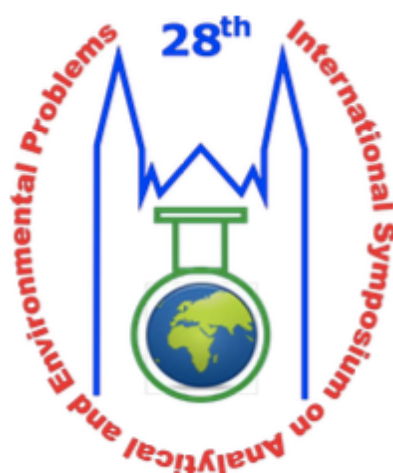




PROCEEDINGS OF THE

28th International Symposium
on Analytical and Environmental Problems

Szeged, Hungary
November 14-15, 2022



University of Szeged

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Publisher:
University of Szeged, H-6720 Szeged, Dugonics tér 13,
Hungary

ISBN 978-963-306-904-2

2022.
Szeged, Hungary

***The 28th International Symposium on Analytical and
Environmental Problems***

Organized by:

SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi Munkabizottsága

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INVESTIGATION OF THE UV/PERSULFATE PROCESS FOR THE ELIMINATION OF TRIMETHOPRIM ANTIBIOTIC – THE EFFECT OF MATRIX AND INORGANIC IONS

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Antimicrobial resistance is one of the most emerging health crises due to the release of antibiotics into the environment. The WHO declared in 2019 that antibiotic resistance is among the ten most serious environmental risks. Nevertheless, antibiotic use increased sharply during the COVID-19 pandemic, as more than half of those infected with the coronavirus received antibiotics to prevent bacterial infection. These antibiotics and their biologically active metabolites are present in domestic and hospital wastewater effluents. Various UV-based advanced oxidation methods can be used in the degradation of pharmaceuticals due to the generation of reactive hydroxyl radicals. Besides these processes, sulfate radical ($\text{SO}_4^{\bullet-}$) based techniques have become widely investigated in recent years.

This study investigated UV photolysis combined with peroxydisulfate ion (PDS) to eliminate trimethoprim, a widely used and hardly biodegradable antibiotic from aqueous solutions. The low-pressure mercury-vapor lamp emits 254 nm UV light as a light source. The direct UV photolysis is negligible for trimethoprim elimination, and the addition of PDS enhanced the transformation and mineralization rate due to the formation of reactive $\text{SO}_4^{\bullet-}$ via direct photolysis.

The effect of inorganic ions, such as Cl^- and HCO_3^- and biologically treated domestic wastewater as a matrix were also investigated. Biologically treated domestic wastewater diminished the transformation and mineralization efficiency. Using 1.0×10^{-4} M trimethoprim and 1.0×10^{-3} M PDS concentration, the transformation stopped after 3 minutes, and no more than 30% degradation was reached. Using doubled PDS concentration, the negative matrix effect was moderated. Since both Cl^- and HCO_3^- react with $\text{SO}_4^{\bullet-}$, their influence was studied separately and together. The degree of inhibition was far below the value expected based on their radical scavenging capacity. The formed secondary radicals, $\text{Cl}^{\bullet}$ and $\text{CO}_3^{\bullet-}$ can react with trimethoprim or initiate the formation of other reactive species, such as $^{\bullet}\text{OH}$. The formation of chlorinated products proved the contribution of $\text{Cl}^{\bullet}$ to the transformation. The presence of HCO_3^- diminished the formation of chlorinated products, most likely due to the reaction between $\text{Cl}^{\bullet}$ and HCO_3^- resulting in Cl^- and $\text{CO}_3^{\bullet-}$. However, the reactions between inorganic ions and $\text{SO}_4^{\bullet-}$ require further investigation due to the complexity of the multi-component solutions containing various reactive species.

Acknowledgment

This work was sponsored by the National Research, Development, and Innovation Office-NKFI Fund OTKA, project number FK132742.

