Summary of PhD Thesis "Tertiary treatment of urban wastewater by advanced oxidation processes"

The increasing demand of food to satisfy the needs of a growing world population alongside the rate of economic development and high population are putting incomparable pressure on water resources. As a result of this impact, water resources quality is steadily decreasing. Several organic pollutants such as pesticides, pharmaceuticals, hormones, personal care products and their metabolites also known as contaminants of emerging concern (CECs) are continuously released into the environment from urban wastewater treatment plants (UWWTPs) effluents. Although occurring at low concentrations (ng/L−μg/L) they can persist into the environment resulting in significant acute and chronic toxicity, with potential collateral effect on human health and aquatic ecosystems. Unfortunately, conventional UWWTPs are unable to provide an effective removal of several CECs. To overcome this problem, in recent years research has been focused on the investigation of new processes/technologies for tertiary treatment of urban wastewater in the attempt to effectively remove CECs and pathogens before effluent disposal or reuse. Advanced Oxidation Processes (AOPs), which are based on the formation of highly oxidative species (mainly hydroxyl radicals, $HO^•$), have found to be effective in CECs removal as well as in bacteria inactivation.

The main aim of this PhD thesis work was to investigate the effects of different AOPs as tertiary treatment methods of urban wastewater under realistic conditions using different endpoints: CECs removal, pathogens inactivation and toxicity. In this study, five pollutants have been selected as model CECs (Caffeine, Carbamazepine, Diclofenac, Sulfamethoxazole and Trimethoprim) and three human bacterial pathogens (*E. coli, Salmonella spp and Enterococcus spp*) as model of microbial contamination because they are typically detected in UWWTP effluent.

Firstly, homogeneous solar driven AOPs, namely sunlight/H_2O_2, solar photo-Fenton (SPF) and SPF with EDDS were compared to a new solar driven heterogeneous photocatalytic (namely sunlight/N-TiO_2 doped) process with the aim of contributing to fill the gap between lab scale tests and full scale applications as well as to provide a sustainable solution for tertiary treatment in small UWWTPs. Process efficiency was evaluated in terms of effluent toxicity and degradation of a mixture of three CEC (namely carbamazepine, diclofenac and trimethoprim), at initial concentration of 200 μg/L each, in deionized water (DW) and real

UWWTP effluent (WW). SPF with EDDS was found to be the most effective process (99% removal of CEC from WW in 15 min, Q_{uv} =1.2 kJ/L). Conventional SPF was drastically and negatively affected by water matrix, due to the spontaneous neutral pH and iron precipitation in real WW. Although sunlight/N-TiO_2 process was not so affected by water matrix, it was found to be less efficient than SPF with EDDS. Toxicity values were found to be lower in WW compared to DW matrix. WW samples showed a toxicity reduction up to the no acute toxicity level for sunlight/N-TiO_2 and SPF with EDDS treatments, while sunlight/H_2O_2 and SPF increased the final effluent toxicity up to slightly acute levels.

Subsequently, SPF with EDDS at near neutral pH was investigated in the simultaneous removal of a mixture of CECs and bacteria inactivation in simulated urban wastewater treatment plant effluent (SUWW). Process efficiency was evaluated in terms of (i) degradation of five CECs (namely caffeine, carbamazepine, diclofenac, sulfamethoxazole and trimethoprim) at the initial concentration of 100 μg/L each and (ii) bacteria inactivation (*E. coli*, *S. enteritidis* and *E. faecalis*), at the initial concentration of 10^3 CFU/mL each. The aim of 80% removal of total CECs was selected according to Switzerland regulation in UWWTPs, being the only Country that has established a release limitation for such compounds from UWWTPs into the environment. SPF with EDDS was investigated at lab scale in a solar simulator to evaluate the effect of iron concentration (0.1 mM and 0.05 mM) and Fe:EDDS ratio (1:2 and 1:1). 80% removal of total CECs was not achieved in the experiment with Fe (III) at concentration 0.05 mM with 1:2 molar ratio to EDDS. To evaluate the effect of organic matter, SPF with EDDS was investigated even in SUWW without organic compounds (SUWW-woc). Organic matter negatively affected process efficiency. Total inactivation of all bacteria and 80 % removal of CECs was achieved only in the experiment with Fe:EDDS 1:1 in SUWW-woc, accordingly, such operating condition was chosen for the scaling-up to pilot plant with raceway pond reactor (RPR).

Therefore, in the third part of the work, SPF with EDDS at near neutral pH and sunlight/H_2O_2 processes operated in RPR were compared with ozonation under different end points (CECs removal, bacteria inactivation and toxicity). Process efficiency was evaluated first in terms of simultaneous inactivation of *E. coli*, *Salmonella spp* and *Enterococcus spp*. The effect of inorganic matter was also evaluated. The highest bacteria inactivation rate was observed for ozonation. The detection limit (DL) (1 CFU/mL) was reached for all pathogens in 45 min treatment in WW. The inactivation of all bacteria in WW by sunlight/H_2O_2 (50 mg/L) and SPF with EDDS (at 1:1 molar ratio, 0.1 mM of Fe and 50 mg/L of H_2O_2) showed similar behavior. Although the DL was not reached in WW, faster inactivation kinetics and lower bacterial concentration after 180 min of treatment time was observed for sunlight/H_2O_2 process. In general, the results showed different bacterial inactivation profiles under the same operational conditions, observing for both treatments the following order of inactivation kinetics: *Salmonella spp*>*E. coli*>*Enterococcus spp*. *Enterococcus spp* showed high resistance to solar driven investigated processes. Quantitative microbial risk assessment (QMRA) for the ingestion of a raw-vegetable (lettuce) irrigated with untreated and treated WW was also estimated. Disinfection by ozonation and sunlight/H_2O_2 processes was found to drastically decrease the associated microbiological risk. Then, degradation of five CECs (namely caffeine, carbamazepine, diclofenac, sulfamethoxazole and trimethoprim) at the initial concentration of 100 μg/L each and toxicity were investigated. Treatment of CECs by SPF and ozonation at neutral pH was demonstrated in CEC-enriched simulated and real WW. SPF has shown to be strongly affected by water matrix, since in SUWW-woc the 80 % removal of the total CECs was reached in 10 min while in WW after 180 min. 80% removal of total CECs could be achieved in 15 minutes by ozonation in real WW. Toxicity of treated effluents keeps as a hot topic to address. Acute toxicity test was not conclusive and chronic toxicity should be also measured to avoid a dispose/ reuse tertiary treated WW more toxic than secondary treated one.

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