Proceedings of the 3rd International Conference on Environmental Science and Applications (ICESA'22)
Seoul, South Korea - November 24 - 26, 2022
Paper No. 128
DOI: 10.11159/icesa22.128

UV/Persulfate and UV/VUV/Persulfate Methods for Removal Trimethoprim from Waters - Special Attention to the Effect of Matrix Components

Tünde Alapi[1], Luca Farkas[1], Adrienn Szirmai[1]
[1]University of Szeged,
H-6720 Szeged, Hungary
alapi@chem.u-szeged.hu; fluca@chem.u-szeged.hu; adri.szirmai@gmail.com

Abstract - VUV (185 nm) and UV light (254 nm) was recently used to promote the performance of UV-based advanced oxidation processes. In this study, UV and UV/VUV photolysis was combined with the peroxodisulfate process (UV/PDS and VUV/UV/PDS) for enhanced degradation of trimethoprim (TRIM, $c_0 = 1.0 \times 10^{-4}$ M) antibiotic from waters. Without PDS, the efficiency of UV/VUV photolysis exceeds that of UV photolysis due to the $^{\bullet}$OH formation. The addition of PDS (5.0×10^{-4} M - 3.0×10^{-3} M) highly enhanced the transformation and mineralization rate in both cases. The relative contribution of radical-based reactions ($^{\bullet}$OH and $SO_4^{\bullet-}$) were studied using terc-butanol, a radical scavenger. The contribution of $^{\bullet}$OH and $SO_4^{\bullet-}$ to the transformation and mineralization depended on the PDS concentration – above 1.0×10^{-3} M PDS, the $SO_4^{\bullet-}$ became the dominant reaction partner even in the case of UV/VUV photolysis. The effect of biologically treated wastewater as a matrix and its main inorganic components, such as HCO_3^- and Cl^- were also studied. The results proved that, however, both inorganic ions react with $^{\bullet}$OH and $SO_4^{\bullet-}$, the reactions between TRIM and formed $CO_3^{\bullet-}$ and $Cl^{\bullet}$ are involved in the conversion. The AOX content of the treated solution increased in the presence of Cl^-, and this effect was moderated in the presence of HCO_3^-.

Keywords: VUV, hydroxyl radical, biologically treated wastewater, persulfate, radical scavenger, antibiotics, pharmaceuticals

1. Introduction

Antimicrobial agents have been essential for the treatment of many human and animal diseases since the 1900s. The amount of antibiotics which is consumed for human disease treatment decreased from 2009 to 2018, but the total antibiotic consumption increased significantly in recent years, mainly thanks to industrial-scale animal husbandry [1]. During the last years, the pandemic situation also increased the consumption of various pharmaceuticals, especially antibiotics to prevent bacterial superinfection of patients infected with the COVID-19 virus. As a result, a large amount of drug residues is discharged into the wastewater [2,3] and reaches the surface waters [4,5]. The increase in the number of antibiotic-resistant bacterial strains is a dangerous consequence of the presence of antibiotics in the environment and causes a global problem [6,7]. The European Antimicrobial Resistance Surveillance Network [8] recently estimates that more than 670.000 infections are caused by antibiotic-resistant bacterial strains in the European Union each year, and this causes approximately 33000 deaths [8].

The low-pressure mercury vapor (LPM) lamp emitting at 254 nm is a widely used light source for water disinfection, but its effectiveness in eliminating organic pollutants is highly limited. The LPM lamps, equipped with special high-purity quartz, emit at 254 and 185 nm, and are suitable for high-purity water production due to the $^{\bullet}$OH, which originated from the direct VUV photolysis of water:

$$H_2O + h\nu_{185nm} \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad \Phi({}^{\bullet}OH)_{185nm} = 0.33 \qquad [9] \qquad (1)$$

Due to the formed $^{\bullet}$OH, VUV photolysis is an efficient and chemical-free method for the elimination of trace organic pollutants [10].

