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Evaluation of electrochemical processes assisted by solar energy for water depuration

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PhD Thesis

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Summary

Nowadays society's lifestyle encourages a high rate of consumption of natural resources; many of them are non-renewable, meaning that an inadequate management will lead to a certain degree of scarcity in the medium to long term. The most illustrative example is water, used in almost any human activity, for human consumption, cleaning and domestic use or in industrial processes (even in energy production), either as cooling medium or directly intervening in the productive process, water is present. It was up to the 2000s that the Legislative Authorities were considering water no more than a commercial asset being the implementation of the Water Framework Directive (2000/60/CE) the inception to a mentality change towards water, considering it now more an heritage deserving protection and laying the foundations for the development of specific regulations that will establish minimum quality limits to be achieved prior to the discharge of the effluents into the environment.

Specifically, chemical industry undergone a strong development owed to a growing demand for new products to satisfy the needs of the consumers. The manufacture of drugs, personal care products, or pesticides and fertilizers to improve agricultural production has led to the appearance, development and deployment of new organic substances. These are usually toxic, non-biodegradable and highly recalcitrant, thus they are difficult to assimilate for microorganisms, being active in the environment for long periods of time and with unknown effects on the discharge ecosystems.

That situation motivates arisen, development and application of new highly oxidizing technologies, aiming the degradation of these emerging compounds and even, depending to their complexity, enhancing the biodegradability of the whole effluent. For this reason, electrochemical processes pose a versatile, useful and powerful tool since only by applying an electric current or potential on the electrodes it is able to generate oxidizing species that interacts with a broad spectra of contaminants, facilitating their removal.

Some electrochemical processes have been widely used at industrial scale. For example, electrocoagulation implies an advantage over the conventional coagulation-flocculation physicochemical process, since avoids the addition of chemical reagents by the use of sacrificial electrodes, generating a lower amount of sludge, and presenting higher efficiency in the colloids removal. On the other hand, electrodialysis, an electrically assisted membrane process, is able to separate the ions from an influent, yielding a high-

quality effluent of low ionic charge, being mainly applied in desalination processes aimed to produce drinking water.

In spite of involving great advantages such as an easy control of the process and therefore easy automatization, as well as the absence of external reagents, some electro-oxidative processes have not been evaluated further than at laboratory scale. In fact, most of the studies reported in the literature are focused in the development of new materials for electrodes manufacturing, to improve effectiveness and reduce costs associated to this technology. However, it must be highlighted that electrochlorination has been implemented on a larger scale due to the low cost of the electrodes.

The scarcity of studies facing these technologies under a realistic approach and for the purification of complex water matrices, has limited the possibilities of electro-oxidative systems from a commercial standpoint. It is important to note that from the ions species naturally contained in certain waters, a large amount and variety of oxidizing species can be generated, which entails an intrinsic improvement over the basic studies using a supporting electrolyte whose only function is to allow the transition of electrons. Furthermore, many of these electrogenerated species are photoactive, which means that just by irradiating the solution with ultraviolet light the generation of even more oxidizing species could be promoted, which results in an increase of the contaminants degradation rate. This has meant that the development, implementation, start-up and evaluation of these systems on a larger scale have not been also addressed in depth, hindering the scale-up of the electro-oxidative process.

In this context, the opportunity of this PhD Thesis arises bringing the study of electrochemical technology to a new level closer to reality. The application of electro-oxidative processes at pilot plant scale in actual wastewaters is addressed, assessing the operating conditions seeking to improve contaminants removal and water depuration. Combination of electro-oxidative systems with a natural and renewable energy source such as sunlight is also tackled.

