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## INVESTIGATION OF UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> AND UV/VUV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> PROCESSES ON THE DEGRADATION OF TRIMETHOPRIM

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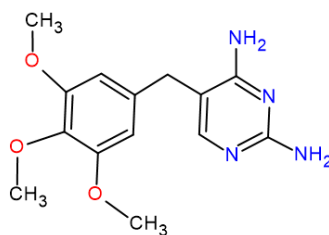
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### Abstract

Several environmental and public health problems are caused by toxic pharmaceuticals with biological activity released into the environment. Conventional biological water treatment methods are generally not effective enough to completely remove pharmaceuticals, especially antibiotics from waters, so advanced oxidation processes should be used as a complementary method. In this study, the removal efficiency of trimethoprim (TRIM) was investigated using UV (254 nm), UV/VUV (254/185 nm) photolysis, and UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and UV/VUV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> treatments. Opposite to the relatively high molar absorbance of TRIM at 254 nm, the simple UV photolysis was ineffective for its elimination. Its removal and mineralization were significant in the case of UV/VUV photolysis due to the <sup>•</sup>OH formation from water via absorption of 185 nm VUV light. The addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> highly increased the transformation and mineralization rate in both cases due to the formation of SO<sub>4</sub><sup>•-</sup>. At the highest concentration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, both UV and UV/VUV<sub>185nm</sub> photolysis removed the total TOC content within 45 minutes.

### Introduction

The consequences of the release of pharmaceuticals into the environment have become a global problem in the last decade and caused several environmental and public health problems. According to the published literature, the global use of antimicrobials could reach 200,000 tons per year [1], and a significant part of that enters the wastewater. A considerable amount of pharmaceuticals, primarily antibiotics, are also used as veterinary drugs. The conventional biological wastewater treatment method is not suitable for completely removing these components, so the increasing use of antibiotics significantly increases the risk of developing antibiotic-resistant bacteria, dangerous for animals and humans [1]. In this study, trimethoprim (TRIM), a widely used antibiotic, was used as a model compound, detected several times in wastewaters and grey waters [2]. TRIM has been used for treating various infections (e.g., urinary tract infection) since the '60s and is often applied together with sulfonamides to enhance their effect. TRIM consists of a pyrimidine-2,4-diamine and a 1,2,3-trimethoxybenzene ring connected via a methylene bridge (Fig. 1).



**Fig. 1.** The chemical structure of TRIM

The Advanced Oxidation Processes are chemical water treatment processes based on the radical generation and suitable for removing small amounts of harmful organic contaminants that cannot be removed by biological water treatment. In this work, the transformation and mineralization of TRIM were investigated using UV, UV/VUV, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and UV/VUV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> methods. While 254 nm UV radiation is generally used for water disinfection and adsorbed by the dissolved organic and inorganic substances, 185 nm VUV light having small intensity is adsorbed by water and produces <sup>•</sup>OH (2.8 V). Persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) is a potent oxidizing agent (2.1 V) that can be activated by 254 nm UV light to form highly reactive and more potent oxidizing agents, sulfate radicals (SO<sub>4</sub><sup>•-</sup>) (2.5–3.1 V) [3]. Consequently, in UV/VUV radiated solutions containing S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, both <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> can form and cause the degradation.

## Experimental

Two low low-pressure mercury vapor (LPM) lamps were used as light sources. UV lamp emitting at 254 nm (GCL307T5L/CELL, produced by LightTech, having 227 mm arc length) covered by commercial quartz envelope was used for UV photolysis. For UV/VUV photolysis low-pressure mercury-vapor lamp having the same electric and geometric parameters (GCL307T5VH/CELL produced by LightTech, having 227 mm arc length) was used. The UV/VUV<sub>185nm</sub> lamp's envelope was synthetic quartz to transmit the VUV<sub>185nm</sub> photons. The UV (254 nm) photon flux was determined by ferrioxalate actinometry and that was the same ( $3.68 \times 10^{-6}$  mol<sub>photon</sub> s<sup>-1</sup>) for both LPM lamps. The flux of the 185 nm VUV photons was determined by methanol actinometry and found to be  $3.23 \times 10^{-7}$  mol<sub>photon</sub> s<sup>-1</sup>.

