különböző gyökátalakító anyagok adagolásával

   XVIII. International Conference on Chemistry, ISSN 1843-6293 (75. p.)

   BAILE FELIX (**ROMANIA**) 2012. 11. 22-25.   (Hungarian presentation)

Local conferences:

1. **<u>Kozmér Zsuzsanna</u>**, Póta Liliána, Alapi Tünde, Takács Erzsébet, Wojnárovits László, Dombi András, Hernádi Klára: Nagyhatékonyságú oxidációs eljárások hatékonyságának tanulmányozása gyöktranszfer anyagok jelenlétében

   IV. Interdiszciplináris Doktorandusz Konferencia 2015 (53-54. p.)

       PÉCS 2015. 05. 14-15.   (Hungarian presentation)

2. **<u>Kozmér Zsuzsanna</u>**, Arany Eszter, Alapi Tünde, Takács Erzsébet, Wojnárovits László, Dombi András, Hernádi Klára: Hangyasav, mint hidroxilgyökfogó koncentrációjának hatása a fenol vákuum-ultraibolya fotolízisére és γ-radiolízisére

   III. Interdiszciplináris Doktorandusz Konferencia 2014, ISBN 978-963-642-597-5 (263. p.)

       PÉCS 2014. 04. 15-17.   (Hungarian presentation)

3. **<u>Kozmér Zsuzsanna</u>**, Arany Eszter, Alapi Tünde, Dombi András, Takács Erzsébet, Wojnárovits László: Hasonlóságok és különbségek a fenol vákuum-ultraibolya fotolízise és γ-radiolízise között, a reakciókörülmények befolyása

   XXXVI. Kémiai Előadói Napok, ISBN 978-963-315-145-7 (296. p.)

       SZEGED 2013. 10. 28-30.   (Hungarian presentation)

4. **<u>Kozmér Zsuzsanna</u>**, Arany Eszter, Alapi Tünde, Dombi András, Hernádi Klára: Terc-butanol, hidroxilgyökfogó koncentrációjának hatása a fenol vákuum-ultraibolya fotolízisére

   XI. Környezetvédelmi Analitikai és Technológiai Konferencia, ISBN 978-963-9970-40-3 (72. p.)

       HAJDÚSZOBOSZLÓ 2013. 10. 02-04.   (Hungarian presentation)

5. **<u>Kozmér Zsuzsanna</u>**, Alapi Tünde, Arany Eszter, Wojnárovits László: A reaktív köztitermékek szerepe fenol vizes oldatának vákuum-ultraibolya fotolízisében és γ-radiolízisében

   XXXI. Országos Tudományos Diákköri Konferencia, ISBN 978-963-08-6206-6 (140. p.)

       EGER 2013. 04. 4-6.   (Hungarian presentation)

6. **<u>Kozmér Zsuzsanna</u>**, Alapi Tünde, Arany Eszter, Dombi András, Takács Erzsébet, Wojnárovits László: A reaktív intermedierek szerepe fenol vizes oldatának radiolízisében

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Journals: Σ IF: **4.636**

Georgina Rózsa, **Zsuzsanna Kozmér**, Tünde Alapi, Krisztina Schrantz, Erzsébet Takács, László Wojnárovits: Transformation of Z-thiacloprid by three advanced oxidation processes: Kinetics, intermediates and the role of reactive species, *Catalysis Today,* 284 (**2017**) 187-194

DOI: 10.1016/j.cattod.2016.11.055

Number of citations: 2 (1)   **IF: 4.636**

Full-length publications y:

1. Milán Molnár, Krisztina Schrantz, **Zsuzsanna Kozmér**, Klára Hernádi, Tünde Alapi: Effect of various radical transfers and scavengers on the transformation of phenol over UV irradiated TiO_2

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   SZEGED 2016. 10. 10.   (English poster)

2. Georgina Rózsa, **Zsuzsanna Kozmér**, Tünde Alapi, Krisztina Schrantz, Erzsébet Takács, László Wojnárovits: Transformation of thiacloprid, a new insecticide, by gamma radiolysis in aqueous solutions

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   SZEGED 2016. 10. 10.   (English poster)

3. Georgina Rózsa, Eszter Arany, **Zsuzsanna Kozmér**, Tünde Alapi, András Dombi: The effect of the simultaneous presence of four non-steroidal anti-inflammatory drugs during the vacuum ultraviolet photolysis

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   SZEGED 2015. 09. 28.   (English poster)

4. Rózsa Georgina, Arany Eszter, **Kozmér Zsuzsanna**, Simon Gergő, Alapi Tünde, Dombi András: Ibuprofen, ketoprofen, naproxen és diklofenák vákuum-ultraibolya fotolízise: Gyöktranszferek hatása

XXXVII. Kémiai Előadói Napok, ISBN 978-963-9970-53-3 (152-156. p.)

SZEGED 2014. 11. 03-05. (Hungarian presentation)

5. Georgina Rózsa, Eszter Arany, **Zsuzsanna Kozmér**, Gergő Simon, Tünde Alapi, András Dombi: The effect of radical transfer materials (O_2, HCOOH, HCOONa) on vacuum ultraviolet photolysis of ibuprofen

20th International Symposium on Analytical and Environmental Problems, ISBN 978-963-12-1161-0 (259-263. p.)

SZEGED 2014. 09. 22. (English poster)

6. Arany Eszter, **Kozmér Zsuzsanna**, Apáti László, Alapi Tünde, Gajdáné Schrantz Krisztina, Dombi András: Reakciókörülmények hatása aromás vegyületek vákuum-ultraibolya fotolízisére

Környezettudományi Doktori Iskolák Konferencia, ISBN 978-963-284-242-4 (211-218. p.)

