Xe*-EXCIMER LAMP VERSUS LOW PRESSURE MERCURY VAPOR LAMP – THE COMPARISON OF THE EFFICIENCY OF 185 nm WITH 172 nm RADIATION, BASED ON H₂O₂ FORMATION AND COUMARIN OXIDATION

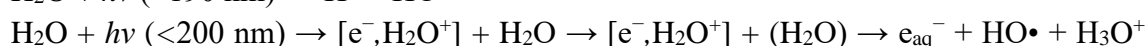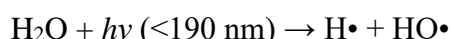**Tünde Alapi, Luca Farkas, Daniele Scheres Firak**

Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
Email: alapi@chem.u-szeged.hu

Abstract
VUV photolysis is a widely used method for producing high purity water by efficiently removing organic substances present in low concentrations. This process is based on the direct photolysis of water, which results in the formation of HO• and •H radicals. In the case of photo-initiated Advanced Oxidation Processes (AOPs), such as VUV photolysis, the lamp type determines the effectiveness. There are two types of light sources commonly used in VUV photolysis: the low-pressure mercury vapor (LPMV) lamps and the Xe* excimer lamp. In this work, the efficiency of the low-pressure mercury vapor (LPM) lamp, which emits at 254 and 185 nm (UV/VUV$_{185\ nm}$ lamp), and the Xe* excimer lamp, which emits at 172 nm (VUV$_{172\ nm}$) photons, were compared. The comparison of the efficiency of the VUV light sources was based on the formation of H₂O₂ in the case of the pure water as well as on the transformation of coumarin (COU) and formation of its hydroxylated product, umbelliferone (7-HO-COU).

Introduction
The VUV photolysis is mainly used and investigated for the elimination and mineralization of various organic pollutants in aqueous solutions [1,2]. Organic and inorganic molecules or ions have high absorption coefficients in the VUV region. However, in aqueous solutions, the VUV radiation is absorbed almost exclusively by water because its concentration (55.5 mol dm^{-3}) highly exceeds those of the dissolved compounds. Absorption of the VUV radiation results in the homolysis and, with lower quantum yield, the photochemical ionization of water molecules:

$$H_2O + h\nu\ (<190\ nm) \rightarrow H\bullet + HO\bullet$$
$$H_2O + h\nu\ (<200\ nm) \rightarrow [e^-, H_2O^+] + H_2O \rightarrow [e^-, H_2O^+] + (H_2O) \rightarrow e_{aq}^- + HO\bullet + H_3O^+$$

There are some characteristic differences between the 185 and 172 nm VUV light irradiated solutions, which are the consequence of the extremely high absorption coefficient and low penetration depth of the 172 nm VUV light.

Table 1. The molar absorption coefficient and the penetration depth of 185 and 172 nm VUV light in water and the quantum yields of the formation of reactive species [3-5]

	absorption coefficient (cm^{-1})	penetration depth in water (mm)	quantum yield	
			Φ(•OH)/ Φ(H•)	Φ(e$_{aq}^-$)
172 nm	550	0.036	0.42	0.05
185 nm	1.53	11	0.33	0.05

The extremely low penetration depth of 172 nm photons results in a very thin (0.04 mm) photoreaction zone containing high concentrations of primary radicals. The carbon-centered

radicals, formed by the reaction of organic substances with H• and HO•, react immediately with dissolved O_2 and form organic peroxyl radicals. As a result, an O_2-depleted layer is formed next to the lamp wall.

The VUV photon flux of the Xe-excimer lamp generally highly exceeds that of the low-pressure mercury vapor lamps that emits both 254 nm and 185 nm photons. Although several authors published results about the efficiency of the low-pressure mercury-vapor lamp for the elimination of organic substances from waters [6-9], the studies about the Xe-excimer lamp [10], especially the comparison of these two light sources [5] , are quite rare.

Experimental

For the $VUV_{172\,nm}$ radiation, a Xe_2* excimer lamp (Radium Xeradex^{TM}, 130 mm long, 46 mm diameter, 20 W) was used, which was centred in a high purity silica quartz envelope (53 mm diameter), able to transmit the 172 nm light. The aqueous solution was circulated continuously (375 mL min^{-1}) between the reactor and the reservoir. A double walled, water-cooled reactor was used, and the temperature was set to 25 ± 0.5 °C. Samples were taken from the reservoir. The volume of the treated solution was 500 mL, the thickness of the irradiated water layer was 5 mm.

The low-pressure mercury vapour (LPMV) lamp (UV/VUV$_{185\,nm}$ lamp GCL307T5VH/CELL, 227 mm arc length, produced by LightTech) was used for the UV/VUV (254 nm/185 nm) photolysis. The UV/VUV$_{185\,nm}$ lamp's envelope was made of synthetic quartz to be able to transmit the VUV$_{185\,nm}$ photons. The volume of the treated solution was 500 mL, the thickness of the irradiated water layer was 20 mm.

