



INVESTIGATION OF UV/S₂O₈²⁻ AND UV/VUV/S₂O₈²⁻ PROCESSES ON THE DEGRADATION OF TRIMETHOPRIM



Luca Farkas, Adrienn Szirmai, Tünde Alapi

Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm square 7, Hungary
e-mail: fluca@chem.u-szeged.hu

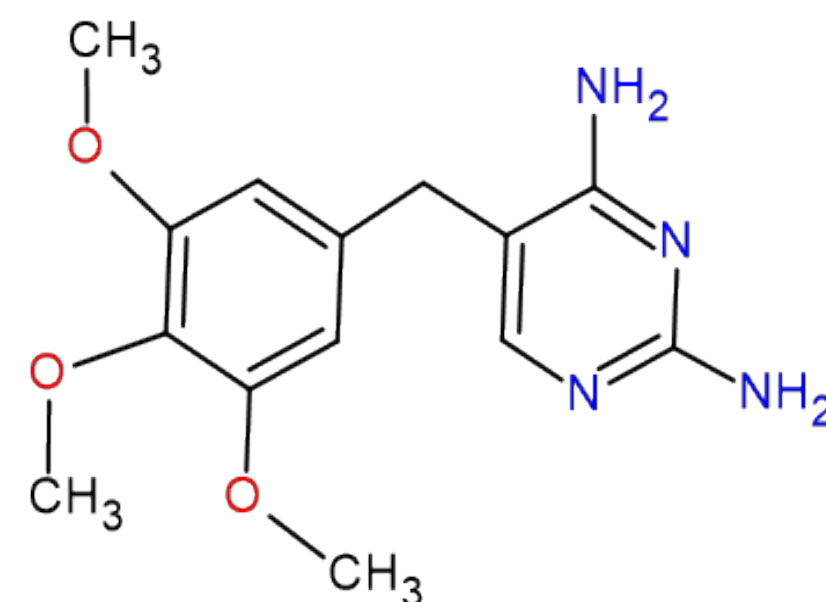
Several environmental and public health problems are caused by toxic pharmaceuticals with biological activity released into the environment.

Antibiotics deserve increased attention; their appearance in the environment leads to the emergence of antibiotic-resistant bacterial strains and cause severe environmental and public health problems.

The use of low-pressure mercury vapor lamps (LPMV), emitting 254 nm UV and 185 nm VUV light, makes it possible to remove pollutants from the water, in particular by combining photolysis with the persulfate (S₂O₈²⁻) method.

Trimethoprim:

- Antibiotic
- Frequently used with sulfonamides
- Hardly biodegradable
- Presented in wastewater
- Serious risk: antibiotic resistance



Light sources, reactive species and possible transformation ways

UV LPM lamp

Emission wavelength: 254 nm

$$\Phi_{254\text{ nm}} = 3.68 \times 10^{-6} \text{ mol}_{\text{photon}} \text{ s}^{-1}$$

TRIM + $h\nu_{254\text{ nm}}$ → direct photolysis

$$\epsilon_{254\text{ nm}} = 2942 \text{ M}^{-1} \text{ cm}^{-1}$$

UV/VUV LPM lamp

Emission wavelength: 254 and 185 nm

$$\Phi_{254\text{ nm}} = 3.68 \times 10^{-6} \text{ mol}_{\text{photon}} \text{ s}^{-1}$$

TRIM + $h\nu_{254\text{ nm}}$ → direct photolysis

$$\Phi_{185\text{ nm}} = 3.23 \times 10^{-7} \text{ mol}_{\text{photon}} \text{ s}^{-1}$$