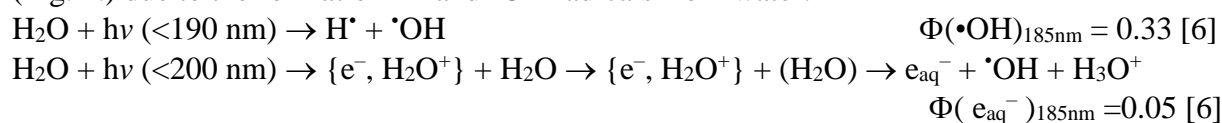
In the case of UV (254 nm), and UV/VUV<sub>185 nm</sub> photolysis, air was bubbled continuously through the solution. Gas bubbling was started at least 20 min before the measurement. TRIM (Sigma-Aldrich, ≥98.5%) solution with an initial  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> concentration was made in ultrapure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16).

Separation of the aromatic components in the treated solutions was performed by Agilent 1100 type HPLC, equipped with a diode array detector (DAD). For the analysis of TRIM and its degradation products, Kinetex 2.6u XB-C18 100A column (Phenomenex) was used at 30 °C. The eluent contains 20% acetonitrile and 80% phosphate buffer, the flow rate was 0.8 mL min<sup>-1</sup>, and 20 μL sample was injected. The wavelength of the detection was 285 nm. Total organic carbon (TOC) measurements were performed using an Analytik Jena N/C 3100 analyzer. The concentration of H<sub>2</sub>O<sub>2</sub> was measured with a cuvette test by Merck, having a 0.015 - 6.00 mg L<sup>-1</sup> measuring range.

## Results and discussion

During 254 nm UV irradiation, direct photolysis is the main pathway for the transformation of TRIM. The efficiency of UV photolysis primarily depends on the molar absorbance of the target compound. Opposite to the relatively high molar absorbance of TRIM at 254 nm ( $2942 \text{ M}^{-1} \text{ cm}^{-1}$  [4]), its transformation is negligible during the first 20 minutes due to the very low quantum yield [5]. After this induction period, a slow degradation can be observed in the air-saturated solution. One plausible explanation could be a slow accumulation of low-reactivity species, such as HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup> or CO<sub>3</sub><sup>•-</sup>.

Opposite to the low intensity, the presence of 185 nm VUV light highly improved the efficiency (Fig. 2.) due to the formation H<sup>•</sup> and <sup>•</sup>OH radicals from water:



In the presence of dissolved  $O_2$ ,  $H^+$  and  $e_{aq}^-$  transforms into the less reactive  $HO_2^{\bullet}$  and  $O_2^{\bullet-}$ , and the main reactive species is the  $\bullet OH$ , which is a non-selective, strong oxidant.

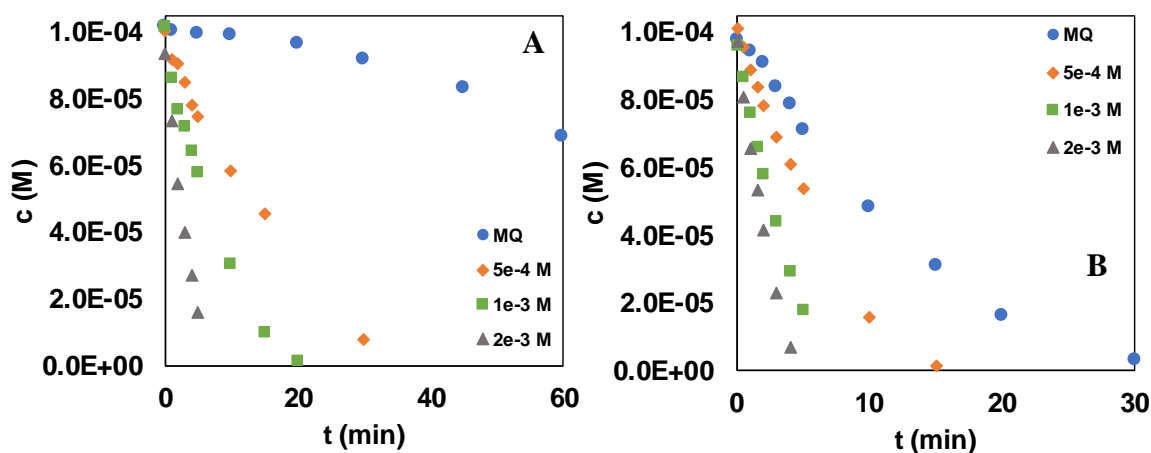
**Table 1.** Initial transformation rates of TRIM at  $1.0 \times 10^{-4}$  M initial concentration