In the case of VUV$_{172\,nm}$ and UV/VUV$_{185\,nm}$ photolysis, O_2 or N_2 gas was bubbled continuously through the solution. Coumarine (Sigma-Aldrich, ≥98,5%) solutions were made in ultrapure Milli-Q water (MILLIPORE Milli-Q Direct 8/16).

The transformation of coumarin (COU) was followed by a spectrophotometer (Agilent 8453). The concentration was determined from the absorbance of the solution at 277 nm. Fluorescence spectroscopy (Hitachi F4500) was applied to determine the concentration of umbelliferone (7-HO-COU). The wavelength of excitation was 387 nm. The determination of its concentration was based on the intensity of the emitted fluorescence light at 455 nm.
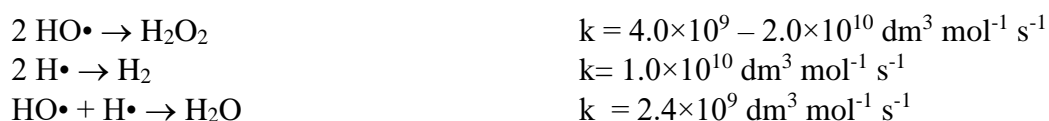
The concentration of H_2O_2 was measured with a cuvette test by Merck, with a 0.015 - 6.00 mg dm^{-3} measuring range.
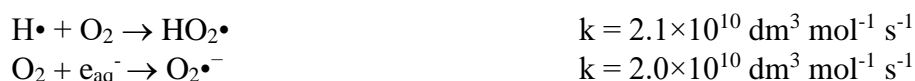
Results and discussion

In the case of the VUV photolysis, the 172 nm and 185 nm VUV light is absorbed by water to form reactive species, such as hydrogen radicals (H•), hydroxyl radicals (HO•), and, with a lower yield, hydrated electrons (e_{aq}^-) [2]. The VUV flux of light sources determines their efficiency in terms of radical formation and consequently the removal of organic matter from water.

The VUV photon flux was determined with methanol actinometry [11], and was found to be 32 times higher for the excimer lamp (1.04×10^{-5} mol$_{photon}$ s^{-1}) than for the LPM lamp (3.23×10^{-7} mol$_{photon}$ s^{-1}). The UV photon flux was 3.70×10^{-6} mol$_{photon}$ s^{-1}.

The recombination of primer radicals results in the formation H_2O, H_2 and H_2O_2 [12]:

$$2\ HO• \rightarrow H_2O_2 \qquad\qquad k = 4.0 \times 10^9 - 2.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$$
$$2\ H• \rightarrow H_2 \qquad\qquad k = 1.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$$
$$HO• + H• \rightarrow H_2O \qquad\qquad k = 2.4 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$$

In the presence of dissolved O_2, the reaction of O_2 with H• hinders the recombination of primary radicals [12]:

$$H• + O_2 \rightarrow HO_2• \qquad\qquad k = 2.1\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$O_2 + e_{aq}^- \rightarrow O_2•^- \qquad\qquad k = 2.0\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The further reactions of $HO_2•$ and $O_2•^-$ also produce H_2O_2 [13]:

$$HO_2• + H_2O \leftrightharpoons H_3O^+ + O_2•^- \qquad\qquad pK_a = 4.8$$
$$O_2•^- + HO_2• + H_2O \rightarrow O_2 + H_2O_2 + HO^- \qquad k = 9.7\times10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
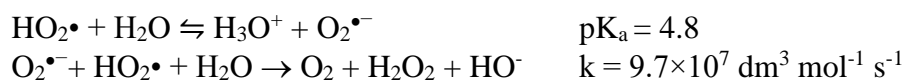
At first, the H_2O_2 concentration and its formation rate were determined and compared in the case of both lamps, in O_2 saturated and O_2-free Milli-Q waters. In O_2 saturated waters, the rate of H_2O_2 formation was about twice as high, while the equilibrium concentration was almost 50-fold higher in the 172 nm irradiated solution than in the 254/185 nm irradiated Milli-Q water. This result reflects well the nearly 30-fold higher VUV photon flux of the Xe*-excimer lamp. In the case of 172 nm VUV photolysis, the formation rate and equilibrium concentration of H_2O_2 in O_2-free solution was about 20% of the values determined in O_2-saturated water. There was no H_2O_2 formation in O_2-free water for irradiation at 254/185 nm.

