PhD Thesis´ title

New perspectives in the application of the Advanced Oxidation Processes

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Thesis´ summary

The Advanced Oxidation Processes (AOPs) have been widely studied as they can degrade many types of organic contaminants, due to the action of the hydroxyl radicals which are generated in this type of processes. Previous studies performed in the BIOSUV group demonstrate the AOPs are an efficient alternative for the remediation of different effluents.
In the current context, this PhD Thesis was focused on the use of the AOPs in the treatment of effluents with high organic load (such as the winery solutions), or with emerging contaminants (such as pesticides, drugs or ionic liquids). What is more, the treatment of micro-polluted effluents was assessed, as the vast majority of pollutants are detected at very low concentrations. For that, the combination of adsorption, as a pre-concentration step, and AOPs, as an adsorbent regeneration step, was presented as solution.

Different AOPs were studied for the degradation of the aforementioned pollutants: i) The Fenton process, because of its easy application and for the detection of its main limitations, ii) the electro-Fenton process ,where an electric field is applied to overcome the aforementioned limitations, iii) the photo-Fenton process, carried out with an external ultraviolet radiation to enhance the Fenton performance, iv) the photo-electro-Fenton process, which combines the aforementioned processes in a synergistic way which was demonstrated, v) the photocatalysis, where the light radiation is used to activate photoactive compounds which can lead to chain reactions generating oxidant and reductive species and vi) the poorly reported photocatalysis-electro-Fenton which is the combination of TiO_2 photocatalysis and photo-electro-Fenton processes. This latter proposed process leverages the application of the light radiation, which was already necessary for the application of the photo-electro-Fenton process, enhancing the efficiency around 20 % in the studied cases.

The effect of the working parameters in the AOPs was studied, so the production of hydroxyl radicals and, undeniably, the degradation of the contaminants were increased. In this context, different reactor´s configurations were used to maximize the processes´ efficiency. Specifically, the physical separation of electrochemical-based and photolysis-based processes within the reactor, arose as a good alternative for enhancing the performance of the photo-electro-Fenton process in the so-called two-chamber reactor. This configuration was raised to the next level with the separation of both photo and electrochemical-based processes in two cyclic columns so i) the distance between electrodes can be minimal (which was been demonstrated favours the electro-Fenton degradation), ii) the radiation is completely applied on the photo-column and iii) the column configuration is closer to future applications.

During the PhD realization, some limitations of AOPs were detected and then overcome. For instance, the operational costs associated to the utilization of a mercury lamp were reduced to a half by the utilization of a LED lamp which even enhance slightly the results and avoid the temperature increase. The slow performance and the low reusability of graphite electrodes made the utilization of carbon felt, BDD or PTFE-air diffusion synthesized electrodes a better alternative. In order to avoid an extra contamination and to ensure the industrial application of these processes, some alternatives were proposed to get the catalyst immobilization. Thus, expanded perlite was used as a floating support to enhance the activation of the photo-catalyst when using an above-radiated reactor. The synthesis of magnetic catalysts was also proposed as a good alternative to maintain the easy separation of the photocatalysts after use. These alternatives were validated by the use of the immobilized catalysts during different batches and with the successful treatment of real wastewaters.

What is more, the optimization of the operational variables, using either the one-factor-at-a-time or response surface methodologies, was carried out. Therefore, the optimization of the catalysis dosage, voltage, distance between electrodes, type of electrode, etc. was successfully accomplished. Under the optimal conditions, all the treated pollutants (Prednisolone, winery wastewaters, Pirimicarb, Pyrimethanil, ionic liquid 1-butyl-2,3-dimethyl imidazolium chloride) were successfully degraded (80 %) even when being in real wastewater matrixes.

The treatment of micro-polluted effluents was done by adsorption into naturally available adsorbents, in order to also propose a process which is suitable for the treatment of wide amounts of low polluted effluents. The regeneration of the spent adsorbents under the electro-Fenton slurry configuration or electro-kinetic-Fenton process was accomplished, being the selection of the processes dependent on the interaction pollutant-adsorbent. Under the optimal conditions, in terms of electrolyte composition, 80 % of the adsorbed ionic liquid was eliminated.

To sum up, this PhD Thesis helped the understanding of AOPs and highlighted the importance of its synergistic combination and the optimization process for making its industrial application more realistic. All these results were published in eight JCR journals and spread in national and international courses and conferences.