Assessment of solar photo-Fenton in raceway pond reactors for micropollutant removal in secondary effluents from agro-food industry and municipal WWTPs

Candidate: Gracia Rivas Ibáñez [a,b]
Supervisor: José Antonio Sánchez Pérez, Ph.D.[a,b]
Co-Supervisors: José Luis Casas López, Ph.D.[a,b]

[a]Department of Chemical Engineering, University of Almería
[b]Solar Energy Research Center (CIESOL): Joint Centre of the University of Almería-Energy, Environment and Technology Research Center (CIEMAT), Almería

Abstract

There is increasing environmental concern about the presence of organic micropollutants in aquatic systems. One of the main factors behind their release into the environment is the poor efficiency of their degradation in conventional wastewater treatment plants, commonly based on biological processes. As such, it involves the continuous release into the water cycle of substances which have been recognised as a potential hazard to the environment and human health even when detected at very low concentrations. To overcome this problem, research is being carried out to remove them by including a tertiary stage in wastewater treatment plants. In this regard, advanced oxidation processes have been widely used due to the generation of highly reactive hydroxyl radicals, which help to oxidise organic compounds. Amongst them, the photo-Fenton process has proven to be effective in micropollutant removal. However, more research is still needed for their application in wastewater treatment plants at real scale.

This study was designed to assess different operating strategies of the photo-Fenton process as tertiary treatment to remove micropollutants in secondary effluents from the agro-food industry ("Cítricos del Andarax S.A.", Almería, Spain) and municipal wastewater treatment plants. The evaluation was based on the characteristics of the water matrix to be studied, and the feasibility to scale up the process to a realistic levels applying the recently proposed low-cost photoreactor: the raceway pond reactor (RPR). It is

extensive non-concentrating photoreactor which allows large volumes of water to be treated and consists of channels where water is set in motion by a paddlewheel system.

For agro-food industry wastewater, research was focused on solving the accumulation of bicarbonates during the biological treatment of wastewater with high organic strength. Furthermore, the effect of the bicarbonates as hydroxyl radical scavengers during the removal of micropollutants by chemical oxidation was studied. To this end, a lab-scale sequencing batch reactor (SBR) was operated at circumneutral pH to avoid inorganic carbon accumulation. Following this, the obtained agro-food industrial effluents were doped with acetamiprid as a model pollutant at 100 µg/L and then treated by Fenton and photo-Fenton processes. Results showed that controlling pH at circumneutral values in the biotreatment reduced the high accumulation of bicarbonates in the effluents, the SBR efficiency in organic carbon removal not being affected. This led to a significant reduction in reagent costs (~80%) since less acid or iron was needed to carry out further catalytic processes for micropollutant removal, even with photo-Fenton being carried out at pH 2.8.

Additionally, attention was paid to solve other environmental and economic questions related to the agro-food industry wastewater biological treatment such as the excess sludge and the presence of organic micropollutant absorbed in the sludge. The degradation of micropollutants (pesticides) absorbed in agro-food industrial sewage sludge was investigated during its excess reduction by disintegration with low-frequency ultrasound (US) treatment. Results indicate that the US treatment was efficient not only in sludge disintegration (68.7% solubilisation of the carbon content in the disintegrated biomass) but also in pesticide degradation (90% removal of pesticides absorbed into the sludge). Investigation into the sono-degradation of three characteristic pesticides found in the agro-food industry effluent (thiabendazole, acetamiprid and imazalil) revealed the formation of transformation products already reported in studies on the degradation of these compounds by advanced oxidation processes, thus confirming that ultrasound treatment at low frequencies also involves hydroxyl radical reactions.

In order to extend the use of the low-cost RPR at real scale, the effect of solar irradiance on RPR operation for micropollutant removal by solar photo-Fenton was studied. A 360-L RPR was used at pilot plant scale and the pesticides acetamiprid and thiabendazole found in the agrofood industry were used as model pollutants in a simulated effluent at a concentration of 100 µg/L each. Averaged UV irradiances ranged from 10 to 30 W/m^2

and three values of iron concentration (1, 5.5 and 10 mg/L) were used. Different liquid depths (5-15 cm) were also used to evaluate the relationship between the rate of photon absorption and pollutant removal. A model was proposed to predict degradation rate and treatment capacity (TC) as a function of the volumetric rate of photon absorption (VRPA). Under low irradiance conditions (10 W/m^2) the treatment capacity was not sensitive above 10 cm liquid depth, so a low iron concentration should be used (5 mg Fe/L) to reach TC values of around 40 $mg/h \cdot m^2$. For high irradiance values (30 W/m^2), greater liquid depth (20 cm) and iron concentration (10 mg Fe/L) should be used to take full advantage of photon availability. Treatment capacity values of 133 $mg/h \cdot m^2$ can be reached under these conditions proving the feasibility of RPR for micropollutant removal.

These results led the application of solar photo-Fenton in RPR for micropollutant removal in real secondary effluents being studied. The photo-Fenton process was carried out at neutral pH, since working at acidic pH might be a drawback for its application at large scale due to the associated costs for pH conditioning. As such, two operating strategies were evaluated for micropollutant removal in municipal secondary effluent in RPR: i) sequential iron dosage adding Fe^{2+} to replace the precipitated $Fe(OH)_3$ and ii) using the complex Fe^{3+}/EDDS at 1:2 molar ratio to keep iron dissolved. Additionally, an ecotoxicity evaluation of the treatment was carried out.

A first approach was undertaken to evaluate the sensitivity of different standardised acute and chronic bioassays for ecotoxicity assessment of secondary effluent treated by solar photo-Fenton at neutral pH with the sequential iron dosage strategy. The bioassays were tested before and after the oxidative treatment and results indicated that the solar photo-Fenton process at neutral pH was efficient in micropollutant removal and there was no increase in ecotoxicity for any of the organisms tested.

A more detailed toxicological analysis was performed on enriched samples to increase pollutant concentration, thereby enabling better detection in short-term bioassays during a three-month research stay at the RECETOX center at the Masaryk University (Czech Republic). As such, a battery of tests including low complexity "*in vivo*" and "*in vitro*" cell-based bioassays was applied to evaluate: i) the phytotoxicity in the former and ii) in the latter, cytotoxicity in fish cells and to detect the presence of endocrine disruptors (androgenic-glucocorticoid activity and estrogenicity). This battery was carried out on a municipal WWTP secondary effluent before and after being treated by solar photo-Fenton at neutral pH in a raceway pond reactor by the two operating strategies: the sequential

iron dosage and the use of the Fe^{3+}/EDDS complex. Results indicated the presence of compounds with endocrine disrupting potency as well as compounds toxic for algae and fish cells in the secondary effluent. Both photo-Fenton operating strategies led to high efficiencies for micropollutant and toxicity removal, hence becoming a feasible choice to enhance the quality of municipal effluents from a chemical and toxicological point of view.

In summary, the work presented in this Ph.D. thesis showed that controlling pH in the biological depuration of agro-food industry wastewater enables micropollutant removal by the photo-Fenton process and reduces reactant cost. Additionally, the excess sludge generated during the biological treatment can be reduced by ultrasonication of the purged sludge, which degrades most of the pesticides absorbed in the sludge. Raceway Pond Reactors allow a high treatment capacity for micropollutant removal by solar driven Fenton processes such as the sequential iron dosage and using the Fe^{3+}/EDDS complex. They have proved to be efficient treatments for micropollutant and toxicity removal in WWTP secondary effluents.