EVALUATION OF THE EFFICIENCY OF THE COMBINATION OF A MEMBRANE BIOREACTOR WITH SELECTED ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF ANTIBIOTIC-RELATED MICROCONTAMINANTS

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Abstract

This Ph.D. thesis aims at shedding light into currently open questions regarding the removal of antibiotic-related microcontaminants from urban wastewater. The main goal of this study was to investigate the removal in urban wastewater of antibiotic-related microcontaminants by a pilot-scale Membrane BioReactor (MBR) process combined with selected Advanced Oxidation Processes (AOPs): (i) heterogeneous TiO_2 photocatalysis, ii) photocatalysis with novel TiO_2-reduced graphene oxide (TiO_2-rGO) composites using a photocatalytic (hereby denoted TiO_2-rGO-PH) or hydrothermal synthesis method (hereby denoted TiO_2-rGO-HD) and, iii) homogeneous photo-Fenton oxidation, which was later examined at a pilot-scale setup under real solar irradiation (solar photo-Fenton oxidation).

The examined parameters include: the removal of antibiotics (clarithromycin (CLA), erythromycin (ERY) and sulfamethoxazole (SMX)), the inactivation and re-growth of total and antibiotic-resistant bacteria (ARB) (*Escherichia coli*, *Pseudomonas aeruginosa* and *Klebiella* spp. and their antibiotic-resistant counterparts to the abovementioned antibiotics), the removal of antibiotic resistance genes (ARGs) (*sul*1, *mec*A, *amp*C and *erm*B), taxon-specific markers (*enc* gene for enterococci and *ecf*X gene for *Pseudomonas aeruginosa*) and the reduction of genomic DNA, followed by insights into bacterial community structure changes using 16S rRNA sequencing and DGGE.

TiO_2 and TiO_2-rGO photocatalysis did not achieve complete removal of the antibiotic compounds. However, TiO_2 and TiO_2-rGO-PH photocatalyses achieved a complete inactivation of the examined bacteria (<LOD) but there was re-growth *P. aeruginosa* when using TiO_2-rGO-HD and *Klebsiella* spp. with all materials after treated effluent storage for 24 hours, suggesting the process inability to permanently inactivate these types of bacteria. There was no remarkable impact of treatment with all catalysts on the concentration of ARGs, taxon-specific markers and genomic DNA.

The bench-scale photo-Fenton oxidation achieved a complete removal of the antibiotic compounds (<LOD) and complete inactivation of the total and antibiotic-resistant bacteria to all antibiotics (<LOD) without any re-growth after 24 hours of effluent storage. Moreover, it removed all examined ARGs (<LOD) but did not significantly affect the concentration of the examined taxon-specific markers in the treated effluents.

Overall, the photo-Fenton oxidation outperformed the TiO_2 and TiO_2-rGO photocatalysis, thus it was decided to test the combined pilot-scale MBR-solar photo-Fenton process, under real solar irradiation conditions for its impact on these antibiotic-related microcontaminants.

The combined pilot-scale MBR-solar photo-Fenton oxidation process achieved a high antibiotic (<LOD for ERY and SMX and 84% for CLA) and DOC reduction (90%) along with 99% removal of the bacteria with no re-growth after effluent storage for 24 hours. Moreover, there was a high genomic DNA reduction observed (>99%). However, there was no significant impact of the combined process on ARGs and taxon-specific markers.

The molecular analyses revealed that TiO_2 and TiO_2-rGO-PH photocatalyses and homogeneous photo-Fenton oxidation produced distinct bacterial communities compared to the MBR effluent. Interestingly, the solar photo-Fenton oxidation generated a bacterial community that contains genera previously reported to be thermotolerant, indicating the important role of temperature during wastewater treatment using solar-driven AOPs.

Overall, the combined MBR-solar photo-Fenton process was shown to be an effective method for the removal of antibiotic-related microcontaminants from urban wastewater that is intended for disposal or reuse purposes.