The efficacy of UV photolysis can be enhanced by using various oxidizing agents, such as ozone, hydrogen peroxide, or peroxodisulfate ion ($S_2O_8^{2-}$; PDS) [11]. PDS ($S_2O_8^{2-}$) can be activated to generate highly reactive $SO_4^{\bullet-}$ characterized by a high oxidative potential (E_0 = 2.6 V) [12]. The 254 nm UV light-activated PDS ($\varepsilon_{254\,nm}$ = 20-22 M^{-1} cm^{-1} [13]) is a clean source for producing $SO_4^{\bullet-}$ with high quantum yield [13] via the homolytic bond cleavage [14]:

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^{\bullet-} \qquad \Phi\ (SO_4^{\bullet-})_{254nm} = 1.4 \pm 0.3 \qquad [14] \qquad (2)$$

The $SO_4^{\bullet-}$ is a potent oxidizing agent like the $^{\bullet}OH$ [14]. Comparing their reactivity, $^{\bullet}OH$ is less selective and more reactive toward saturated organic substances than $SO_4^{\bullet-}$. The reaction rate constant of $^{\bullet}OH$ with TRIM is 7.36×10^9 $M^{-1}s^{-1}$ [15], whereas the reaction rate constant with $SO_4^{\bullet-}$ is 3.81×10^9 $M^{-1}s^{-1}$ [16], just slightly lower than with $^{\bullet}OH$.

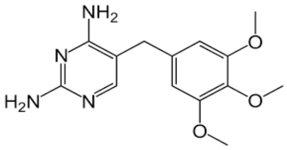

Fig. 1: The chemical structure of TRIM

This research compares and studies the UV photolysis, UV/VUV photolysis producing $^{\bullet}OH$, and their combinations with PDS to eliminate and mineralize the commonly used pharmaceutical, namely trimethoprim (TRIM), an antibiotic drug, which is regularly detected in urban and hospital wastewater [17,18]. The effect of dissolved O_2, PDS concentration, the biologically treated domestic wastewater as matrix, and inorganic ions was also studied.

2. Materials and methods

Two low-pressure mercury vapor (UV and UV/VUV) lamps were used as light sources. UV lamp emits 254 nm UV photons (GCL307T5L/CELL, produced by LightTech), while UV/VUV lamp (GCL307T5VH/CELL produced by LightTech) emits both 254 nm UV and 185 nm VUV photons. Both lamps have the same electric (15 W) and geometric (227 mm arc length and 20,5 mm diameter) parameters. The UV/VUV lamp envelope was made from synthetic quartz to transmit the VUV_{185nm} photons. The UV photon flux was determined by ferrioxalate actinometry [19] and found to be the same (3.70×10^{-6} mol_{photon} s^{-1}) for both lamps. The flux of the 185 nm VUV photons was determined by methanol actinometry and found to be one magnitude lower, 3.23×10^{-7} mol_{photon} s^{-1}. The experiments were carried out in a 400 mL cylindrical glass reactor with a 45 mm inner diameter and 300 mm height. The thickness of the irradiated water layer was 13 mm, which is enough for the complete absorption of 185 nm photons [20]. The initial concentration of TRIM was 1.0×10^{-4} M in each case.

The concentration of model compounds was performed by Agilent 1100 HPLC system, equipped with a diode array detector (DAD). For the analysis of TRIM (≥99%, Sigma-Aldrich) and its degradation products, Gemini 3u C6-phenyl 110A column was used (thermostated at 40 °C). The eluent contains 10% methanol (HPLC grade, VWR) and 90% formate buffer (≥99%, Sigma-Aldrich); the flow rate was 0.4 mL min^{-1}. The detection wavelength was 275 nm.