Table 2. *The initial transformation rates and equilibrium concentration of H_2O_2 determined in Milli-Q water*

		O_2 saturated Milli-Q water	O_2-free Milli-Q water
Xe-excimer lamp, 172 nm	r_0 *(×10^{-8} mol dm^{-3} s^{-1})*	**10.53**	**2.85**
	c_{eq} *(×10^{-6} mol dm^{-3})*	**102**	**19**
LPMV lamp 254/185 nm	r_0 *(×10^{-8} mol dm^{-3} s^{-1})*	**4.83**	**-**
	c_{eq} *(×10^{-6} mol dm^{-3})*	**2.1**	**-**

The transformation of COU is negligible in 254 nm irradiated solutions, its transformation is due to the reaction with HO• ($k = 6.9\times10^9$ mol^{-1} dm^3 s^{-1}) and H• ($k = 2.5\times10^9$ mol^{-1} dm^3 s^{-1}) [14], in both UV/VUV$_{185nm}$ and VUV$_{172nm}$ irradiated solutions. Although the reaction of dissolved O_2 with H• inhibits the transformation of COU via H• initiated reaction, it has no negative effect in the 172 irradiated solution, and increased the transformation rate by 20% in the UV/VUV$_{185nm}$ irradiated solution. Dissolved O_2 generally has a positive effect on the radical based transformation of organic substances due to the formation of organic peroxyl radical (R-COO•) from carbon-centered radicals (R-C•). The formation of R-COO• opens up a new pathway for the transformation of organic substances and hinders the backward reactions. In terms of COU transformation rate, it is likely that the negative and positive effects of O_2 are compensated for each other.

The formation of 7-HO-COU starts with the addition of HO• to the aromatic part of COU. From the carbon-centered radical, there are two possibilities of the 7-HO-COU formation: without dissolved O_2 the reaction of two carbon-centered radical results in the formation of hydroxylated product and COU (Fig. 1). However, in the presence of O_2, 7-HO-COU is formed exclusively through organic peroxyl radicals (Fig. 2). Consequently, the dissolved O_2 highly enhances the formation of hydroxylated products, such as 7-HO-COU.

Taking into account the different photon fluxes, we compared the efficiency of photolysis at 172 nm and 185 nm in the transformation of COU and formation of 7-HO-COU. Despite the photon flux more than 30 times higher, the conversion rate of COU was only 5-6 times higher, while the formation rate of 7-HO-COU was only 2-3 times higher in the case of the excimer lamp compared to the LPMV lamp. It has to be mention that, in 172 nm irradiated aqueous solutions of organic substances, due to the extremely high HO• concentration close to the wall of the lamp, an O_2-depletion layer forms. Thus, the positive effect of O_2 via peroxyl radical formation is less pronounced.
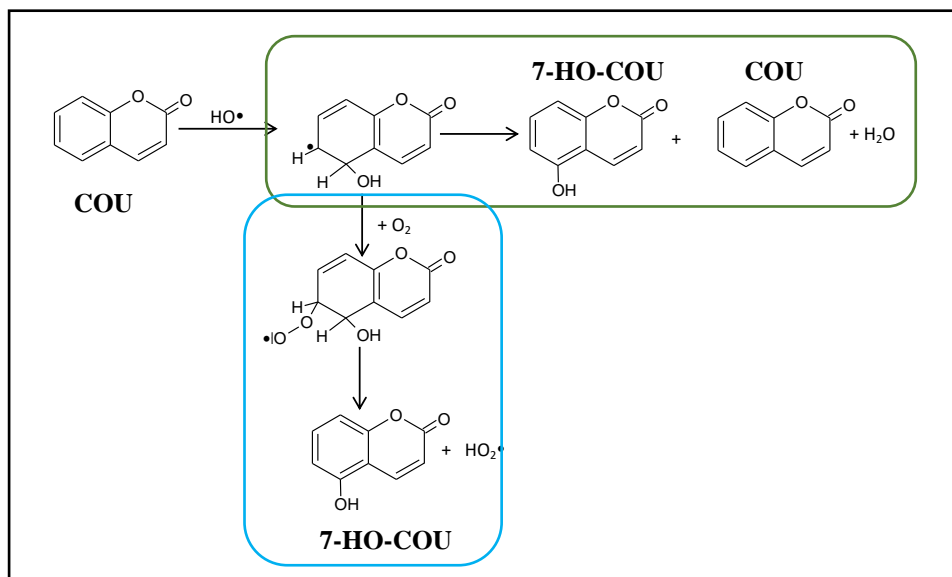

Fig. 1 *The HO• initiated formation of 7-HO-COU from COU in the presence (light blue frame) and absence (dark green frame) of O_2*

Table 3. The initial transformation rate of COU and the formation rate of 7-HO-COU in UV/VUV$_{185nm}$ and VUV$_{172nm}$ radiated solutions (c_0^{COU} = 1.0×10⁻⁴ M)