The first objective addressed was characterization, start-up and optimization of the main operational parameters of a solar photoelectro-Fenton (SPEF) pilot plant able to treat up to 100 L of water developed and installed at Plataforma solar de Almería (PSA) (CIEMAT). The system consists of four electro-cells equipped with a niobium-supported boron doped diamond anode (Nb-BDD) and a carbon-polytetrafluoroethylene (carbon-PTFE) gas diffusion cathode (GDE) (Electro MP-Cells from ElectroCell). The cells are connected in parallel to a recirculation tank and this, in turn, to a solar photo-reactor based on compound parabolic collectors (CPC) with 2 m^{-2} of illuminated surface. Optimization of the main input variables, pH and current density (*j*), was carried out to maximize onsite H_2O_2 electrogeneration with the maximum current efficiency (CE). A central composite experimental design was defined, and after the completion of the 19 experiments proposed in the matrix, by means of the statistical analysis of the results, the adjustment model for H_2O_2 concentration was obtained: $[H_2O_2] = 2.19 - 0.31 \cdot pH + 0.81 \cdot j - 0.05 \cdot pH \cdot j + 0.15 \cdot pH^2 - 2.42 \times 10^{-3} \cdot j^2$, as well as for the CE percentage: $\%CE = 61.68 - 0.43 \cdot pH - 0.18 \cdot j - 0.0275 \cdot pH \cdot j$, and the corresponding response surface graphs. Finally, the model was validated, corroborating that, at pH 3 and applying 73.66 mA cm^{-2}, the maximum production of H_2O_2 is achieved (64.9 mg min^{-1}) with a CE associated of 89.3%. Once these parameters were established, the influence of the water and air flows, as well as the concentration of the electrolyte on the H_2O_2 electrogeneration was also studied, reaching the maximum applying a water flow of 5.6 L min^{-1}, an air flow of 10 L min^{-1}, and with 50 mM of Na_2SO_4. Afterwards, preliminary tests were developed assessing the efficiency in the removal of reference compounds, pyrimethanil and methomyl in a concentration of 50 mg L^{-1} and 90 mg L^{-1}, respectively, by the application of the different oxidation processes that are able to be developed in the pilot plant system: anodic oxidation (AO), electro-Fenton (EF) and solar SPEF, having as supporting electrolyte a solution of Na_2SO_4 50 mM. The highest degradation rates were attained by SPEF process: 55% of pyrimethanil and 50% of methomyl after only 5 minutes. This research was performed with the collaboration of Prof. Anastasios J. Karabelas and Dr. Konstantinos V. Plakas of the Chemical Processes and Energy Resources Institute of the Centre for Research and Technology-Hellas (Greece) in the framework of the European project SFERA-II at PSA facilities.

Second objective was focused on a real application of the previously optimized electrochemical pilot plant through its combination with a pre-treatment consisting of a nanofiltration (NF) membrane system. Urban wastewater treatment plant effluent was pre-treated for increasing the concentration of organic microcontaminants (OMCs) in the NF retentate stream, together with reducing the total volume to be treated in the tertiary electro-oxidation system. Also noteworthy is the increase in water salinity achieved after the NF system in the retentate, decreasing ohmic resistance and thus facilitating a subsequent tertiary treatment based on electro-oxidation. For studying the behavior of the SPEF system in highly saline and complex matrices, a recipe of simulated NF concentrate was developed from the characterization of concentrates previously reported in literature. Aiming to work at the effluent natural pH, avoiding the addition of reagents for acidification and neutralization, the use of ethylenediamine-N,N'-disuccinic acid (EDDS) as an iron complexing agent in the electro-Fenton (EF) process was evaluated. It was also checked the stability of Fe^{3+}:EDDS complex in the EF process, which was degraded after 15 min of treatment, although iron did not precipitate completely until 30 min. Thereupon, the degradation of four OMCs was studied: pentachlorophenol, terbutryn, chlorfenvinphos and diclofenac (at 200 and 500 µg L^{-1} of initial concentration each); by AO, EF, SPEF and solar-assisted AO at natural pH, using Fe^{3+}:EDDS (1:2) at 0.1:0.2 mM in EF and SPEF treatments.