$S_2O_8^{2-}$ c ( $\times 10^{-4}$ M)	UV/air	UV/VUV/air	
	$r_0$ ( $\times 10^{-7}$ M/s)	$r_0$ ( $\times 10^{-7}$ M/s)	$r_0^{UV}/r_0^{UV/VUV}$
0.0	–	0.817	–
5.0	0.860	1.883	0.457
10.0	1.492	3.383	0.441
20.0	2.983	5.267	0.566

The addition of  $S_2O_8^{2-}$  highly enhanced the transformation rate in the case of both light sources. Due to the 254 nm UV radiation from  $S_2O_8^{2-}$  highly reactive sulfate radicals ( $SO_4^{\bullet-}$ ) are formed:  $S_2O_8^{2-} + h\nu \rightarrow 2 SO_4^{\bullet-}$ .  $\Phi(SO_4^{\bullet-})_{254nm} = 1.4 \pm 0.3$  [7,8]

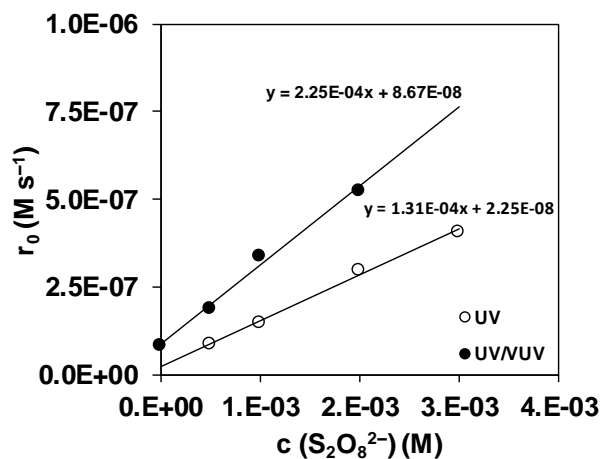
The  $SO_4^{\bullet-}$  has similar reactivity to  $\bullet OH$ ; however, it is more selective and less reactive towards organic substances. The reaction rate constants of SMT with  $\bullet OH$  and  $SO_4^{\bullet-}$  were calculated from the competition kinetics method by Luo et al. [4] and found to be  $6.02 \pm 0.13 \times 10^9 M^{-1}s^{-1}$  and  $3.88 \pm 0.07 \times 10^9 M^{-1}s^{-1}$ , respectively.

In the UV/ $S_2O_8^{2-}$  process, the relative contribution of the direct photolysis to the TRIM transformation is negligible, and  $SO_4^{\bullet-}$  based transformation is dominant. Comparing the molar absorbances of TRIM ( $2942 M^{-1} cm^{-1}$ ) and  $S_2O_8^{2-}$  ( $20\text{--}22 M^{-1} cm^{-1}$  [8]), a higher portion of the photons absorbed by TRIM even at the highest concentration of  $S_2O_8^{2-}$ . (Table 1, Fig. 2). In the case of UV photolysis, the effect of  $3 \times 10^{-3}$  M  $SO_4^{\bullet-}$  was also investigated, which is slightly enhanced the transformation.



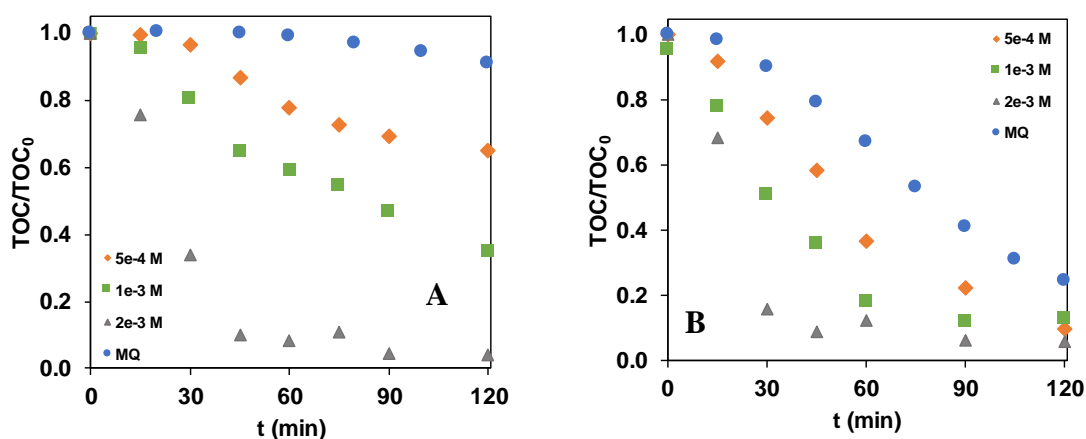
**Fig 2.** Effect of  $Na_2S_2O_8$  dosage on the degradation of TRIM in the case of UV (A) and UV/VUV<sub>185nm</sub> (B) photolysis

