The presence of persistent pollutants in water bodies has encouraged the scientific community to investigate advanced water processes which degrade them. Wastewater treatment plants are often based on biological processes as secondary treatment. Nevertheless, these systems are not sufficient to remove non-biodegradable contaminants or contaminants at a very low concentration. As a result, recalcitrant compounds can be detected in rivers, lakes and other aquatic systems. Stronger types of treatment are therefore required. Advanced Oxidation Processes (AOPs) have gained the reputation over the last few decades of being effective in this regard. Amongst them, homogeneous photocatalysis, or the photo-Fenton process, has been reported as being successful in the removal of organic pollutants. Nonetheless, its application at commercial scale has not yet become widespread.

This study investigated the application of several operating strategies to carry out the solar-driven photo-Fenton process. It was comprised by two parts: (i) the oxidation of pollutants in the mg/L range (medium concentration level) and (ii) in the μg/L range (micropollutants). For medium concentration of pollutants, the first strategy proposed was the use of the complexes iron d-glucinate, iron lactate and fertilizer ferroactive, and the iron chelate deferoxamine mesylate to operate the process at natural pH and mineralise 0.5 mM acetaminophen (50 mg DOC/L) in a compound parabolic collector (CPC). The strategy was compared with the addition of ferrous iron salt. Results showed that the addition of ferrous salt was analogous or better than the use of iron complexes. Based on these results, the dosage of iron salt was further investigated at pilot plant scale and under realistic conditions as secondary wastewater was used as an example of complex matrix where model contaminants were added. The removal of 50 mg DOC/L of a mixture of five commercial pesticides - Vydate® (10% w/v oxamyl), Metomur® (20% w/v methomyl), Couraze® (20% w/v imidacloprid), Perfekthion® (40% dimethoate) and Scala® (40% w/v pyrimethanil) - was evaluated under different iron dosage strategies, paying special attention to iron
concentration per dose and addition time. Complete pesticide removal and up to 50% mineralisation were achieved.

For the study of micropollutant removal, sequential and continuous iron salt dosage strategies were also applied. All the strategies used to operate the photo-Fenton process at micropollutant level were evaluated using a mixture of pesticides found in the effluent of an agro-food industry: acetamiprid, thiabendazole and imazalil, each at a concentration of 100 μg/L. Sequential and continuous iron salt dosages were investigated at pilot plant scale in a flat-reflector tubular photoreactor. Continuous dosage provided the shortest degradation time in real wastewater (15 min and 80 mg Fe/L in total).

At micropollutant level, the interrelationship between iron concentration and UV solar light was also studied. These two factors are the key variables in photoreactor design and process operation. Iron concentration was varied between 1-20 mg/L and UV-light between 5-30 W/m². The experimentation was carried out in deionised water and simulated secondary effluent as well as at laboratory and pilot plant scale. Results indicated that above 15 W_{UV}/m² and a light path length of 5 cm (the most commonly used path for this type of application) iron concentration limited the process and there was irradiance excess under these conditions. It was concluded that wider path lengths of more than 5 cm (typical of CPC) are recommended since more wastewater volume can be treated with a higher process rate per surface unit. A simplified model was also suggested to corroborate the phenomenology observed.

These conclusions led to the proposal of raceway pond reactors (RPRs) as a new technology for the application of solar photo-Fenton as tertiary treatment wastewater. RPRs are extensive photoreactors traditionally used for microalgal mass culture. A 360-L RPR was used to study the degradation of commercial formulations of acetamiprid and thiabendazole (100 μg/L each) in water from the supply network in CIESOL and in simulated secondary effluent. Iron concentration (1-10 mg/L) and liquid depth (5-15 cm) were studied as process
A process time of 40 min was needed to treat 360 L until complete pollutant degradation was achieved. A higher treatment capacity per surface area than for CPC was obtained (48 mg/h·m$^2$ with 5.5 mg Fe/L and 15 cm liquid depth compared to 29 mg/h·m$^2$ for the same iron concentration in the CPC), proving the feasibility of using RPRs for micropollutant removal. Transformation products of thiabendazole and acetamiprid, the two most persistent model micropollutants, were detected in collaboration with the Environmental Analysis and Water Treatment research group in the CIESOL. They were monitored at laboratory scale and during the treatment of real agro-food wastewater in the RPR thanks to the use of highly sensitive liquid chromatography-triple quadrupole-linear ion trap-mass spectrometry (LC-QqLiT-MS/MS).

With the strategies learned, the operation of the photo-Fenton process was also studied under artificial light during a three-month placement at Cranfield University, UK. Firstly, UVC low pressure lamps were used to compare the performance of the photo-Fenton process with other AOP systems such as persulphate, hydrogen peroxide photolysis and heterogeneous photocatalysis to remove the most persistent model pollutant, acetamiprid. Results indicated that photo-Fenton and UVC/persulphate were the most effective AOPs tested in real wastewater. Secondly, high intensity UVC light emitting diodes (LEDs) were also tested as low energy-consuming technology for photo-Fenton applications, with high intensity LEDs emerging as a promising and novel technology for lamp-driven photo-Fenton.

Most of the work presented in this Ph.D. thesis showed that the efficient operation of solar-driven photo-Fenton is possible. The results indicated that iron dosage could be an effective strategy to operate the solar photo-Fenton process at natural pH to oxidise either mg/L or μg/L of pollutants. At micropollutant level, irradiance requirements are not high, so extensive and low-cost photoreactors such as RPRs can be used. They demonstrate a high treatment capacity and this finding involves an approach to commercial scale application. Finally, lamp-driven photo-Fenton is also a promising process thanks to high intensity LEDs.