

# **Electrochemical Advanced Oxidation Processes: Application to the Degradation of Synthetic and Real Wastewaters**

Candidate: Maria Francisca da Costa Moreira\*  
Supervisor: Vítor Jorge Pais Vilar, Ph.D.\*  
Co-Supervisors: Enric Brillas Coso, Ph.D. (University of Barcelona)  
Rui Alfredo da Rocha Boaventura, Ph.D.\*

\*Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto

## **Abstract**

Water pollution by organic compounds arising from human activities is a major global environmental problem that requires a rapid and effective answer. In the last years, electrochemical advanced oxidation processes (EAOPs) have been acquiring high relevance for water treatment. These processes are able to degrade recalcitrant organic compounds, mainly via the electrochemical generation of strong oxidants such as hydroxyl radicals ( $\bullet\text{OH}$ ).

The current thesis focuses on the assessment of the technical feasibility of using some EAOPs for the degradation of recalcitrant organic compounds of five solutions: (i) a  $290 \text{ mg L}^{-1}$  Sunset Yellow FCF (SY) azo dye aqueous solution in  $7.0 \text{ g Na}_2\text{SO}_4 \text{ L}^{-1}$ , (ii) a  $20.0 \text{ mg L}^{-1}$  trimethoprim (TMP) antibiotic aqueous solution in  $7.0 \text{ g Na}_2\text{SO}_4 \text{ L}^{-1}$ , (iii) a wastewater collected after secondary treatment of a municipal wastewater treatment plant (MWWTP) spiked with TMP at  $\text{mg L}^{-1}$  levels or 19 pharmaceutical compounds at  $\mu\text{g L}^{-1}$  levels, (iv) a winery wastewater, and (v) a municipal sanitary landfill leachate. EAOPs were directly applied to the both pure solutions, hereinafter also referred to synthetic wastewaters, and also to the secondary MWWTP effluent. For the winery wastewater and the landfill leachate, these processes were combined with other technologies. The winery wastewater was subjected to biological oxidation before EAOPs to remove the biodegradable organic fraction. For the sanitary landfill leachate treatment, the following multistage strategy was applied: (i) initial biological treatment for ammonium oxidation, removal of alkalinity and biodegradation of organics, (ii) coagulation for removal of humic acids and suspended solids, (iii) EAOP for degradation of recalcitrant organic compounds and biodegradability enhancement, and (iv) final biological treatment. The following five EAOPs were under focus: anodic oxidation (AO), anodic oxidation with electrogenerated hydrogen peroxide (AO- $\text{H}_2\text{O}_2$ ), electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF). EAOPs were performed in four lab- and pilot-scale experimental

units, all equipped with a boron-doped diamond (BDD) or a platinum (Pt) anode and a carbon-PTFE air-diffusion cathode. Two of these units were designed and constructed within this thesis.