Total organic carbon (TOC) measurements were performed using an Analytik Jena N/C 3100 analyzer. For the investigation of matrix effect, biologically treated wastewater was used with high ionic ($c(HCO_3^-)$ = 526 mg dm^{-3} and $c(Cl^-)$ = 120 mg dm^{-3}) and relatively low organic content (TOC = 6 mg dm^{-3}). The concentration of adsorbable organic halogens (AOX) was quantified in an AOX analyzer (Analytik Jena, Multi X 2500) using the column method with adsorption in quartz containers filled with activated carbon. Samples were prepared in a sample preparation module (Analytik Jena, APU 2).

3. Results

3.1. UV and UV/VUV photolysis

The efficiency of UV photolysis is determined by the molar absorbance of the target substance at 254 nm and the quantum efficiency of the transformation. However, the molar absorbances of TRIM is relatively high (4045 M^{-1} cm^{-1}), there is practically no transformation in the O_2-free solution and starts with a long induction period in the O_2-containing one (Fig. 2a). TRIM emitted an intensive fluorescent light having maximum intensity at 340 nm due to the excitation with 254 nm UV light. The dissolved O_2 decreased the intensity of fluorescent light, suggesting that O_2 can quench the excited state of TRIM (Fig. 2b). The formed singlet oxygen ($^1O_2$) is probably responsible for the positive effect of O_2 on the on the transformation of TRIM in the case of UV photolysis.

For UV/VUV photolysis, the low intensity 185 nm photons highly enhanced the transformation rate both in aerated and and O_2-free solutions (Fig 2a) due to the formation of $H^\bullet$ and $^\bullet OH$ radicals from water (1). Besides radical-based reactions, dissolved O_2 is also required for the enhanced mineralization. The mineralization was negligible in UV radiated solution, while in UV/VUV irradiated one about 80% of TOC was removed during 2 h in the presence of dissolved O_2. (Fig 2c).

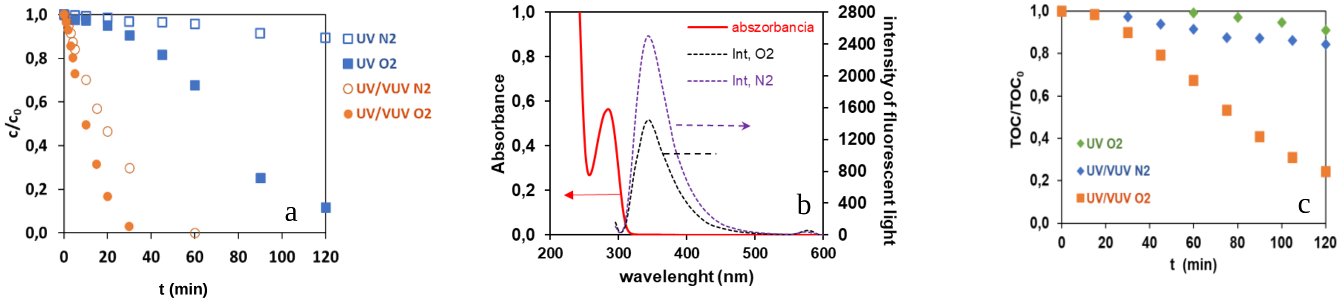

Fig. 2: The transformation (a) and mineralization (c) of 1.0×10^{-4} M TRIM, and the absorbance and the fluorescent spectra ($\lambda_{excitation} = 254$ nm)

3.2. UV/PDS and UV/VUV/PDS methods

Using both light sources, the effect of the initial PDS concentration in the range of 5.0×10^{-4} M – 3.0×10^{-3} M, i.e., 5 – 30-fold excess of PDS compared to TRIM was examined. In the case of the UV/PDS process, the transformation of TRIM takes place mainly via reaction with $SO_4^{\bullet-}$. For UV/VUV/PDS, additionally, the reactions with $^\bullet OH$ must be taken into consideration. Comparing the molar absorbance of TRIM and PDS (30 M^{-1} cm^{-1}) at 254 nm, 1.0×10^{-4} M TRIM absorbs 75%, while PDS absorbs no more than 27% of the 254 nm photons. Opposite this, the contribution of direct photolysis to the TRIM transformation is negligible besides $SO_4^{\bullet-}$ and/or $^\bullet OH$ initiated reactions at the given PDS concentrations.