UV photolysis of S₂O₈²⁻



$$\Phi(\text{SO}_4^{\bullet-})_{254\text{ nm}} = 1.4 \pm 0.3$$



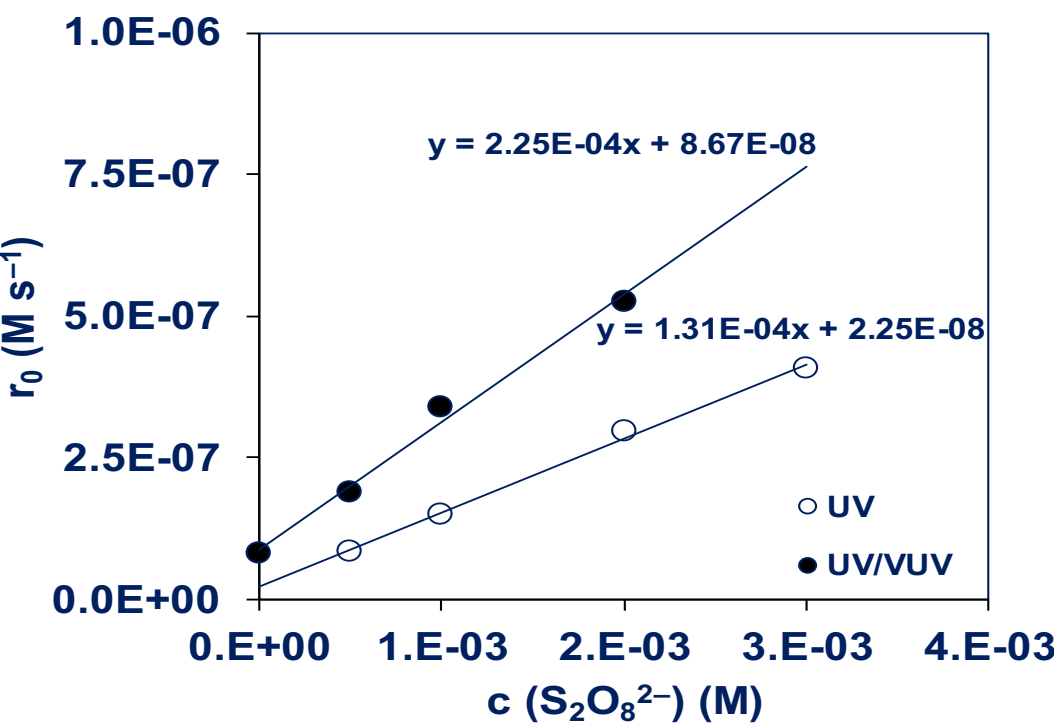
$$k = 3.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

Depending on the light source, the transformation of TRIM can take place via direct UV photolysis (UV LPM lamp) or reaction with $\text{}^\bullet\text{OH}$ (UV/VUV LPM lamp). The addition of S₂O₈²⁻ opens up a new possibility for the transformation due to the formation of highly reactive SO₄^{•-}.

The aim of this work was the comparison the efficiency of UV/S₂O₈²⁻ and UV/VUV/S₂O₈²⁻ processes in particular the effect of VUV light in the case of the combined method.

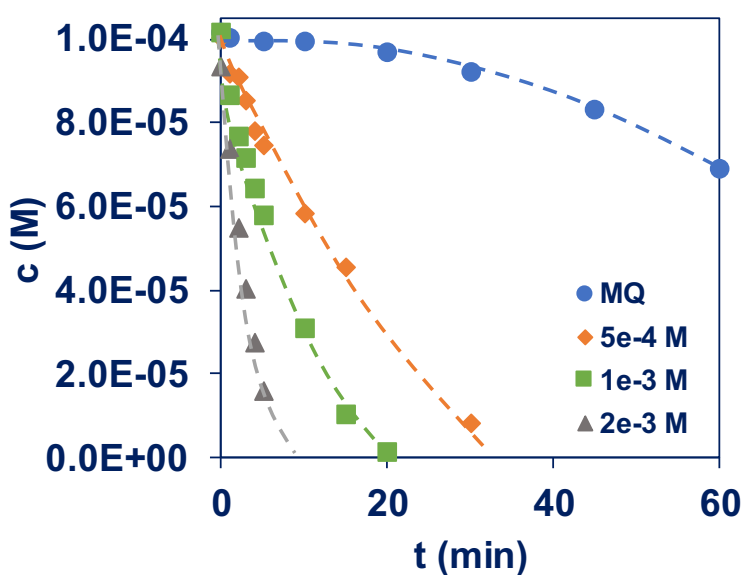
UV/S₂O₈²⁻ and UV/VUV/S₂O₈²⁻

The transformation rate of TRIM increases linearly with the initial S₂O₈²⁻ concentration. The effect of S₂O₈²⁻ addition is more pronounced in the case of UV/VUV/S₂O₈²⁻.

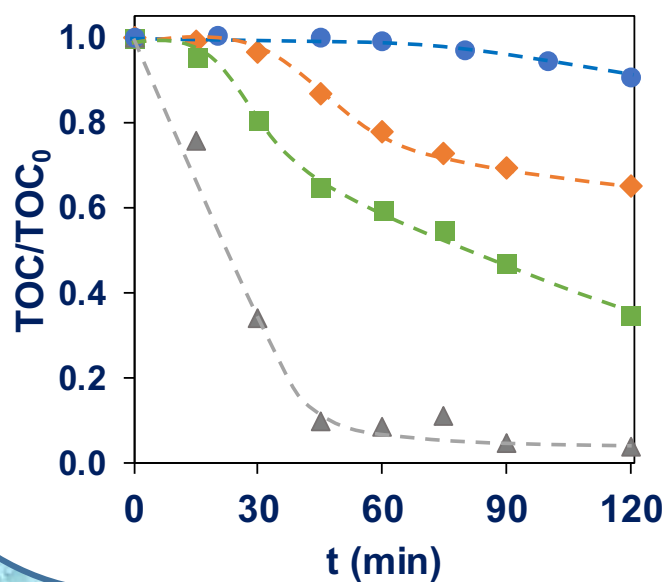


- •OH and SO₄^{•-} based reaction also contributes to the transformation in the case of UV/VUV/S₂O₈²⁻
- Due to the absorption of 185 nm VUV light by the formed SO₄^{•-} the regeneration of the SO₄^{•-} is supposed.