BUDAPEST 2012. 08. 30.-31. (Hungarian presentation)

Conference presentations, posters:

International conferences:

1. Rózsa Georgina, **Kozmér Zsuzsanna**, Alapi Tünde, Schrantz Krisztina, Takács Erzsébet, Wojnárovits László: Tiakloprid átalakítása nagyhatékonyságú oxidációs eljárásokkal vizes közegben

XXII. International Conference on Chemistry (140. p.)

TIMIŞOARA (**ROMANIA**) 2016. 11. 03-06. (Hungarian presentation)

2. Pap Zsolt, Fodor Szilvia, Gyulavári Tamás, Kovács Gábor, Tóth Zsejke-Réka, Kása Zsolt, Bárdos Enikő, Rózsa Georgina, Simon Gergő, **Kozmér Zsuzsanna**, Rusu Mihai, Hernádi Klára, Lucian Baia, Monica Baia, Székely István, Kedves Zsolt, Boga Bíborka, Ravasz Alpár, Hampel Boglárka, Kovács Zoltán, Saszet Kata, Virginia Danciu, Veronica Cosoveanu, Vajda Krisztina, Karácsonyi Éva, Lucian, Cristian Pop, Czekes Zsolt, Székely Zsuzsanna, Magyari Klára, Milica Todea, Adriana Vulpoi, Veréb Gábor, Orbán Eszter, Dombi András: Új nanokompozitok és nanoszerkezetek a víztisztításban
XXII. International Conference on Chemistry (140. p.)
TIMIŞOARA (**ROMANIA**) 2016. 11. 03-06. (Hungarian presentation)

3. **Zsuzsanna Kozmér**, Éva Karácsonyi, Zsolt Pap, Andrzej Sienkiewicz, László Forró, Tünde Alapi, András Dombi: Investigation of the photocatalytic properties if intercalated WO_3/TiO_2 composites
18th International Symposium in Intercalation Compounds (149. p.)
STRASBOURG (**FRANCE**) 2015. 05. 31-06. 04. (English poster)

4. **Zsuzsanna Kozmér**: Hydroxyl radical generation during TiO_2 based heterogeneous photocatalysis - an ESR study
Closing Conference of Swiss-Hungarian Cooperation Program
LAUSANNE (**SWITZERLAND**) 2015. 03. 29. - 04. 01. (English presentation)

5. Georgina Rózsa, Eszter Arany, Tünde Alapi, **Zsuzsanna Kozmér**, Gergő Simon, András Dombi: The effect of formate ion and pH on vacuum ultraviolet photolysis of NSAIDs
XX. International Conference on Chemistry, ISSN 1843-6293 (145. p.)
CLUJ-NAPOCA (**ROMANIA**) 2014. 11. 06-09. (Hungarian poster)

6. **Zsuzsanna Kozmér**, Andrzej Sienkiewicz, László Forró, András Dombi, Klára Hernádi: ESR study of the effect of different e^-/h^+ traps on hydroxyl radical generation during TiO_2 based heterogeneous photocatalysis
XX. International Conference on Chemistry, ISSN 1843-6293 (35. p.)
CLUJ-NAPOCA (**ROMANIA**) 2014. 11. 06-09. (Hungarian presentation)

7. **<u>Zsuzsanna Kozmér</u>**, Andrzej Sienkiewicz, László Forró, András Dombi, Klára Hernádi: Hydroxyl radical generation during heterogeneous photocatalysis in presence of TiO_2 and tert-butanol/methanol/phenol - an ESR study

   12th International Congress of Young Chemists, ISBN 978-83-61037-28-6 (82. p.)

   SZCZECIN (**POLAND**) 2014. 10. 08-12.   (English poster)

8. **<u>Zsuzsanna Kozmér</u>**, Andrzej Sienkiewicz, László Forró, András Dombi, Klára Hernádi: Hydroxyl radical generation during heterogeneous photocatalysis in presence of TiO_2 / Ag^+ - an ESR study

   38th International Symposium on Environmental Analytical Chemistry (135. p.)

   LAUSANNE (**SWITZERLAND**) 2014. 06. 17-20.   (English poster)

Local conferences:

1. Rózsa Georgina, **Kozmér Zsuzsanna**, Alapi Tünde, <u>Schrantz Krisztina</u>, Takács Erzsébet, Wojnárovits László: A Z-tiakloprid átalakítása három nagyhatékonyságú oxidációs eljárással: Kinetika, köztitermékek és a reaktív részecskék szerepe

   60. Magyar Spektrokémiai Vándorgyűlés és XIII. Környezetvédelmi Analitikai és Technológiai Konferencia, ISBN:978-963-9970-77-9 (88. p.)

   DEBRECEN 2017. 08. 23-25.   (Hungarian presentation)

2. <u>Rózsa Georgina</u>, Arany Eszter, **Kozmér Zsuzsanna**, Alapi Tünde, Dombi András: Nem szteroid gyulladáscsökkentő hatóanyagok együttes hatásának vizsgálata vákuum-ultraibolya fotolízissel

   II. Soós Ernő Tudományos Konferencia

   NAGYKANIZSA 2015. 10. 28.   (Hungarian poster)

3. **<u>Kozmér Zsuzsanna</u>**, Gyurcsik Béla: Vizes oldatok Hg(II)-ion koncentrációjának meghatározására alkalmazható fluoreszcencián alapuló módszer kidolgozása

   XXXI. Országos Tudományos Diákköri Konferencia, ISBN 978-963-08-6206-6 (40. p.)

   EGER 2013. 04. 4-6.   (Hungarian presentation)