The transformation rate increased with the initial concentration of added PDS for UV/PDS and UV/VUV/PDS processes (Fig. 3a and b), and synergism can be observed for UV/VUV/PDS method compared to its efficiency to the UV/VUV and UV/PDS methods, especially at lower PDS concentrations. Using 5.0×10^{-4} M PDS, for UV/VUV/PDS the transformation rates are higher (approximately doubled) than for the UV/PDS process, which suggests that the consequences of low-intensity VUV light remain important even in the presence of PDS. The addition of PDS enhanced not only the transformation but also the mineralization of TRIM (Fig. 3c and d), but the difference between the efficiency of UV/PDS and UV/VUV/PDS methods became negligible above 20-fold excess (2.0×10^{-3} M) of PDS. The relative contribution of $^\bullet OH$ initiated reaction was investigated using t-BuOH as a radical scavenger. The addition of 3.0×10^{-2} M t-BuOH (96% $^\bullet OH$ radicals scavenging capacity) decreased by 74% the initial transformation rate in the case of UV/VUV photolysis, while in the presence of 1.0×10^{-3} M PDS the decrease was only 15%. Taking into consideration the photon flux of UV and VUV light, molar absorbance of water at 185 nm and PDS at 254 nm, and reaction rate constants of $^\bullet OH$ and $SO_4^{\bullet-}$ with each other and with TRIM, the contribution of $^\bullet OH$ decrease with the increase of PDS concentration and probably became negligible above 1.0×10^{-3} M PDS.

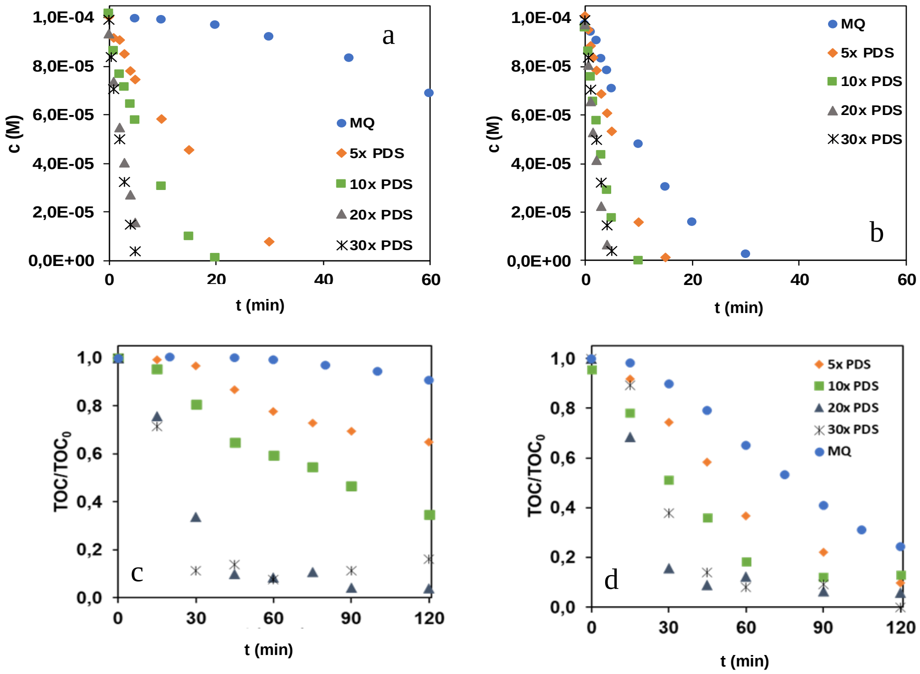

Fig. 3: The transformation (a, b) and mineralization (c, d) of TRIM, in the case of UV/PDS (a, c) and UV/VUV/PDS (b, d) processes