The effect of dissolved O_2				
	UV/VUV$_{185nm}$		**VUV$_{172\ nm}$**	
VUV photon flux φ ($mol_{photon}\ s^{-1}$)	**3.23×10⁻⁷**		**1.04×10⁻⁵**	
	O_2	**N_2**	**O_2**	**N_2**
r_0^{COU} (×10⁻⁸ $mol\ dm^{-3}\ s^{-1}$)	**3.77**	**3.12**	**20.2**	**19.5**
Φ (r_0^{COU}/ φ)	**0.23**	**0.38**	**0.039**	**0.038**
$r_0^{7-HO-COU}$ (×10⁻⁹ $mol\ dm^{-3}\ s^{-1}$)	**1.03**	**0.29**	**2.53**	**9.60**
$r_0^{COU}{}_{O2}$/ $r_0^{COU}{}_{N2}$	**1.21**		**1.04**	
$r_0^{7-HO-COU}{}_{O2}$/ $r_0^{7-HO-COU}{}_{N2}$	**3.58**		**2.63**	
Comparison of the VUV$_{172nm}$/VUV$_{185\ nm}$ photolysis				
	O_2		**N_2**	
$r_0^{COU}{}_{172nm}$/$r_0^{COU}{}_{185nm}$	**5.36**		**6.25**	
$r_0^{COU}{}_{172nm}$/$r_0^{COU}{}_{185nm}$	**2.46**		**3.33**	

The quantum yield of the COU transformation was one magnitude lower for VUV$_{185\ nm}$ photolysis than VUV$_{172\ nm}$ photolysis (Table 3.). The reason is probably the extreme inhomogeneity of the 172 nm irradiated aqueous solutions of organic substances.

Conclusion

In this work, we compared the efficiencies of two VUV light sources, the low-pressure mercury vapor lamp (UV/VUV185nm) and the Xe-excimer lamp (VUV172nm). The H_2O_2 concentration formed in the 185 and 172 nm Milli-Q irradiated waters well reflects the almost 30-fold higher VUV photon flux of the Xe * -excimer lamp. The high photon flux and the low penetration depth of VUV light at 172 nm causes extreme inhomogeneity in VUV photolysis of an aqueous solution of organic matter. This inhomogeneity is the reason why the apparent quantum yield of the COU transformation is one order of magnitude lower in the 172 nm irradiated solution than with 185 nm irradiation.

Acknowledgements

References

[1] Alapi, T. Schrantz., K.; Arany, E., Kozmér Zs., Chapter 3: Vacuum UV radiation-driven processes, in Advanced Oxidation Processes for Water Treatment, Editor: Stefan, M.I., 2017. IWA Publishing

[2] Oppenländer, T., *Photochemical Purification of Water and Air*. 2003. Wiley-VCH, Weinheim

[3] Weeks, J. L., Meaburn, G. M. A. C., Gordon, S., Radiation Research, 1963. 19(3), 559–567.

[4] Heit, G., Braun, A. M., Water Sci. Technol., 1997. 35(4), 25–30.

[5] Al-Gharabli, S., Engeßer, P., Gera, D., Klein, S., Oppenländer, T., Chemosphere, 2016. 144, 811–815.

[6] Rozsa, G.; Nafradi, M.; Alapi, T.; Schrantz, K.; Szabo, L.; Wojnarovits, L.; Takacs, E.; Tungler, A Appl. Cat. B-Environ. 250. 429-439

[7] Rozsa, G; Fazekas, A; Nafradi, M; Alapi, T; Schrantz, K; Takacs, E; Wojnarovits, L; Fath, A; Oppenlander, T. Environ. Sci. and Poll. Res. 26(23) 23268-23278

[8] Geng, C; Liang, ZJ; Cui, FY; Zhao, ZW; Yuan, C; Du, JY; Wang, C., Chem. Eng. J. 2020. 383. Article number 123145

[9] Arany E., Szabó R.K., Apáti L., Alapi, T., Ilisz, I., Mazellier, P., Dombi, A., Gajda-Schrantz, K., J. Hazard. Mater., 2013. 262, 151–157.

[10] Oppenlander, T. J. Environ. Eng. and Sci. 2007. 6(3) 253-264

[11] Heit, G., Neuner, A., Saugy, P.-Y., Braun, A. M., J. Phys. Chem. A, 1998. 102 (28), 5551–5561.

[12] NDRL/NIST solution kinetics database on the web, https://kinetics.nist.gov/solution/

[13] Bielski, B. H. J. Cabelli, D. E., Arudi, L.R., J. Phys. Chem. Ref. Data, 1985. 14 (4), 1041–1100.

[14] Náfrádi, M., Farkas, L., Alapi, T., Hernádi, K., Kovács, K., Wojnárovits, L., Takács, E. Radiat. Phys. Chem., 2020. 170, 108610