Universidade Vigo

Bioengineering & Sustainable Processes
BIOSUV
Universidade Vigo

Towards a future actual implementation of the heterogeneous electro-Fenton treatment for water remediation

PhD Candidate: Verónica Poza Nogueiras

Supervisors: Mª Ángeles Sanromán Braga

Marta Mª Pazos Currás

Abstract

The pollution of water environments worldwide is a pressing issue. In particular, the detection in water bodies of the so-called contaminants of emerging concern (e.g. pharmaceuticals, pesticides or ionic liquids) constitutes a challenge since traditional wastewater treatments are generally ineffective for the degradation of these compounds. In this context, alternative treatments such as the electrochemical advanced oxidation processes (EAOPs) have gained traction in the last decades as suitable techniques for water remediation. Among EAOPs, the electro-Fenton treatment has been widely investigated. This process relies on the generation of hydroxyl radicals by means of the catalytic decomposition of hydrogen peroxide in the presence of the ferrous ion, being those reagents continuously formed at the cathode ensuring the Fenton reaction continuity. However, despite the research efforts devoted to electro-Fenton over the past years and the promising results obtained, this technique has not yet been applied at full scale.

For the electro-Fenton process to move from being *promising* to *applicable to real-world situations*, some issues should be tackled. One of the main limitations of electro-Fenton is the separation of the dissolved iron from the solution at the end of the treatment, and the disposal of the resulting iron sludge, which entails an environmental problem and an additional cost. This can be overcome by using heterogeneous catalysts, as demonstrated by the numerous investigations conducted on this matter, regretfully most of them at lab scale. Other issues of

electro-Fenton are related to the low solubility of oxygen in the solution and mass transfer limitations, which affect the generation of hydrogen peroxide and, consequently, the degradation of the pollutant. Additionally, electro-Fenton suffers from relatively high energy consumption.

Some aspects as the selection of the heterogeneous catalyst, optimization of the process, design of the reaction system and evaluation of the cathode material are key to address the limiting factors of electro-Fenton and promote its full-scale applicability. Therefore, it is crucial to further investigate those aspects.

With all this in mind, this PhD Thesis is focused on contributing to ***approach the heterogeneous electro-Fenton treatment of water polluted with organic compounds to a more realistic operation***. To achieve this general goal, the following specific objectives have been stablished:

- *Analysis of the literature on different heterogeneous catalysts*. To gain insight into the different catalysts that have been used in the heterogeneous electro-Fenton treatment and to select the catalysts for this investigation, a comprehensive review of the literature is required.
- *Optimization of operational parameters*. To validate the incorporation of a solid catalyst into the system and to increase the heterogeneous electro-Fenton process efficiency, it is necessary to identify the most relevant variables and optimize them.
- *Development of a monitoring technique*. To follow the evolution of the heterogeneous electro-Fenton treatment and the formation of intermediate products, the implementation of a monitoring analytical tool is of paramount interest.
- *Scaling-up of the heterogeneous electro-Fenton treatment*. To take the treatment one step closer to a real application, the design of a bench-scale reactor configuration that addresses several of the electro-Fenton limitations is of utmost importance.
- *Evaluation of new cathode materials*. To reduce the costs associated with energy consumption and electrodes, it is interesting to explore the use of alternative cathodes. Moreover, this brings the possibility of investigating a different heterogeneous catalysis approach: the incorporation of iron onto the cathode material.

Those specific objectives have been assigned into four different research areas in which the investigation workload of the PhD Thesis was divided, as shown in Fig. 1.