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Pharmaceuticals are essential elements of medical and veterinary practice, but conventional wastewater treatment plants are not designed to eliminate wastewater.



Releasing human and veterinary drugs into the environment results in antibiotic-resistant bacterial strains. Drug-resistant infections already cause 700,000 deaths each year globally. This number is estimated to increase to 10 million by 2050....



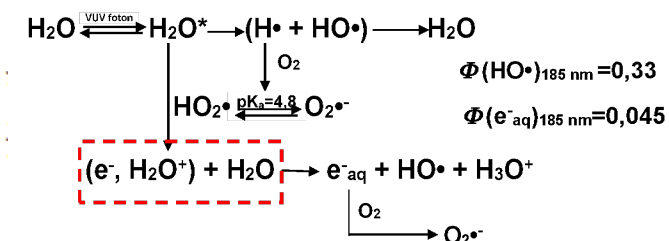
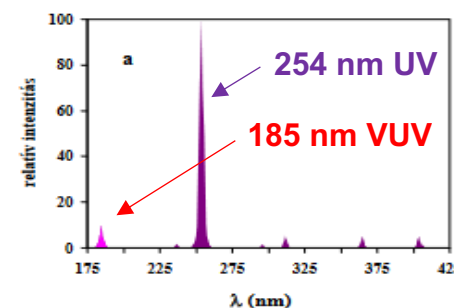
The COVID-19 pandemic has caused a considerable increase in the use of antibiotics in recent years with unpredictable consequences...



Upgrading of wastewater and drinking water treatment plants is necessary
→ Effective post-treatment methods are required → Advanced Oxidation Processes?



Low-pressure mercury vapor lamp in water treatment



UV photons are absorbed by dissolved organic or inorganic substances.

VUV photons absorbed by the water and result in reactive radicals

UV photolysis of $\text{S}_2\text{O}_8^{2-}$ results in reactive $\text{SO}_4^{\bullet-}$



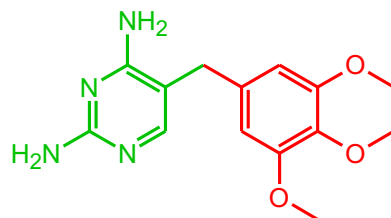
$$\Phi(\text{SO}_4^{\bullet-})_{254\text{ nm}} = 1.4 \pm 0.3$$



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

Trimethoprim

- antibiotic
- applied in large quantities in husbandry
- persistent, difficult to biodegrade
- detected regularly in surface waters worldwide ($\mu\text{g/L}$)