When using simulated NF retentate, whose chloride concentration was 555 mg L^{-1}, the highest degradation of OMCs (500 µg L^{-1} of initial concentration each) was obtained using SPEF reaching 85% of total contaminants removal. The reason is that chlorine species generated by solar-assisted AO were not enough to degrade OMCs (75% of total amount), despite the presence of lower organic matter in solution due to the absence of EDDS. On the other hand, EF process was discarded since no improvement was observed with respect to AO, consuming the hydroxyl radicals produced by the Fenton reaction in the degradation of the EDDS instead of the OMCs.

The evaluation of the SPEF system for the tertiary treatment of actual wastewater, was carried out by collecting effluent from the secondary treatment of El Ejido WWTP (in Almería, South-East of Spain), after its pre-treatment in the NF pilot plant installed at PSA until reducing the initial volume 4 times. The salinity of the effluent increased from 2.1 - 2.3 mS cm^{-1} to 6.1 - 6.8 mS cm^{-1}, and the chloride concentration reached 1182 - 1960 mg L^{-1}. The concentrate was spiked with the four target OMCs (100 µg L^{-1} each) and their degradation was studied by AO, SPEF (with the carbonates naturally contained in the concentrate and reducing them to 20 mg L^{-1} to diminish the scavenger effect on hydroxyl radicals) and solar-assisted AO. The percentages of degradation of the sum of OMCs after 180 minutes of each applied treatment were 84% (AO), 69% (SPEF with carbonates), 75% (SPEF with low carbonates) and 84% (solar-assisted AO), respectively. In this occasion, the highest percentage of degradation with the lowest electricity consumption, 5.3 kWh m^{-3}, was obtained by solar-assisted AO, since the higher concentration of chlorides promoted a higher generation of active chlorine species. Finally, tertiary treatment by applying solar-assisted AO was chosen for the degradation of 44 OMCs actually contained in the secondary effluent of the WWTP and detected by LC-QqLIT-MS/MS, resulting in the elimination of 80% of the sum. This work was performed in collaboration with Prof. Ana Agüera and Dr. Ana Martínez-Piernas from CIESOL (mixed center CIEMAT-UAL) at the University of Almería.

After the experimental program conducted in the electrochemical pilot plant, which began with its start-up and optimization of operation parameters, it was considered to study and diagnose the state of the cathode surface of the cells used in those tests. While cathode usage hours increased, onsite production of H_2O_2 decreased progressively from 43 mg L^{-1} of accumulated H_2O_2 in 30 min, in the first use of the cathode, to 1.5 mg L^{-1} after several experiments. At the moment an important reduction of the H_2O_2 electrogenerated was observed, making impossible the effective development of EF and SPEF processes, the cell was disassembled and the autopsy of the cathode surface was carried out by means of scanning electron microscopy and X-rays in order to try to identify the main reasons for the contamination of the cathode and the consequent loss of efficiency. In the images obtained, a loss of the carbon-PTFE coating was detected as well as the formation of iron deposits, justifying the drop in H_2O_2 electrogenerated with the loss of the electrode active surface.

In the framework of the Marie Curie - ALICE project "AcceLerate Innovation in urban wastewater management for Climate change", H2020- MSCA-RISE, the PhD candidate carried out a research internship at the Nanotechnology and Integrated Bioengineering Centre (NIBEC) of the University of Ulster (UK), in collaboration with the Photocatalysis Research Team lead by Prof. John Anthony Byrne. The goal of this collaboration was the development and application of a laboratory-scale photoelectrocatalytic reactor for the simultaneous elimination of OMCs and pathogenic microorganisms in natural water. As a core part of the reactor, two nanotube photo-anodes of titanium dioxide were manufactured by anodizing a titanium mesh at 30 V for 3 h and then annealing it at 500°C to promote the anatase phase. The reactor consists of a 190 mL cell with a double photo-anode of titanium dioxide nanotubes illuminated by a 9 W UV-A lamp through a quartz window, with an applied irradiation of 50 W m^{-2}. The main objective was the simultaneous removal of OMCs (terbutryn, chlorfenvinphos and diclofenac at 500 µg L^{-1} of initial concentration each) and pathogens (*E. coli* as reference bacteria at an initial concentration of 106 CFU mL^{-1}), at the same time that a possible improvement by replacing a counter cathode with no contribution to the degradation process (platinum-coated titanium) by a carbon-felt cathode able to electrogenerate H_2O_2, was evaluated. Assessing separately the degradation of OMCs and the inactivation of *E. coli*, when applying the photoelectrocatalytic process with platinum cathode, a clear improvement in the inactivation of bacteria was observed (2 Log reduction after 120 minutes of treatment), compared to the photo-catalytic process on its own (0.8 Log reduction in the same treatment time). However, degradation of OMCs remained at the same ratio;

