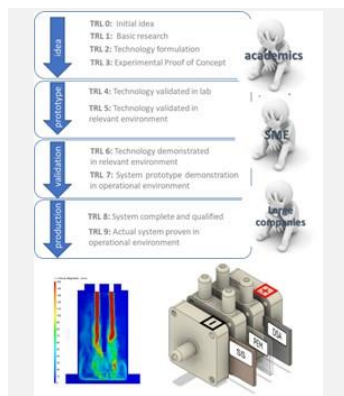


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The main topics of interest in the development of Electrochemical Advanced Oxidation Processes during the last two decades are reviewed in terms of the technology readiness levels reached. Based on this evaluation, the present and the future and how it is faced the increase in the TRL is discussed. Special emphasis is made in the targets of topics of interest within the TRL 4-5, including the enhancement in the electrosynthesis of oxidants, expanding the applicability from the treatment of wastewater and water to gaseous streams and the novel electro-refinery concept. As well, new instrumental tools that will help to increase the TRL of EAOPs will be discussed including the impact of 3-D printing manufacturing, the development of process integration tools and the energy powering of electrochemical processes.

A little recent history: What happened up to 2020

Over the last decades, a very important progress has been noticed in the development of electrochemical advanced oxidation processes (EAOPs). Following the pioneering demonstration of the formation of free hydroxyl radical in electrolytic processes of aqueous wastes when anodes consisting of diamond coatings are used, at the turn of the century, direct electrochemical processes (also known as anodic oxidation processes) were started to be considered as advanced oxidation processes. Then, mechanisms to explain the role of these hydroxyl radicals in other electrodes were proposed, involving in many cases the transient modification of the surface of the electrodes (so called active behaviour of mixed metal oxides based on iridium or ruthenium), in what it was really an improvement in the understanding of electrocatalytic processes.

Simultaneously, an alternative route for the application of electrochemical processes as advanced oxidation processes was proposed: the electrosynthesis of powerful oxidants that can be activated as radicals, either by the electrochemical process itself or with the contribution of other activation mechanisms such as the photolysis of the addition of catalyst. The most important oxidant for these mediated processes has been hydrogen peroxide which it transformed into hydroxyl radicals not only by Fenton catalyst (electroFenton processes) but also by light irradiation (photoelectrolytically assisted hydrogen peroxide

AOPs). The evaluation of these processes first with synthetic wastewater and later with real water samples was the objective of the works published in the first decade of the XXI century. Then, the search for synergistic combinations with other technologies trying to approach a solution for the reduced efficiency obtained in the treatment of wastes polluted with low concentrations of pollutants (e.g. removal of CECs for the effluents of municipal WWTP) focused the interest during the second decade. As well, the development of electrochemically assisted disinfection processes.

And...Where are we now?

Currently, the technology readiness level (TRL) of all these processes can be fixed in between 4 (Technology validated in lab) and 5 (Technology validated in relevant environment), not being a surprise to state that, as with most AOPs, closer to the lower level. In fact, most of the works published corresponds to the testing of devices built in a laboratory environment with lab to bench scale plants and synthetic feedstock in discontinuous operation mode, and the more advanced correspond to evaluations tested in intended environment with real feedstock or with pilot scale plants in situ or in continuous operation for long periods to test robustness and operation procedures, but rarely combining the three inputs, which is what it is needed to reach a technology readiness level of 6 (Technology demonstrated in relevant environment) for which what it is required is

that the systems is tested in intended environment close to expected performance. This explains that only some cases are above this level and reach TRL 7 (System prototype demonstration in operational environment) for which operating in operational environment at pre-commercial scale. Examples such as the electrochemical treatment and disinfection of water for reuse within the eu funded project Safewaterafrica project are good examples of this level of maturity, which requires the strong collaboration between academia and industry. Of course, the value chain for TRL 8 (System complete and qualified) and 9 (Actual system proven in operational environment) is not developed.

What is the interest now

In this context, in this third decade of the century, the interest of researchers has been moved importantly with several topics that still belong to the TRL 4 and 5 such as: 1) the enhancement the electrosynthesis of oxidants; 2) expanding the applicability from the treatment of wastewater and water to gaseous streams; 3) the electro-refinery concept.

The first of this topic deals with the last blows to the most important research topic in EAOPs in the second decade of the XXI century, trying to get advantage of the recent findings of other AOPS, in which sulfate radicals have been found as promising alternative (or synergitic ally) of hydroxyl radicals and motivate researchers to go further not only on the development of processes for the electrogeneration of peroxospecies but also in other oxidants. In this context, the development of gaseous oxidants such as ozone or chlorine dioxide are extremely promising because they can be separated easily from the electrolyte during production and avoid the addition of other species to the wastes when applied. The second topic is a natural extension of the initial application of EAOPs: most of the treatment of gases are based on the retention of the pollutants in liquids(absorption) or solid matrices(adsorption), where electrochemically assisted technologies can be used to destroy the pollutants, based on the experience gained in the evaluation of the treatment of wastewater. Finally,

Conclusions

Past and present of EAOPs are used to forecast future in the research an applications of these interesting technologies how it is going to be impacted in the raise of their TRL

Acknowledgments

This work is part of the research project PID2022-138401OB-I00 funded by MCIN/AEI/ and “Unión Europea Next Generation EU/PRTR.

the third is the most impactful technology. Why the production of carbon dioxide should be the target of the treatment? why do not attempt to produce valuable species from the pollutants. Versatility of electrochemical technologies is giving here an important advantage which, according to the circular economy precepts, helpt to improve the suisnatility of our Society.

In addition to these topics, researchers are also motivated to raise the TRL above 5, where it is needed a strong collaboration with industrial partners, not always easy because of the strong cultural differences between academia and industry, and in which three instrumental tools are considered to be of a primary importance: 1) the impact of 3-D printing manufacturing; 2) the development of process integration tools; 3) energy powering of electrochemical processes.

Regarding the first, the improvement in the electrode composition and structure has been the main target in the search of increasing the efficiency of electrochemical processes. This means that the chemical has prevailed over the chemical engineering view to improve electrochemical processes. However, the electrochemical cell is a complex heterogeneous reactor, strongly dependent on fluidynamics, mass and heat transfer, for which a suitable mechanical desing can help to obtain important improvements. Recents works in the production of oxidants have demonstrated that while the improvement in an electrocatalyst can only obtain few percentual points of improvement, the mechanical desing can multiply this points by one fold. The second point also intensify the view of chemical engineers by properly connecting processes that not only avoid inefficiencies but generate synergisms. Finally the third point deals with the necessity of taking advantage of the key necessity of electorchemical processes (electricity) and provide it in the most sustainable way: powering with green energies. Many cases of studies are illustrate that this is not as simple as connecting the devices but many points not only technological but also of energy management have to be considered in the search of really sustainable processes