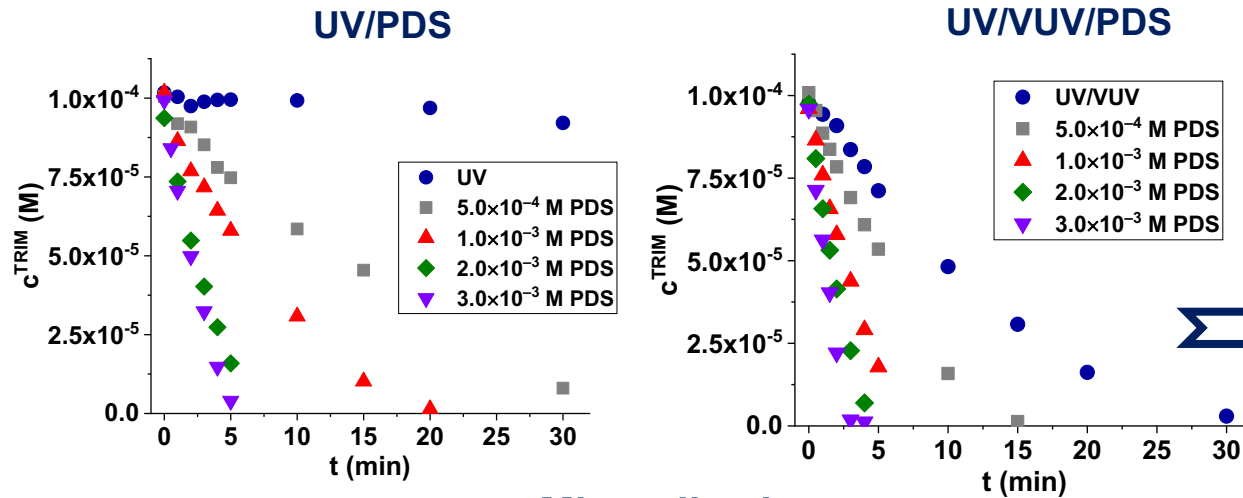


The aim of this work was the investigation of the

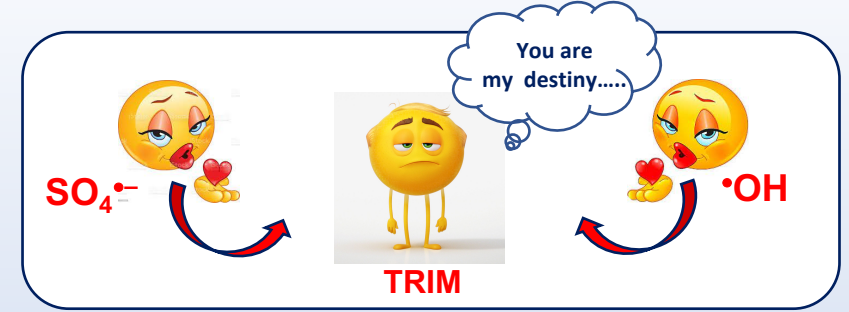
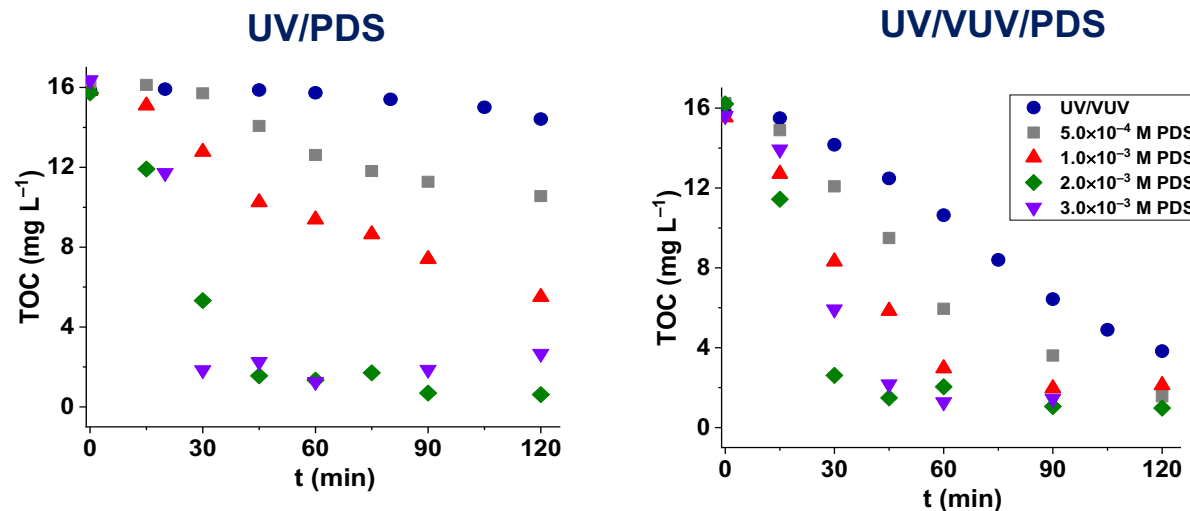
- TRIM transformation and mineralization by UV/PDS and UV/VUV/PDS processes
- effects of PDS concentration
- role of radicals ($^\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) and the importance of VUV photolysis
- effect of biologically treated domestic wastewater and inorganic ions of the matrix (Cl^- and HCO_3^-)