around 70% of the sum after 60 min. Replacement of the platinum cathode by a carbon-felt cathode increased the efficiency of *E. coli* inactivation, reducing its concentration in 2.7 Log, although OMCs showed similar degradation percentages. When finally the degradation of OMCs was carried out simultaneously to the inactivation of bacteria by photoelectrocatalysis with carbon cathode, a significant increase in disinfection was observed, reaching the detection limit of the method through a reduction of 4.5 Log. This improvement could be attributed to the presence of methanol from the stock solution where OMCs were pre-dissolved, that acts as a hole scavenger increasing the photocurrent and getting oxidized so generating formaldehyde, a highly toxic substance for microorganisms (LC50 for *E. coli* = 1 mg L^{-1}). As a consequence of this outcome, the effect of hole scavengers presence in disinfection was evaluated, using acetate and methanol at a concentration of 5 mM. In both cases, as described in literature, an increase in the photocurrent was observed under their presence, observing also an increase in the rate of bacteria inactivation, which was greater in the case of methanol due to the generation of formaldehyde.

Finally, as a result of the strong collaboration between the PhD student and the Solar Water Treatment Unit with the electrochemical company DeNora built during transnational access program within SFERA-II project, the evaluation of a commercial electro-oxidation system specially designed for the abatement of chemical oxygen demand in industrial waters and supported by the action of active chlorine spices was carried out. Within the framework of this collaboration, and as part of the objectives developed in this PhD Thesis, the evaluation of a pilot plant equipped with a dimensionally stable anode cell (DSA) manufactured by DeNora was performed, combining it with a solar CPC photo-reactor (3.08 m^2), reaching a total capacity of 38 L, and with the aim of evaluating the possible improvement in efficiency of two batches of landfill leachates. These leachates were characterized by high organic loads (>2000 mg L^{-1} of dissolved organic carbon (DOC)) and a high toxicity in one of the batches (53 % of inhibition on activated sludge) so the main purpose was to reduce the toxicity and increase the biodegradability enough for a subsequent combination with a conventional biological treatment (thus reducing the associated operation costs). First step was the treatment of two batches by solar photo-Fenton process, which required an excessive accumulated UV energy (142.2 kJ L^{-1}) to achieve only a 30% reduction of DOC in the first batch of leachate (diluted 1:1 with distilled water). In the second batch it was not possible to perform solar photo-Fenton treatment due to the large amount of foams generated, causing large oscillations of the DOC along the process. Later on, the two batches were treated by electro-oxidation, electro-oxidation by adding H_2O_2 and electro-oxidation combined with solar radiation, being the second batch the one that showed the highest DOC and total nitrogen removal rates, 3.5 g DOC kWh^{-1} and 18 g TN kWh^{-1} in the first batch of leachate and 13.4 g DOC kWh^{-1} and 45.2 g TN kWh^{-1} in the second batch. After the application of electro-oxidation assisted by solar energy, a reduction on toxicity from 53% to 6% of inhibition, and a sufficient improvement of biodegradability were observed in both batches. This study corroborates the improvement caused by the application of sunlight to the electrochemical treatment of industrial wastewater, which may represent a step forward towards the application of these powerful oxidation systems, presenting themselves as a feasible, sustainable and green alternative to purely electrochemical treatments, with lower operation costs due to lower energy consumption.