3.4. The effect of biologically treated domestic wastewater and inorganic ions (HCO_3^- and Cl^-)

Biologically treated wastewater (TOC_0 = 6 mg dm^{-3}; $c(HCO_3^-)$ = 526 mg dm^{-3} and $c(Cl^-)$ = 120 mg dm^{-3}) completely inhibited the transformation of TRIM after 2 min. in the case of UV/PDS, using 1.0×10^{-3} M PDS concentration (Fig 4a). The doubled PDS dose (2.0×10^{-3} M) caused a similar transformation rate in this matrix than 1.0×10^{-3} M PDS in ultrapure water. Not only transformation but mineralization was also inhibited (Fig 4b). For UV/VUV/PDS process, the presence of VUV light significantly reduced the inhibitory effect of the matrix compared to the UV/PDS method. The matrix TOC content is about the half of the TOC content of 1.0×10^{-4} M TRIM solution (14 mg dm^{-3}) and has high ionic (HCO_3^- and Cl^-) content.

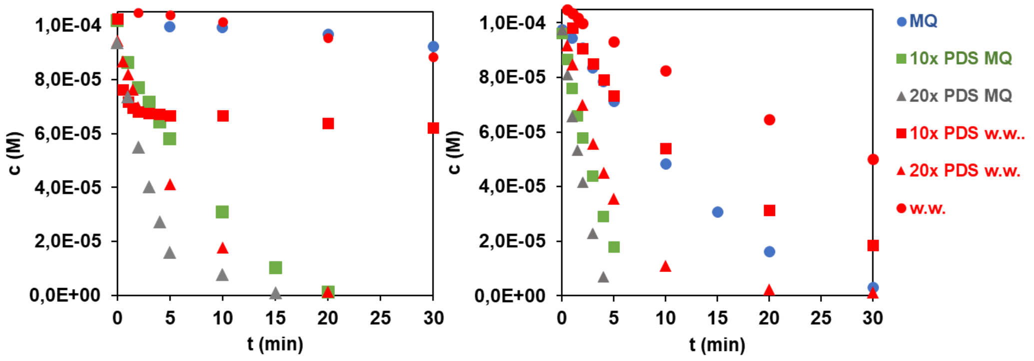

Fig. 4: The transformation of TRIM, in the case of UV/PDS (a) and UV/VUV/PDS (b) processes

Besides organic substances, HCO_3^- and Cl^- also react with $^{\bullet}OH$ and $SO_4^{\bullet -}$:

$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet -} + H_2O$ $k = 8.6\times10^{6}\ M^{-1}\ s^{-1}$ [21] (25)

$HCO_3^- + SO_4^{\bullet -} \rightarrow CO_3^{\bullet -} + SO_4^{2-}$ $k = 2.8\times10^{6}\ M^{-1}\ s^{-1}$ [22] (26)

$Cl^- + {}^{\bullet}OH \rightarrow Cl^{\bullet} + HO^-$ $k = 4.3 \times 10^{9}\ M^{-1}\ s^{-1}$ [23] (27)

$Cl^- + SO_4^{\bullet -} \rightarrow Cl^{\bullet} + SO_4^{2-}$ $k = 3.6 \times 10^{8}\ M^{-1}\ s^{-1}$ [24] (31)

The effect of HCO_3^- and Cl^- were studied separately and in their mixture, using the same ion concentrations as in the matrix. Although Cl^- react fast with both radical, the further transformation of $Cl^{\bullet}$ besides the reaction with organic substances, can regenerate ${}^{\bullet}OH$ radical [25] in the solution having a relatively high Cl^- concentration. Opposite to the high scavenging capacity of $Cl^{\bullet}$, it has no negative effect on the transformation rate (Table 1.), indeed, enhances that for UV/PDS process. The scavenging capacity of HCO_3^-, is much lower than that of Cl^- and the formed $CO_3^{\bullet -}$ can react with TRIM ($k = 1.37 \times 10^{7}\ M^{-1}\ s^{-1}$ [26]), which could be the reason for that, its effect is negligible or slightly positive (Table 1.). These new, selective species ($CO_3^{\bullet -}$ and $Cl^{\bullet}$) can partially take over the role of the $SO_4^{\bullet -}$ and contribute to the TRIM transformation. It was confirmed by the fact that, although the transformation rate of TRIM did not change significantly, the mineralization rate decreased due to the change of the radical set.