Transformation and mineralization of TRIM – effect of PDS and VUV photolysis

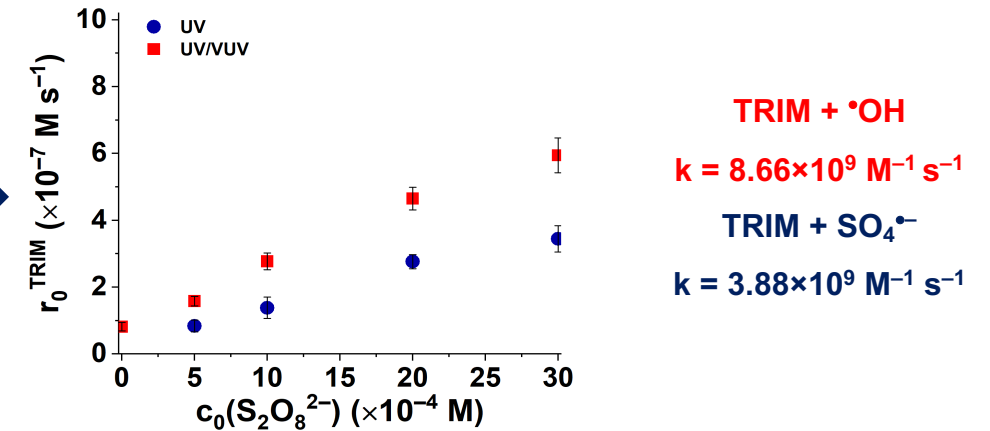
Transformation



Mineralization



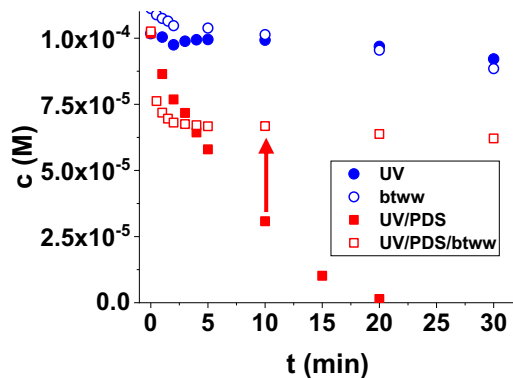
Initial transformation rate of TRIM



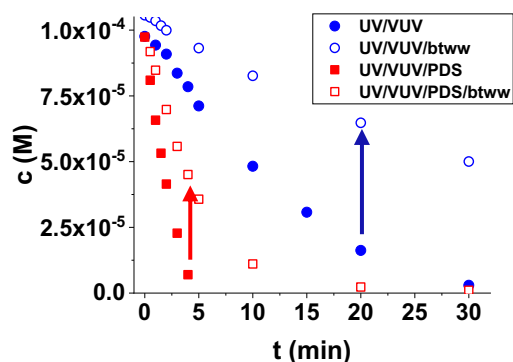
- UV photolysis is not efficient for TRIM transformation
- Low-intensity VUV light enhances the transformation and mineralization due to the •OH formation from water
- The UV/VUV/PDS method is more efficient than UV/PDS at each investigated PDS concentration.
- The relative contribution of low-intensity VUV light is significant, even in the case of the UV/VUV/PDS process.
- The mineralization rate of TRIM increases with increasing PDS concentration in both cases.
- Above 2.0×10^{-3} M PDS there is no difference between the mineralization rate of UV/PDS and UV/VUV PDS processes.

