Michael Irene

Nireas International Water Research Center, University of Cyprus (Cyprus) (michael.irene@ucy.ac.cy)

Investigating the solar-driven advanced chemical oxidation of ofloxacin and trimethoprim in sewage and other aqueous matrices

ABSTRACT

The Ph.D. thesis investigated preliminary the application of two solar-driven advanced oxidation processes (AOPs) for the degradation of two antibiotic compounds in secondary treated domestic effluents at a bench-scale setup. Ofloxacin (OFX) and trimethoprim (TMP) were chosen as the model contaminants while the two AOPs examined were the homogeneous solar Fenton process ($hv/Fe^{2+}/H_2O_2$) and the heterogeneous photocatalysis with titanium dioxide (TiO_2) suspensions. The influence of various operational parameters was evaluated by studying the degradation/removal of the antibiotics in the wastewater solution by UV/Vis spectrophotometry and chromatographic analysis (UPLC-MS/MS) and by monitoring the reduction of dissolved organic carbon (DOC) during the process. A Daphnia magna bioassay was also used to evaluate the potential toxicity of the parent compounds and their transformation products generated during the different stages of the oxidation processes. The results indicated that solar Fenton ($[Fe^{2+}]0$=5 mg L-1; $[H_2O_2(OFX)]0$=2.714 mmol L^{-1}; $[H_2O_2(TMP)]0$=3.062 mmol L-1) has been demonstrated to be more effective than the solar TiO_2 process ($[TiO_2]$=3 g L-1), yielding complete degradation of the examined substrates within 30 min of illumination and DOC reduction of about 41% and 44% at the end of the photocatalytic treatment for OFX and TMP, respectively. The respective values for the TiO2 process under the optimum conditions were 60% and 68% degradation of OFX and TMP respectively within 120 min of treatment and 10-13% DOC removal. Kinetic analyses indicated that the homogeneous photodegradation of OFX and TMP can be described by a pseudo first-order reaction whereas the Langmuir-Hinshelwood (L-H) kinetic expression was used to assess the kinetics of the heterogeneous photocatalytic process. The toxicity of the treated samples was decreased by the end of both processes and the toxicity variations which have been observed illustrated the participation of different oxidation mechanisms during each process.

The solar Fenton process was further investigated in a pilot-scale setup. All the experiments were carried out in a two compound parabolic collector (CPC) pilot plants installed at the PSA and at the sewage treatment plant at the UCY for solar photocatalytic applications. The main objectives of the pilot-scale study were: (a) the optimization of the solar Fenton process for the determination of the degradation kinetics of the two antibiotics in relatively low concentration level (100 μg L^{-1}); and (b) the structure elucidation of the major oxidation by-products formed during the TMP solar Fenton treatment in four different environmental matrices (demineralized water (DW); simulated natural freshwater (SW); simulated effluent from municipal WWTP (SWW); and real effluent from municipal WWTP (RE)).

DOC removal was lower in the case of SW compared to DW, which can be attributed to the presence of inorganic anions which may act as scavengers of the hydroxyl radicals. On the other hand, the presence of organic carbon and higher salt content in SWW and RE led to lower mineralization per dose of hydrogen peroxide compared to DW and SW. A large number of

compounds generated by the photocatalytic transformation of TMP were identified by UPLC-ToF/MS. The degradation pathway exhibited differences among the four matrices; however hydroxylation, demethylation and cleavage reactions were observed in all matrices.

Solar Fenton process using low iron and hydrogen peroxide doses ($[Fe^{2+}]0$=5 mg L^{-1}; $[H_2O_2]0$=75 mg L^{-1}) was proved to be an efficient method for the elimination of these compounds at low concentration level (μg L^{-1}) with relatively high degradation rates. The process was mainly evaluated by a fast and reliable analytical method based on a UPLC-MS/MS technology which was optimized and validated for studying the degradation kinetics of both compounds. Moreover, the solar Fenton application in wastewater treatment at neutral pH had a beneficial impact onto the substrates' degradation due to the formed ferric iron complexes with the dissolved organic matter (DOM). The results demonstrated the capacity of the applied advanced process to reduce the initial toxicity of the non-treated sewage to the examined plant species (Sorghum saccharatum, Lepidium sativum, Sinapis alba) and to the water flea Daphnia magna. The phytotoxicity in the treated samples expressed as root or shoot growth inhibition, was higher compared to that observed on the inhibition of seed germination. Enterococci, including those resistant to OFX and TMP, were completely eliminated at the end of the treatment. Solar Fenton was proved to be an efficient and cost effective method considering the requirement for safe wastewater reuse for agriculture irrigation purposes.