Transformation of Sulfamethazine and Sulfamethoxypyridazine Using TiO₂ and ZnO Photocatalysts Irradiated with Mercury-Vapor and UV-LED Light Sources

<u>Máté Náfrádi</u>, Luca Farkas, Gellért Farkas, Benjámin Vas, Tünde Alapi Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary

Antibiotics are essential in modern medicine, but their extensive use may cause serious environmental and health hazards. A well-known problem is the appearance of antibiotic-resistant bacteria. Several antimicrobial drugs have been detected in commercial and agricultural wastewaters, and since traditional wastewater treatment methods do not remove them completely, they can be found in natural waters too. Sulfonamides are a group of antibiotic drugs extensively used, especially in animal therapy. They are used in large doses, and their utilization is low, therefore a high amount is excreted to the environment. Since their removal is not solved with the classic wastewater treatment methods, additional processes are needed. Advanced Oxidation Processes (AOPs) are a promising method for the removal of such low concentration, recalcitrant organic pollutants.

In the current work the heterogeneous photocatalytic removal of two sulfonamide antibiotics - sulfamethazine and sulfamethoxypyridazine - has been investigated. TiO_2 (P25), and ZnO have been used as photocatalysts. For light sources, a mercury vapor lamp emitting in the 300-400 nm wavelength range, a LED light source emitting at $398(\pm 10)$ nm (LED_{398nm}), and UV-LEDs emitting at $365(\pm 10)$ nm (LED_{365nm}) have been used. LED light sources are promising for different AOPs due to their high efficiency, low cost, and flexible application possibilities.

The photon flux of the different light sources has been measured using ferrioxalate actinometry. The removal efficiency of the two sulfonamides has been determined, and both TiO₂ and ZnO were efficient for their removal. The products forming during the photocatalytic treatment have been determined using HPLC-MS, and a possible reaction mechanism has been proposed. The mineralization efficiency has been investigated by measuring the Total Organic Carbon (TOC) concentration, where TiO₂ proved to be more efficient, except in the case of the LED_{365nm} where both have shown similar – and very high efficiency. Experiments were performed in real water matrices (drinking water and biologically treated wastewater), and artificial matrices containing Cl⁻, HCO₃⁻ (the most abundant anions), and methanol (as 'OH-scavenger). The LED_{365nm} has shown the best efficiency in both matrices, and the effect of the matrix-components was dependent on the model compound, the photocatalysts, and the irradiation source used.

Acknowledgement

This publication was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, and the new national excellence program of the Ministry for Innovation and Technology (ÚNKP-20-5-SZTE-639). The authors thank the financial support of the National Research, Development and Innovation Office – NKFIH (project number FK132742).