UV/S₂O₈²⁻ Degradation

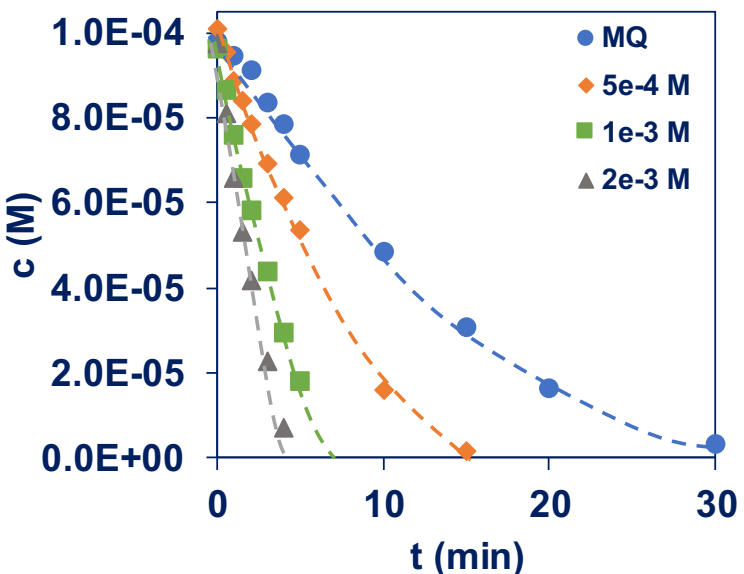


Mineralization

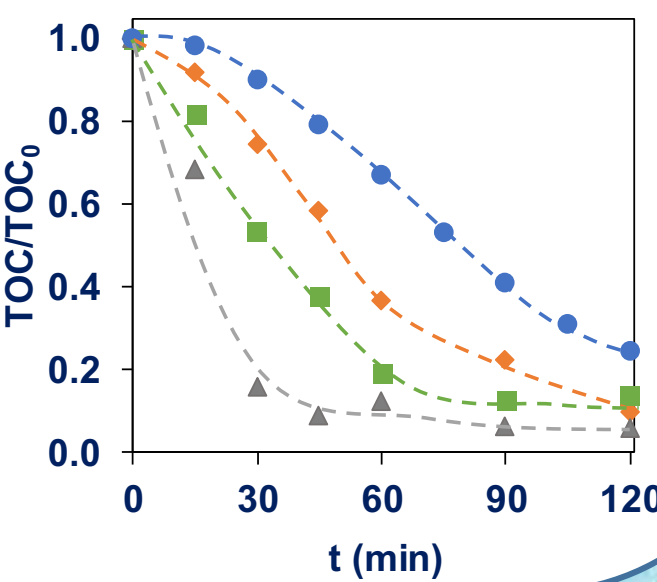


- Direct UV photolysis is not effective for TRIM transformation. Without the addition of S₂O₈²⁻, the transformation and mineralization is significant only in the case of UV/VUV due to the formation of •OH.
- With increasing the initial concentration of S₂O₈²⁻, the transformation and mineralization rate highly increased in both cases.
- The effect of VUV light remains significant at lower concentration of S₂O₈²⁻. At the highest concentration of S₂O₈²⁻, the transformation and mineralization rates are similar for UV and UV/VUV irradiation.

UV/VUV/S₂O₈²⁻ Degradation



Mineralization



		c(S ₂ O ₈ ²⁻) × 10 ⁻⁴ M			
		0	5	10	20
TRIM ^{90%}	UV	108	27	14	8
	UV/VUV _{185nm}	24	12	8	4
TOC ^{90%}	UV	—	233	142	68
	UV/VUV _{185nm}	127	108	108	54

At the highest applied S₂O₈²⁻ concentration, using UV and UV/VUV light sources, the difference between the mineralization rates and energy consumption became negligible.

The additive effect of VUV light and the formed •OH is more significant at lower S₂O₈²⁻ concentrations.



NEMZETI KUTATÁSI, FEJLESZTÉSI ÉS INNOVÁCIÓS HIVATAL

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*Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged,
Dóm tér 7, Hungary
e-mail: fluca@chem.u-szeged.hu*

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/S₂O₈²⁻ and UV/VUV/S₂O₈²⁻ 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 [•]OH formation from water via absorption of 185 nm VUV light. The addition of S₂O₈²⁻ highly increased the transformation and mineralization rate in both cases due to the formation of SO₄^{•-}. At the highest concentration of S₂O₈²⁻, both UV and UV/VUV_{185nm} 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).