Matrix effect

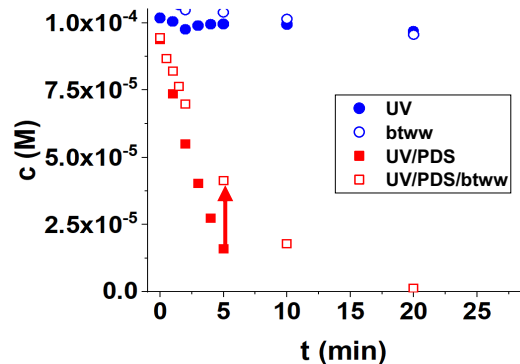
UV/ 1.0×10^{-3} M PDS



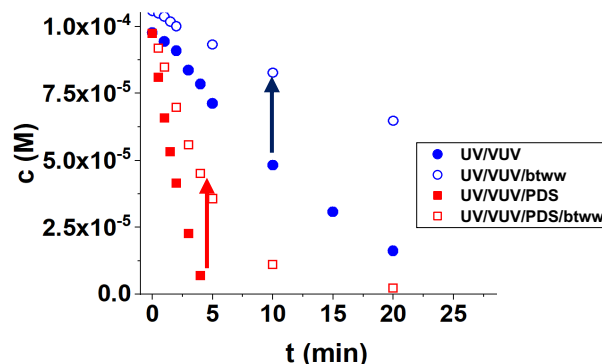
UV/VUV/ 1.0×10^{-3} M PDS



UV/ 2.0×10^{-3} M PDS



UV/VUV/ 2.0×10^{-3} M PDS



- The matrix (biologically treated domestic wastewater (btww)) reduced the transformation and mineralization rate in all cases
- The VUV light significantly reduced the negative matrix effect.
- For the UV/PDS method, the matrix completely inhibited the transformation in the case of 1.0×10^{-3} M PDS.
- The increase of PDS concentration reduces the matrix negative effect

Matrix effect

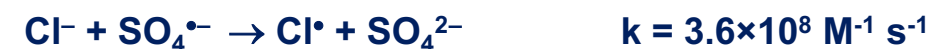
Biologically

treated domestic wastewater was used as a matrix.

Analytical parameters

pH	7,8
Conductivity ($\mu\text{S cm}^{-1}$)	1258
COD (mg L^{-1})	24.4
$\text{HCO}_3^- - \text{C}$ (mg L^{-1})	103.4
$\text{NO}_3^- - \text{N}$ (mg L^{-1})	3.37
Cl^- (mg L^{-1})	120
TOC (mg L^{-1})	5-7

Both organic and inorganic compounds in the matrix can act as radical scavengers.



