



INVESTIGATION OF THE USE OF PERSULFATE SALTS IN ADVANCED OXIDATION PROCESSES USING TRIMETHOPRIM AS MODEL COMPOUND

Anett Covic, Gyöngyi Orosz, Tünde Alapi

Department of Molecular and Analytical Chemistry, University of Szeged, Dóm tér 7, H-6720 Szeged, Hungary

e-mail: covicanett@chem.u-szeged.hu

ABSTRACT

Traditional 3-stage wastewater treatment does not completely remove all organic matter, even non- or hardly-biodegradable substances. Among others, advanced oxidation processes can efficiently remove these pollutants via processes based on the application of various oxidizing agents and radical-based reactions. The low-pressure mercury vapor (LPM) lamps emitting 254 nm UV light have an excellent germicidal effect and are widely used in water treatment for disinfection. The combination of UV light with oxidizing agents, such as hydrogen peroxide (H_2O_2) and persulfate (PS) ions (peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$, PDS) and peroxomonosulfate (HSO_5^- , PMS)) results in $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$ and initiate the transformation of organic substances. In the case of a PS-based process, a sulfate ion is formed; the limit of its concentration in drinking water is 250 mg L^{-1} , which must be considered when dosing. The LPM lamp covered with high-purity quartz envelope, have a small-intensity emission of 185 nm VUV light, which can be used for radical generation directly from water.

The efficiency of UV/ H_2O_2 , UV/PMS, and UV/PDS processes and UV/VUV photolysis were investigated and compared in eliminating trimethoprim (TRIM) from aqueous solutions. The model compound TRIM, is a non-biodegradable, widely used antibiotic for treating urinary, respiratory and gastrointestinal tract infections and frequently detected in wastewater and surface waters and resistant for the UV-initiated transformation.

Due to the UV photolysis of H_2O_2 , PMS, and PDS $\text{HO}\cdot$, $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$, and $\text{SO}_4\cdot^-$ forms. Both $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$ react with TRIM ($k(\text{HO}\cdot) = 8.66 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{SO}_4\cdot^-) = 3.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The rate of TRIM decomposition and mineralization increased with increasing the concentration of oxidizing agent. The dissolved oxygen has no effect on the photolysis of H_2O_2 or PS, but enhanced the transformation and mineralization of TRIM due to the formation of organic peroxy radicals ($\text{ROO}\cdot$), which have an essential role in the mineralization of each organic substances. The relative contribution of various radicals to the transformation was investigated with radical scavenger methanol and *tert*-butanol. The results proved the essential role of $\text{HO}\cdot$ for UV/VUV and UV/ H_2O_2 processes and $\text{SO}_4\cdot^-$ for UV/PDS processes. However, the $\text{HO}\cdot$ formation can not be excluded in the case of UV/PDS process via hydrolysis of $\text{SO}_4\cdot^-$. The efficiency of UV/VUV photolysis can be reached or even exceeded with PMS and PDS dosage lower than 1,0 mM. However, the additive role of low-intensity VUV radiation is manifested in the presence of H_2O_2 and PS and caused the further increase of the efficiency.

The effect of the matrix was investigated using biologically treated domestic wastewater (BTWW) having high Cl^- (120 mg L^{-1}) and HCO_3^- (524 mg L^{-1}) content. The inorganic ions



can inhibit the transformation of the organic pollutant to a different extent due to their reactions with $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$. The matrix effect depended on the quality of the oxidizing agent and the dominant radical. The PS-based processes were found to be more sensitive to the presence of inorganic ions and less effective for mineralization. The positive effect of VUV radiation was well-pronounced in the compensation of the negative matrix effect.

Keywords: Trimethoprim, Advanced Oxidation process, UV/VUV, UV/PDS, UV/PMS

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