Table 1: The effect of inorganic ions and biologically treated domestic wastewater as a matrix on the transformation rate of TRIM ($c_{PDS} = 1.0 \times 10^{-3}$ M)

	r ($\times 10^{-7}$ mol dm^{-3} s^{-1})		
	UV/PDS	UV/VUV	UV/VUV/PDS
Milli-Q water	**1.49**	**0.92**	**3.38**
Cl^- (120 mg dm^{-3})	2.15	1.00	2.78
HCO_3^- (526 mg dm^{-3})	1.65	2.85	3.23
Cl^- (120 mg dm^{-3}) and HCO_3^- (526 mg dm^{-3})	1.67	0.73	3.42
biologically treated domestic wastewater	-	0.43	1.13

The formation and contribution of $Cl^{\bullet}$ to the transformation of TRIM and its products was proved by the formation of chlorinated organic substances. AOX value of the treated solution was determined after the decomposition of TRIM in the case of each process. In Cl^- containing solutions, the AOX value increased to 23, 51 and 57 μg dm^{-3} for UV/PDS, UV/VUV and UV/VUV/PDS methods, respectively. These values decreased to 20, 40 and 40 μg dm^{-3} in the presence of HCO_3^-, most probably because of the reaction between HCO_3^- and $Cl^{\bullet}$ ($k = 2.8 \times 10^{8}\ M^{-1}\ s^{-1}$, [27]) competing for the reaction of $Cl^{\bullet}$ with organic substances and decrease the $Cl^{\bullet}$ concentration but increase the $CO_3^{\bullet -}$.

4. Conclusion

In this work, the combination of UV and UV/VUV photolysis with PDS addition was studied. The transformation and mineralization rate of TRIM, a widely used antibiotic, highly increased with the addition of PDS due to the formation of reactive $SO_4^{\bullet -}$. In UV/VUV irradiated solutions, the effect of t-BuOH proved that the contribution of ${}^{\bullet}OH$-based reactions became negligible above 1.0×10^{-3} M PDS concentration. The biologically treated domestic wastewater decreased the transformation and mineralization rate, especially in the case of UV/PDS method. The effect of inorganic ions, such as HCO_3^- and Cl^- were studied separately and in their mixture, using the same ion concentrations as in the matrix. Our results proved that radicals formed from these ions ($CO_3^{\bullet-}$ and $Cl^{\bullet}$) partially take over the role of the $SO_4^{\bullet-}$ and contribute to the TRIM transformation.

Acknowledgments

Tünde Alapi thank for the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences the New National Excellence Program of the Ministry for Innovation and Technology (ÚNKP-21-5-SZTE-594). Luca Farkas thanks for the financial support from the National Talent Programme (NTP-NFTÖ-21-B-0064). This work was sponsored by the National Research, Development and Innovation Office-NKFI Fund OTKA, project number FK132742.

References

[1] T.P. Van Boeckel, E.E. Glennon, D. Chen, M. Gilbert, T.P.Robinson, B.T. Grenfell, S.A. Levin, S. Bonhoeffer, R. Laxminarayan, “Reducing antimicrobial use in food animals,” *Insigths*, vol. 357, no. 6358, pp. 2–5, 2017.

[2] A. Galani, N. Alygizakis, R. Aalizadeh, E. Kastritis, M. A. Dimopoulos, and N. S. Thomaidis, “Patterns of pharmaceuticals use during the first wave of COVID-19 pandemic in Athens, Greece as revealed by wastewater-based epidemiology,” *Sci. Total Environ.*, vol. 798, p. 149014, 2021.