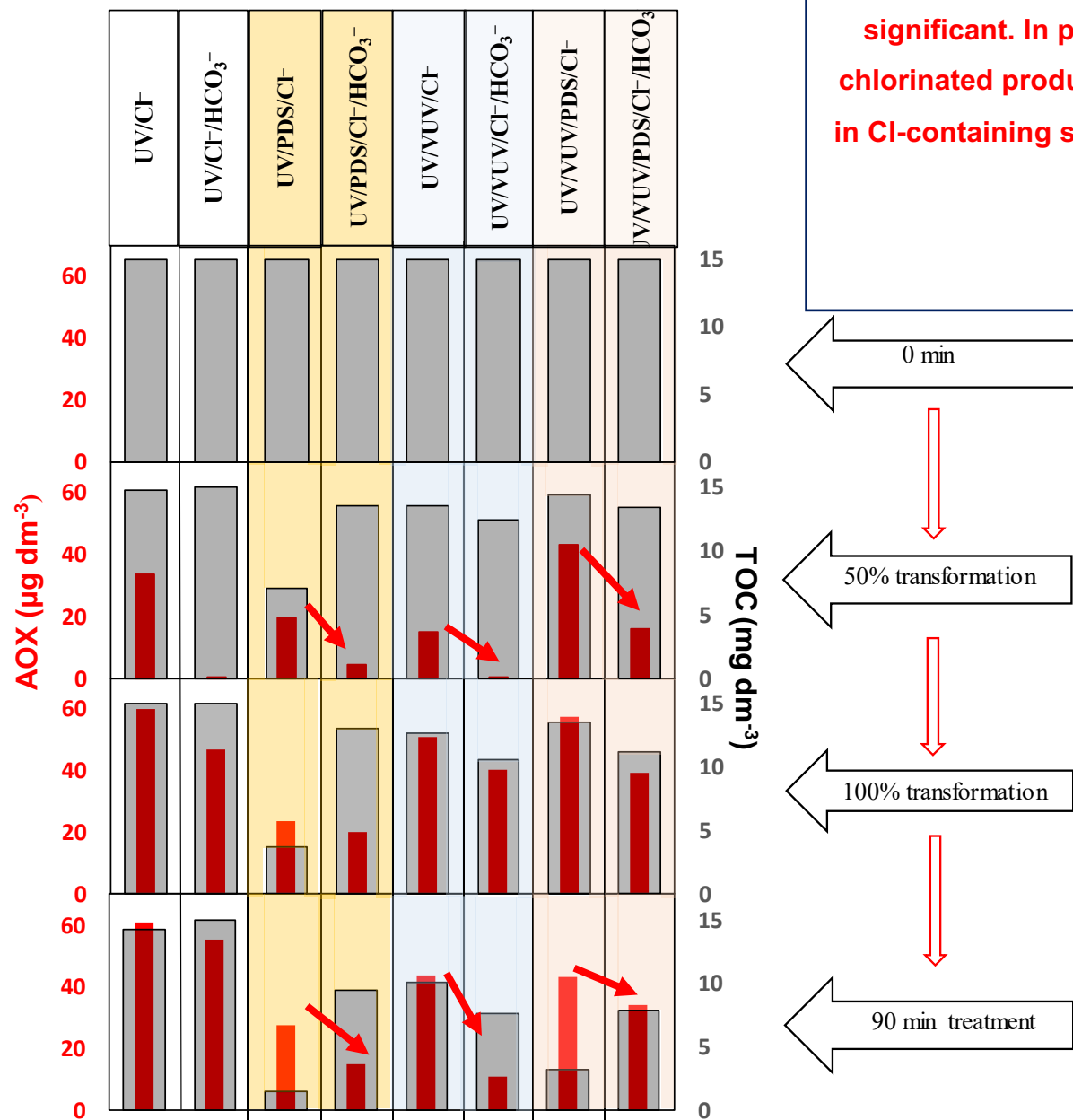
The effect of the inorganic ions together does not reflect well the inhibition effect of the matrix.



The reactions of $\text{Cl}\cdot$ generate $\cdot\text{OH}$

Secondary radicals react with TRIM:





The role and contribution of new reactive species to the transformation and mineralization can be significant. In particular, the additional role of $\text{Cl}^\bullet$ is important due to the possibility of forming chlorinated products. AOX measurements proved the formation and significant contribution of $\text{Cl}^\bullet$ in Cl-containing solution. The chlorination of organic substances was moderated in the presence of HCO_3^- due to the reaction between HCO_3^- and $\text{Cl}^\bullet$.



Summary

- PDS addition (UV/PDS and UV/VUV/PDS process) enhances the transformation and mineralization rate
- additive effect of VUV light is essential even in the case of the UV/VUV/PDS process – due to the $\text{OH}^\bullet$ formation from water and probably via direct VUV photolysis of PDS
- At higher PDS concentrations, $\text{SO}_4^{\bullet-}$ is the dominant reaction partner for both UV/PDS and UV/VUV/PDS process
- Biologically treated domestic wastewater as a matrix significantly reduced the transformation and mineralization rate – VUV light diminished the inhibitory effect
- The role and importance of secondary radicals formed from $\text{Cl}^\bullet$ and HCO_3^- could not be neglected, even though the inhibition effect of inorganic ions is much smaller than that of the matrix.

Luca Farkas thanks the support of the ÚNKP-22-3-SZTE-398 New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development, and innovation fund. This work was sponsored by the National Research, Development, and Innovation Office-NKFI Fund OTKA, project number FK132742.