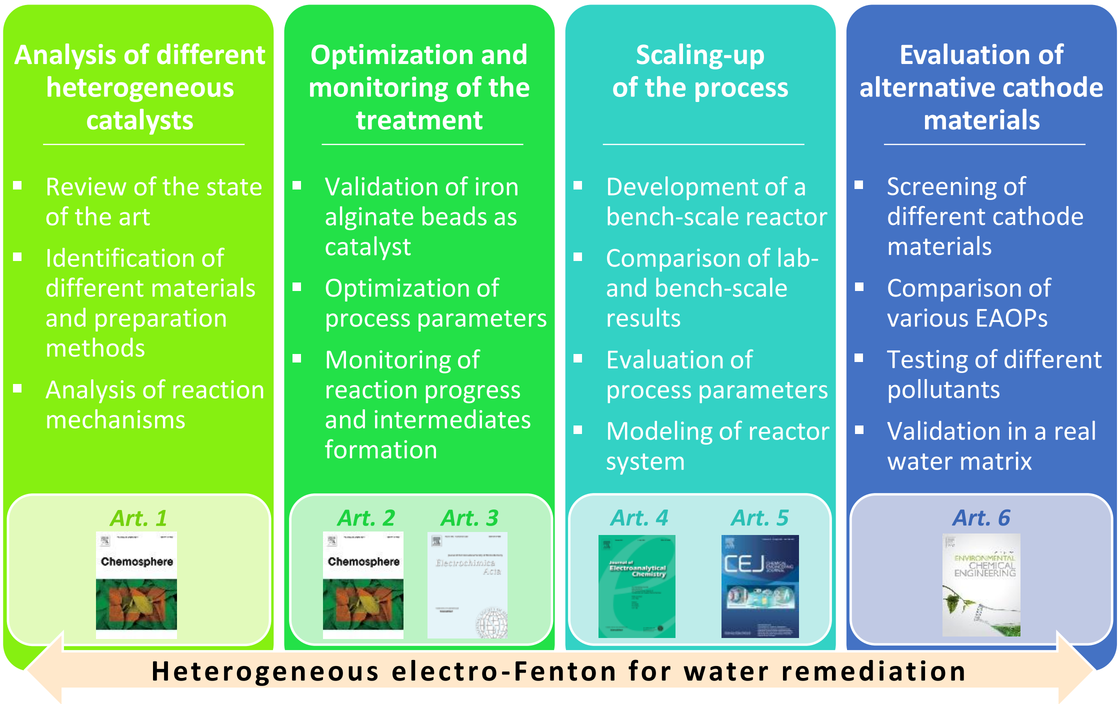

Fig. 1. Scheme of the working plan carried out, relating objectives, milestones and obtained scientific articles

As schematized in Fig. 1, the results obtained in the different research areas of the PhD have been published in various scientific articles:

- Article 1: V. Poza-Nogueiras, E. Rosales, M. Pazos, M.A. Sanromán, 2018. Current advances and trends in electro-Fenton process using heterogeneous catalysts – A review. *Chemosphere* 201, 399-416. https://doi.org/10.1016/j.chemosphere.2018.03.002
- Article 2: V. Poza-Nogueiras, M. Arellano, E. Rosales, M. Pazos, E. González-Romero, M.A. Sanromán, 2018. Heterogeneous electro-Fenton as plausible technology for the degradation of imidazolinium-based ionic liquids. *Chemosphere* 199, 68-75. https://doi.org/10.1016/j.chemosphere.2018.01.174
- Article 3: V. Poza-Nogueiras, M. Pazos, M.A. Sanromán, E. González-Romero, 2019. Double benefit of electrochemical techniques: Treatment and electroanalysis for remediation of water polluted with organic compounds. *Electrochimica Acta* 320, 134628. https://doi.org/10.1016/j.electacta.2019.134628

- Article 4: V. Poza-Nogueiras, A. Moratalla, M. Pazos, M.A. Sanromán, C. Sáez, M.A. Rodrigo, 2021. Towards a more realistic heterogeneous electro-Fenton. *Journal of Electroanalytical Chemistry* 895, 115475. https://doi.org/10.1016/j.jelechem.2021.115475
- Article 5: V. Poza-Nogueiras, A. Moratalla, M. Pazos, M.A. Sanromán, C. Sáez, M.A. Rodrigo, 2021. Exploring the pressurized heterogeneous electro-Fenton process and modelling the system. *Chemical Engineering Journal* 431, 133280. https://doi.org/10.1016/j.cej.2021.133280
- Article 6: V. Poza-Nogueiras, A. Gomis-Berenguer, M. Pazos, M.A Sanromán, C.O. Ania, 2021. Exploring the use of carbon materials as cathodes in electrochemical advanced oxidation processes for the degradation of antibiotics. *Journal of Environmental Chemical Engineering* 10, 107506. https://doi.org/10.1016/j.jece.2022.107506

Firstly, an exhaustive assessment of the state of the art related to the use of heterogeneous catalysts in electro-Fenton process was performed, giving rise to Article 1, a review.

Taking into account the conclusions extracted from the literature review and the previous studies carried out by our research group on the creation of iron-loaded alginate gel beads, that catalyst was selected to validate its use for the electro-Fenton elimination of ionic liquids and optimize the process parameters in Articles 2 and 3. Moreover, the development of a monitoring system based on an electroanalytical technique performed on screen-printed carbon electrodes was accomplished in those articles as well. This method provides in almost real time information on the evolution of the degradation process and the generation of intermediate compounds.

Considering the good results obtained in those studies using the alginate beads in the electro-Fenton process at lab-scale, a scaling-up of the treatment was proposed using the same catalyst. As a result, a bench-scale reactor configuration was developed and tested for the treatment of a pesticide and pharmaceutical metabolite in Articles 4 and 5. The smart design of the proposed system allowed not only the treatment of greater volumes of water, but, more importantly, addressing several of the limitations electro-Fenton suffers from. Those studies provided a great deal of novelty, since heterogeneous catalysis and the pressurization of the system had not been tested in a similar configuration before. Furthermore, the flowing pattern was selected for the bench-scale treatment, among other reasons, to open the possibility for coupling the developed monitoring system with the bench-scale installation in a future investigation.

Finally, the technique used for creating the cathode in bench-scale studies provided the opportunity to explore the use of new cathode materials. Therefore, several carbon materials were tested in self-elaborated cathodes for different EAOPs treatments validating the degradation of pharmaceuticals in Article 6. Additionally, this allowed the analysis of a different heterogeneous catalysis method that was reported in Article 1: the fixation of iron directly on the cathode material, benefiting from having the catalyst right where hydrogen peroxide is generated. As a consequence, an efficient removal of the pollutants was obtained in synthetic and real water matrixes.

From the results obtained inn this PhD Thesis, one may conclude that the goal of approaching the heterogeneous electro-Fenton treatment to a more realistic operation has been fulfilled.