Abstract

The occurrence of contaminants of emerging concern (CECs) in the environment has become a matter of high concern due to the large number of compounds and its recurrent detection in different environmental matrices. Even at trace concentration, when in contact with living beings, these pollutants may cause negative effects such as reduced fish reproduction due to endocrine system disruption, decreased abundance of invertebrates due to sublethal toxicity, and proliferation of antibiotic resistant bacteria. Urban wastewaters are considered a major source of CECs, since conventional technologies used in urban wastewater treatment plants (WWTPs) are not efficient to completely remove them. Several advanced treatment options for water and wastewater contaminated with CECs have been applied over the years. However, issues related to the design of photoreactors, photon and mass transfer limitations may pose as a limiting factor to its industrial implementation.

The present thesis had as main purpose the design and evaluation of diverse innovative photochemical/photocatalytic reactors towards micropollutants mitigation. Five experimental units at lab-scale were used: (i) Jets reactor, (ii) FluHelik reactor, (iii) NETmix mili-photoreactor, and (iv) two membrane reactors. In addition, a FluHelik reactor at pre-pilot scale was also employed. Synthetic solutions fortified with oxytetracycline (OTC) or a mixture of 11 pharmaceuticals were employed. Surface water (SW) and urban wastewaters (UWW) after secondary treatment, spiked with oxytetracycline were used as real matrices. Photochemical (UV photolysis, UVC/H_2O_2), photocatalytic (heterogeneous TiO_2 photocatalysis) and membrane filtration systems were employed as treatment options for the removal of CECs from different water matrices. Furthermore, hybrid systems coupling membrane filtration with the abovementioned processes were also evaluated.

Firstly, an innovative photoreactor, named FluHelik, was employed towards OTC degradation by UVC photolysis and UVC/H_2O_2 photochemical processes, and further compared with a Jets reactor. As expected, the combination of UVC light with H_2O_2 improved the OTC degradation, under all the reactors and conditions studied, until reaching a point where it remained constant or even decreased, given that the H_2O_2 in excess can act as hydroxyl radicals scavenger. Under the best experimental conditions using UWW as reaction matrix, FluHelik photoreactor showed superior performance than the Jets reactor, reaching a mineralization of 71% instead of 56% for the Jets reactor. This fact was attributed to the FluHelik's unique fluid dynamics and irradiation properties. In addition, when using UWW, similar photochemical space time

yields (PSTY) were observed at both scales (0.57 and 0.53 m^3_{water} $m^{-3}_{reactor}$ day^{-1} kW^{-1} at the pre-pilot scale and lab scale, respectively), indicating the feasibility of scaling-up the FluHelik reactor. FluHelik was also able to comply with the Switzerland legislation and to effectively reduce CECs toxicity to zebrafish embryos. Following, OTC degradation by a UVC/H_2O_2 system using the NETmix mili-photoreactor was investigated. The system achieved consistent PSTY values, varying between 0.01 and 0.42 m^3_{water} $m^{-3}_{reactor}$ day^{-1} kW^{-1}. However, although the NETmix mili-photoreactor showed to be a promising system to promote UVC/H_2O_2 photochemical processes, the reactor performance was significantly lower than the FluHelik. A higher matrix effect was also observed for NETmix mili-photoreactor (about 2 to 3 times decrease on OTC degradation rates) than for the FluHelik (1.7 times) reactor. Fact attributed to the higher dissolved organic carbon (DOC) and suspended solids concentrations, turbidity, absorbance at 254 nm, etc. of the urban wastewater sample used in the set-up of experiments with NETmix when compared with the wastewater sample employed with FluHelik reactor. In addition, a kinetic model able to describe the OTC oxidation by the UVC/H_2O_2 photochemical system in the mili-photoreactor was successfully developed, providing reliable reaction kinetic parameters for optimization and photoreactor design purposes. The NETmix mili-photoreactor was also employed for OTC oxidation by heterogeneous TiO_2 photocatalysis. When using UPW solutions, front-side irradiation (FSI) mechanism showed better results than back-side irradiation (BSI) mechanism mainly due to the increment in the illuminated catalyst coated surface, rather than the illumination mechanism itself. UV irradiation intensity and solution pH played an important role in the photocatalytic reaction rates, achieving the best results with a photonic flow of 2.67 J s^{-1} and neutral pH. When using a UWW as solution matrix, only a slightly decrease (about 1.3 times) in the OTC removal rate was perceived, showing the ability of the NETmix mili-photoreactor to overcome matrix effects (when using heterogeneous photocatalysis). However, comparing the NETmix performance for UVC/H_2O_2 or heterogeneous TiO_2 photocatalysis, better results were achieved with the photochemical UVC/H_2O_2 process.

Finally, two membrane reactors were investigated for OTC oxidation. OTC adsorption on the photocatalyst nanoparticles played an important role on OTC removal using both reactors. On the other hand, OTC adsorption on the membrane was detected only using the “membrane reactor A” due to the differences on the membrane material. A higher decline on permeate flux and OTC removal was observed for the UV-UF/MF systems, as consequence of their lower OTC oxidation rates (contributing to the membrane fouling). When using the “membrane

reactor A", the permeate flux and antibiotic oxidation rate proved to be significantly enhanced by increasing the oxidant/photocatalyst concentration. On the other hand, although OTC removal efficiency increased with the increment in the photocatalyst dosage (within the range under study), when using "membrane reactor B", a higher decline on the permeate flux was observed due to the formation of a denser TiO_2-P25 cake layer. Despite the advantages of nano-engineered photocatalytic membranes (i.e. reduced membrane fouling and good photocatalytic stability), the OTC removal efficiencies were significantly lower than those under TiO_2-P25 slurry conditions due to the lower photocatalyst surface area available for adsorption and oxidation of the pollutant. Higher pollutants degradation rates and permeate fluxes were attained for the hybrid system coupling UVC/H_2O_2 process with membrane filtration using "membrane reactor A", due mainly to the fact that UVC/H_2O_2 photochemical processes usually present higher pollutants degradation rates than photocatalytic processes.