In the UV/VUV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> method, <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> based reaction also contributes to the transformation. In both cases, the transformation rate of TRIM increases linearly with the initial S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration, but the effect of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> addition is more pronounced in the case of UV/VUV irradiation (Fig. 3). Due to the absorption of 185 nm VUV light by the SO<sub>4</sub><sup>-</sup>, the regeneration of the SO<sub>4</sub><sup>•-</sup> was supposed.



**Fig 3.** Effect of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dosage on the initial transformation rate of TRIM in the case of UV and UV/VUV<sub>185nm</sub> photolysis

It is essential to study the mineralization of biologically active compounds. During UV photolysis, the mineralization of the treated solution is neglected; the TOC value just slightly decreased (Fig. 4), while in the case of UV/VUV photolysis, the degree of mineralization is significant; the TOC value decreased by approx. 80% (Fig. 4b). With increasing the initial concentration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, the mineralization rate highly increased in both cases. At the highest applied concentration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, the transformation rate of TRIM is higher for UV/VUV photolysis (Table 1.), but the mineralization rate became similar (Fig. 4.).



**Fig 4.** Effect of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dosage on the mineralization of TRIM in the case of UV (A) UV/VUV<sub>185nm</sub> (B) photolysis

The characterization of methods includes the energy investment; thus, the electrical energy required for the 90% transformation of TRIM was calculated (Table 2.).

**Table 2.** The electrical energy required for transformation of 90% TRIM (kJ) and 90% of the TOC content at  $1.0 \times 10^{-4}$  M initial concentration

		$c(\text{S}_2\text{O}_8^{2-}) \times 10^{-4}$ M			
		0	5	10	20
TRIM <sup>90%</sup>	UV	108	27	14	8
	UV/VUV <sub>185nm</sub>	24	12	8	4
TOC <sup>90%</sup>	UV	–	233	142	68
	UV/VUV <sub>185nm</sub>	127	108	108	54

As Table 2. shows, in the case of UV photolysis, even at the lowest concentration of  $\text{S}_2\text{O}_8^{2-}$ , the electrical energy consumption was reduced significantly and approached that required for UV/VUV photolysis. Although the transformation rates (Fig. 2.) and the mineralization (Fig. 4.) were similar at the highest  $\text{S}_2\text{O}_8^{2-}$  concentration using UV and UV/VUV light sources, the energy consumption is much lower.

### Conclusion

The photolysis of TRIM without the addition of  $\text{S}_2\text{O}_8^{2-}$  was only effective during UV/VUV photolysis. The addition of  $\text{S}_2\text{O}_8^{2-}$  highly increased the transformation and mineralization rates in both cases. At the highest  $\text{S}_2\text{O}_8^{2-}$  ( $2.0 \times 10^{-3}$  M) concentration, both UV and UV/VUV photolysis eliminated the TOC within 45 minutes. The electrical energy consumption was lower at each  $\text{S}_2\text{O}_8^{2-}$  concentration using UV/VUV photolysis than UV photolysis, especially for mineralization.

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### References

- [1] M. Cycoń, A. Mroziak, Z. Piotrowska-Seget, *Front. Microbiol.*, 10 (2019) 338.
- [2] H. Kim, M. Homan, *J. Great Lakes Res.*, 46 (2020) 1321-1330.
- [3] N. Karpel Vel Leitner, in: M.I. Stefan (Ed.), *Advanced Oxidation Processes for Water Treatment*, IWA Publishing, London, 2017, pp. 429-460.
- [4] Y. Luo, R. Su, H. Yao, A. Zhang, S. Xiang, L. Huang, *Environ. Sci. Pollut.*, (2021)
- [5] C. Baeza; D.R.U. Knappe, *Water Research*, 45 (2011) 4531-4543.
- [6] N. Getoff and G.O. Schenck, *J. Photochem. Photobiol. A*, 8 (1968) 167-178.
- [7] H. Herrmann, *Phys. Chem*, 9 (2007) 3935–3964.
- [8] G. Mark, M.N. Schuchmann, H.P. Schuchmann, C. von Sonntag C., *J. Photochem. Photobiol. A*, 55 (1990) 157-168.