ABSTRACT

Water is an essential resource for life. However, the low water availability and its increasing demand has provoked worldwide water stress, which is one of the main problems to be faced in the next years. Additionally, the continuous rise in freshwater demand is associated with increased generation of wastewater. Thus, in a water scarcity scenario, the reused wastewater can play an important role to reduce freshwater demand, for instance, in agriculture with around 70% of the total freshwater demand. Nevertheless, the reused wastewater must guarantee the safety for public health and environment. In the last decades, there is an especial concern on removing micropollutants, since they are potentially harmful substances for public health and aquatic ecosystems. Wastewater treatment plants have been identified as a main pathway through which micropollutants can enter to the aquatic ecosystems. This fact is due to the conventional wastewater treatment plants are not designed to remove recalcitrant contaminants at low concentrations.

Advanced oxidation processes have been proven their efficiency in the degradation of several compounds of emerging concern, such micropollutants. Among these techniques, photo-Fenton process is one of the most effective. However, the requirement to work at acidic conditions to keep the iron in solution is one of the drawbacks of the process. Additionally, the need of irradiation rises the treatment operational costs and environmental impact since some conventional lamps comprises mercury. These inconveniences make the processes unattractive for its full scale-application.

The investigation derived from this thesis is focused on different solutions trying to solve these drawbacks. Firstly, LEDs and solar simulated irradiation were used, carrying out the photo-Fenton process more economically and ecofriendly. The employment of organic fertilizers, as a chelating agents of iron, is the second foundation on which the investigation is based. The final objective is the reuse of wastewater in agriculture, facing the current water scarcity scenario.

The study of the conventional photo-Fenton with UV-A LEDs revealed the suitability of the process to remove a recalcitrant compound (Diphenhydramine, DPH) with high conversion efficiencies (total DPH removal in 30 min). COD and TOC removals were 70.2 and 54.2% for 380-390 nm and 79.9 and 60.5% for 390-400 nm. Additionally, the results suggested that synergies on micropollutant, COD and TOC conversion were observed combining two wavelength ranges, because the treatment time was reduced by half (total DPH removal in

15 min, 95.6 and 70.1% of COD and TOC removal, respectively after 1 hour. However, from the results obtained in the comparison between UV-A LEDs in wastewater effluents (52.1% of propranolol (PROP) degradation after 1 hour of treatment in MBR matrix) and BLB lamps (95.3% of PROP abatement after 1 hour of treatment, also in MBR), as a conventional ones, it was evidenced the necessity to optimize the system geometry (photoreactor + lamp) when LEDs are used as irradiation source. This fact is essential in the treatment of wastewater since the turbidity and organic matter present in these matrices influence on the radiation transfer throughout the photoreactor affecting more when LEDs are used, because they are punctual sources of irradiation.

The study in the use of organic fertilizers, as iron chelating agents, revealed that all tested agents (DTPA, HEDTA, EDDS and EDTA, except EDDHA) were effective in photo-Fenton process at circumneutral pH in MBR, CAS and CAS-NE effluents in removing micropollutants. UV-A LEDs and solar simulated light were used to perform the experiments. Propranolol, sulfamethoxazole (SMX) and acetamiprid (ACMP) were used as a model compounds. For instance, PROP degradations higher than 90% were reached in MBR effluent using organic fertilizers and both irradiation sources, UV-A LEDs and solar simulated light at the end of the treatment. The results showed that the efficiency in the degradation is linked to the stability constant of chelates with iron. Low stability corresponds to high reaction rates at initial times but also high iron release. The opposite happens with chelating agents with high stability constant with iron. EDDS and EDTA presented low stability constant, while DTPA and HEDTA have higher ones (in MBR effluent under solar simulated light, using EDTA total removal of PROP and SMX was achieved at 90 and 120 min, respectively and 67.6% of ACMP was observed at 180 min while using DTPA 89.0, 67.6 and 31.0% was reached for PROP, SMX and ACMP, respectively at 180 min). Nevertheless, the iron in solution at 180 min was 52 and 77% for EDTA and DTPA, respectively. The enhancement in removal kinetics and the decrease in iron release was achieved combining organic fertilizers with different stability constant (50%EDDS+50%EDTA, 50%EDDS+50%DTPA, 50%EDTA+50%DTPA). For instance, in MBR matrix, with the mixture 50%EDDS+50%EDTA, total PROP removal was reached 1 hour before compared to only EDTA, which presented better removal than EDDS (total PROP and SMX removal was achieved at 30 min and 90 min, respectively, and 70.0% of ACMP was observed at 180 min). In addition, the total iron in solution at the end of the treatment was 5.5 times higher with the mixture than EDDS. The organic fertilizers mixtures were also tested in two different wastewater effluents to study the effect of the matrix on iron release. It was observed that, in wastewater with higher turbidity, alkalinity and organic matter, the iron precipitation was higher, decreasing the efficiency of the process overall in EDDS, which have the lowest stability constant with iron. Experiments performed with EDDS in CAS effluent achieved 46.8, 30.0 and 10.5% at 180 min for PROP, SMX and ACMP, respectively. While the performances of the same experiments in MBR matrix were better (94.8, 79.9 and 38.5% for PROP, SMX and ACMP, respectively). The experiments carried out in CAS matrix using DTPA the differences between two matrices were low (60.5, 38.0 and 18.3% for PROP, SMX and ACMP, respectively. Differently than MBR, in CAS effluent, the complexes of iron more stables such as DTPA, achieved better final micropollutant's degradations than iron chelates low stables like EDDS. The additional tests of BOD_5 and phytotoxicity analysis confirmed the suitability of final MBR effluent to be reused in agriculture.

Finally, the mechanisms involved in photo-Fenton process, with iron chelates in aquatic environment, cannot be generalized, since each iron complex have its stability constant with iron and its specific absorbance in solar spectrum. The irradiation experiments without H_2O_2 revealed that only EDDS and DTPA were capable to generate ROS. From the photo-Fenton experiments without O_2, it was determined that this specie is involved in the formation of final hydroxyl radicals. Finally, tests with dosing of non-chelated iron revealed that reaction with iron chelates are the main via to hydroxyl radical generation.