[3] H.S. Chung, J.-H. Choi, A. M. Abd El-Aty, Y.-J. Lee, H.S. Lee, S. Kim, H.-J. Jung, T.-W. Kang, H.-C. Shin, J.-H. Shim, “Simultaneous determination of seven multiclass veterinary antibiotics in surface water samples in the Republic of Korea using liquid chromatography with tandem mass spectrometry,” *J. Sep. Sci.*, vol. 39, no. 1, pp. 4688–4699, 2016.

[4] L. Yao, Y. Wang, L. Tong, Y. Deng, Y. Li, Y. Gan, W. Guo, C. Dong, Y. Duan, K. Zhao, “Occurrence and risk assessment of antibiotics in surface water and groundwater from different depths of aquifers: A case study at Jianghan Plain, central China,” *Ecotoxicol. Environ. Saf.*, vol. 135, 2016, pp. 236–242, 2017.

[5] K. Balakrishna, A. Rath, Y. Praveenkumarreddy, K. S. Guruge, and B. Subedi, “A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies,” *Ecotoxicol. Environ. Saf.*, vol. 137, no. November 2016, pp. 113–120, 2017.

[6] M. Kumar, S. Jaiswal, K.K. Sodhi, P. Shree, D.K. Singh, P.K. Agrawal, P. Shukla, “Antibiotics bioremediation: Perspectives on its ecotoxicity and resistance,” *Environ. Int.*, vol. 124, 2018, pp. 448–461, 2019.

[7] T. W. Na, T. W. Kang, K. H. Lee, S. H. Hwang, H. J. Jung, and K. Kim, “Distribution and ecological risk of pharmaceuticals in surface water of the Yeongsan river, Republic of Korea,” *Ecotoxicol. Environ. Saf.*, vol. 181, pp. 180–186, 2019.

[8] A. Cassini, L.D. Högberg, D. Plachouras, A. Quattrocchi, A. Hoxha, G.S. Simonsen, M. Colomb-Cotinat, T. C. Oliveira, M. J. Struelens, C Suetens, D. L. Monnet “Attributable deaths and disability-adjusted life-years caused by infections with antibiotic-resistant bacteria in the EU and the European Economic Area in 2015: a population-level modelling analysis,” *The Lancet Infectious Diseases*, vol. 19, no. 1. pp. 56–66, 2019.

[9] Getoff N. and Schenck G.O., “Primary products of liquid water photolysis at 1236, 1470 and 1849 Å,” *Photochem. Photobiol.*, vol. 8, no. 3, pp. 167–178, 1968.

[10] L. Yang, Y. Feng, and Z. Gao, “Degradation of organic micropollutant by vacuum ultraviolet process: a kinetics study,” *Korean J. Chem. Eng.*, vol. 38, no. 8, pp. 1642–1647, 2021.

[11] S. Hsieh, W. W. Lai, A. Y. Lin, and A. Y. Lin, “Kinetics and mechanism of 4-methylbenzylidene camphor degradation by UV-activated persulfate oxidation,” pp. 18021–18034, 2021.

[12] Q. Yang, H. Choi, Y. Chen, and D. D. Dionysiou, “Heterogeneous activation of peroxymonosulfate by supported cobalt catalysts for the degradation of 2,4-dichlorophenol in water: The effect of support, cobalt precursor, and UV radiation,” *Appl. Catal. B Environ.*, vol. 77, no. 3–4, pp. 300–307, 2008.

[13] G.M. Man, N.Schuchmann, H.-P. Schuchmann, C. von Sonntag “The photolysis of potassium peroxodisulphate in aqueous solution in the presence of tert-butanol: a simple actinometer for 254 nm radiation" *J. Photochem. and Photobiol. A: Chemistry,* vol 5, no 2, pp. 157–168, 1990.