The efficiency of the various EAOPs for recalcitrant organic compound degradation was assessed mainly in terms of mineralization and pollutants concentration decay. The mineralization ability of EAOPs increased in the following order: AO-H<sub>2</sub>O<sub>2</sub> < AO < EF < PEF with UVA radiation (PEF-UVA) < SPEF. The low efficiency of AO-H<sub>2</sub>O<sub>2</sub> can be mainly related to the low oxidation power of either •OH weakly physisorbed at the anode surface or H<sub>2</sub>O<sub>2</sub> electrogenerated at the cathode. The AO process was applied to wastewaters showing chloride ions in their composition and then the superiority of AO over AO-H<sub>2</sub>O<sub>2</sub> can be mainly attributed to the absence of active chlorine species in the latter process due to their reaction with the electrogenerated H<sub>2</sub>O<sub>2</sub>. The mineralization was enhanced in EF by virtue of the attack of •OH produced from Fenton's reaction. The additional •OH generation from the FeOH<sup>2+</sup> photoreduction and the possible direct photolysis of Fe(III)-carboxylate complexes were responsible for the higher efficiency of PEF-UVA process. In SPEF, the mineralization was highlighted due to the ability of natural sunlight to emit in the visible region and its slightly higher UV intensity compared to the employed UVA lamp. However, the SPEF process presented only a slightly superiority over PEF-UVA for the degradation of the winery wastewater and the landfill leachate, diverging from the synthetic solutions. These results indicate the suitability of using UVA lamps, even with low energy power, for the PEF treatment of some wastewaters. Under the best experimental conditions, high degradation rates were attained for all wastewaters when using PEF-UVA and SPEF processes, although with distinct consumptions of electrical energy and UV radiation. To reach a mineralization of 50% by SPEF process, around 2.8 kWh m<sup>-3</sup> and 3.9 kJ L<sup>-1</sup> were consumed both for the synthetic SY wastewater and the winery effluent; 0.26 and 0.89 kWh m<sup>-3</sup> and 3.6 and 9.9 kJ L<sup>-1</sup> were spent for the synthetic TMP wastewater and the secondary MWWTP effluent, respectively, both spiked with a TMP content of 20.0 mg L<sup>-1</sup>; and 30 kWh m<sup>-3</sup> and 4.9 kJ L<sup>-1</sup> were consumed for the landfill leachate. The relative ability of EAOPs to degrade TMP was the same as for mineralization, contrary to what was found for SY removal, for which EF, PEF-UVA and SPEF processes showed quite similar efficiency. This means that the azo dye was mainly destroyed by •OH produced from Fenton's reaction. In the degradation of the secondary MWWTP effluent, the presence of additional dissolved organic matter induced lower degradation rates than in its absence, likely due to the scavenging of •OH and/or filtration of photochemically active light.

The influence of operational variables on EAOPs efficiency was extensively studied. The effect of the anode nature proved to be dependent on the wastewater composition since the BDD anode achieved

only slightly superiority over the Pt one for the treatment of the TMP solution, but its superiority was pronounced for the landfill leachate remediation. In general, the use of higher current densities ( $j$ ) led to increasing degradation rates. However, this improvement came along with higher energy consumptions and, for the winery wastewater and the landfill leachate, almost null/slightly mineralization enhancement was achieved for the highest  $j$ , likely due to the raise of parasitic reactions. Distinct  $j$  values were selected as the best ones for the various solutions: 33, 5.0, 25 and 200 mA cm<sup>-2</sup> for the pure SY solution, the pure TMP solution, the winery wastewater and the landfill leachate, respectively. The increase of the initial total dissolved iron concentration ( $[TDI]_0$ ) improved the efficiency of PEF-UVA up to a value for which this enhancement was decelerated/ceased, suggesting an equilibrium between positive effects coming from the enhancement of Fenton's reaction and negative effects arising from the increase of parasitic reactions and attenuation of light-induced mechanisms. Best  $[TDI]_0$  values of 35 and 60 mg L<sup>-1</sup> were obtained for the treatment of the winery effluent and the landfill leachate, respectively. Typically, a pH value close to 2.8 leads to maximum degradation efficiencies for EAOPs based on Fenton's reaction, mostly due to the presence of higher concentrations of photoactive iron species and absence of iron precipitation. This was observed for the landfill leachate, but the fastest TMP removals occurred at pH of 3.5 and 4.0. This suggests the influence of the wastewater composition on the best pH value. The addition of Fe(III)-carboxylate complexes to the pure TMP solution and to the landfill leachate in 1:1 to 1:9 Fe(III)-to-carboxylate molar ratios allowed working at higher pH values (3.5 to 5.0), with even higher degradation rates. Oxalate, citrate and tartrate ligands revealed to be efficient, contrary to malate. Higher pollutants removal rates were achieved when using greater pollutants contents. The influence of temperature on the efficiency of EAOPs based on Fenton's reaction proved to be dependent on pH and effluent composition since the amount of iron precipitate and photoactive species varies with these parameters. Depending on the wastewater composition, the UVC radiation proved to be able to lead to superior or quite similar degradations to those achieved when using UVA radiation. The employment of artificial UVA-Vis light provided lower mineralization.

EAOPs were compared with the analogous chemical processes, showing higher mineralization efficiency. However, the chemical processes induced faster removal of some pollutants at the reaction beginning due to a higher initial availability of H<sub>2</sub>O<sub>2</sub>. Additionally, the viability of SPEF process at large scale was demonstrated and the by-products generated during pollutants degradation were comprehensively studied.