[14] N. Karpel Vel Leitner, “Sulfate radical ion – based AOPs,” in *Advanced Oxidation Processes for Water Treatment,* M. I. Stefan, Ed. London: IWA Publishing, 2017, pp. 429–460.

[15] L. Wojnárovits, T. Tóth, and E. Takács, “Critical evaluation of rate coefficients for hydroxyl radical reactions with antibiotics: A review,” *Crit. Rev. Environ. Sci. Technol.*, vol. 48, no. 6, pp. 575–613, 2018.

[16] Y. Luo, R. Su, H. Yao, A. Zhang, S. Xiang, L. Huang “Degradation of trimethoprim by sulfate radical-based advanced oxidation processes : kinetics , mechanisms , and effects of natural water matrices,” *Environ Sci Pollut Res Int.* vol 28, pp 62572-62582, 2021.

[17] M. Mahdi Ahmed, S. Barbati, P. Doumenq, and S. Chiron, “Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination,” *Chem. Eng. J.*, vol. 197, pp. 440–447, 2012.

[18] J. Wang, L. Chu, L. Wojnárovits, and E. Takács, “Occurrence and fate of antibiotics, antibiotic resistant genes (ARGs) and antibiotic resistant bacteria (ARB) in municipal wastewater treatment plant: An overview,” *Sci. Total Environ.*, vol. 744, p. 140997, 2020.

[19] H. Heath, C. G. Hatchard, and C. A. Parker, “A new sensitive chemical actinometer - II. Potassium ferrioxalate as a standard chemical actinometer,” *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, vol. 235, no. 1203, pp. 518–536, 1956.

[20] S. Al-Gharabli, P. Engeßer, D. Gera, S. Klein, and T. Oppenländer, “Engineering of a highly efficient Xe2*-excilamp (xenon excimer lamp, λmax=172 nm, η=40%) and qualitative comparison to a low-pressure mercury lamp (LP-Hg, λ=185/254 nm) for water purification,” *Chemosphere,* vol. 144, pp. 811–815, 2016.

[21] C. Duca, G. Imoberdorf, and M. Mohseni, “Effects of inorganics on the degradation of micropollutants with vacuum UV (VUV) advanced oxidation,” *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.*, vol. 52, no. 6, pp. 524–532, 2017.

[22] G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, “Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O− in Aqueous Solution,” *J. Phys. Chem. Ref. Data*, vol. 17, no. 2, pp. 513–886, 1988.

[23] G.G. Jayson, B.J. Parsons, and A.J. Swallow, “Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter,” *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, vol. 69, pp. 1597–1607, 1973.

[24] Z. Zuo, Y. Katsumura, K. Ueda, and K. Ishigure, “Reactions between some inorganic radicals and oxychlorides studied by pulse radiolysis and laser photolysis,” *J. Chem. Soc. - Faraday Trans.*, vol. 93, no. 10, pp. 1885–1891, 1997.

[25] J. De Laat, N. Chramosta, M. Doré, H. Suty, and M. Pouillot, “Constantes cinétiques de réaction des radicaux hydroxyles sur quelques sousproduits d’oxydation de l’atrazine par O_3 ou par O_3/H_2O_2: Rate constants for reaction of hydroxyl radicals with some degradation byproducts of atrazine by O_3 orO_3/H_2O_2,” *Environ. Technol.*, vol. 15, no. 5, pp. 419–428, 1994.

[26] B. A. Wols, D. J. H. Harmsen, E. F. Beerendonk, and C. H. M. Hofman-Caris, “Predicting pharmaceutical degradation by UV (LP)/H2O2 processes: A kinetic model,” *Chem. Eng. J.*, vol. 255, pp. 334–343, 2014.

[27] R. Mertens and C. von Sonntag, “Photolysis (λ = 354 nm of tetrachloroethene in aqueous solutions,” *J. Photochem. Photobiol. A Chem.*, vol. 85, no. 1–2, pp. 1–9, 1995.