New perspectives for Advanced Oxidation Processes

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Abstract

Advanced Oxidation Processes (AOPs) are called to fill the gap between the treatability attained by conventional physico-chemical and biological treatments and the day-to-day more exigent limits fixed by environmental regulations. They are particularly important for the removal of anthropogenic pollutants and for this reason, they have been widely investigated in the last decades and even applied in the treatment of many industrial wastewater flows. However, despite the great development reached, AOP technology cannot be considered mature yet and there are many new fields worthy of research. Some of them are going to be briefly introduced in this Editorial, including hybrid processes, heterogeneous semiconductor photocatalysis, persulphate oxidation and the so-called advanced electrochemical oxidation technologies. The work ends with some perspectives which can be of interest for the ongoing and future research.

Keywords

Advanced oxidation technologies; hybrid processes; heterogeneous photocatalysis; persulphate oxidation; advanced electrochemical oxidation processes

1. Introduction

Nowadays, there is a growing concern about how to minimize the impact of wastewater discharges into environment. For decades the improvement in the removal of pollution by simple coagulation and biological processes have been a topic worthy of research. However, in the last quarter of the 20th century both, the physico-chemical and biological treatments, reached a considerable status of maturity and new technologies started to develop in order to fulfil the gag between the maximum treatability attained by these conventional treatments and the everyday more exigent limits fixed by environmental regulations. This necessity of new technologies was even more important in the treatment of wastewater produced in industry, because the complex molecules of the anthropogenic pollutants are hardly attacked by the microorganisms in biological processes.

This lack of efficiency of the conventional treatment technologies justified the initial interest of the scientific community for other novel environmental processes, such as the Fenton oxidation or the ozonation, and the search of operation conditions capable to improve their applicability and efficiency. These technologies, commonly known as Advanced Oxidation Processes (AOPs) were based on the production of hydroxyl radicals. One of their main advantages with respect to conventional technologies is that they may contribute to minimize the formation of hazardous species in the treated waste from the oxidants dosed. This was especially important since several of the competing technologies failed because of the production of non-desired hazardous species, such as the organo-chlorinated species formed by the chlorine oxidation of organics.

From the turn of the century till now, the number of AOPS have increased drastically with the development of new synergetic processes based on the combination of ozone and hydrogen peroxide with UV light irradiation and also with the coupling of ultrasounds. These combination have helped to overcome the occurrence of refractory species and also to improve significantly the performance of the AOPs.

However, despite this great advancement, there is still slot for more research. Thus, it is generally accepted that degradation rates by AOPs can adversely be affected by several factors including, besides the complexity of the water matrix, the type and concentration of the contaminant, the type and concentration of the oxidants and catalysts, and the reactor configuration. Hence, AOP technology cannot be considered mature yet and there are many new fields of research and development, among which hybrid processes, heterogeneous semiconductor photocatalysis, persulphate oxidation and novel advanced electrochemical oxidation technologies are worth of further discussion in this introductory perspective work.

2. Coupling of AOPs in hybrid processes

The simultaneous application of two or more AOPs is a step to the right direction increasing the oxidative capacity of the combined process due to (i) the increased production of ROS (i.e. cumulative effect), and/or (ii) positive interactions amongst the individual processes (i.e. synergistic effect).

In general, the synergy (S) can be quantified as the normalized difference between the rate constants obtained under the combined process ($k_{combined}$) and the sum of those obtained under the separate processes (k_i) as shown in eq.1, where a positive value stands for synergistic effect, a negative value for an antagonistic effect and 0 stands for a simpler cumulative effect.

$$S = \frac{k_{combined} - \sum_{1}^{n} k_i}{k_{combined}} \qquad (1)$$

Combination of AOPs typically results in a synergistic effect, because of the wider spectra of oxidants involved in the processes. However, although not very common, in few cases AOPs coupling may result in inhibitory (antagonistic) effects, thus leading to decreased degradation rates. A possible reason is the generation of large amounts of ROS that may behave as self-scavengers.

Anyhow, AOPs are not only combined among each other and there are different ways in which selectivity can be improved. Thus, bearing in mind that (i) AOPs are, in general, non-selective processes since the hydroxyl radical (i.e. the dominant oxidizing species) is non-selective itself, and (ii) most wastewaters, and in particular those originating from industrial processes, may contain a wide array of substances with varying physicochemical, biological and ecotoxic properties, a smart strategy is to increase process selectivity against the "nastier" chemicals of the effluent. Some examples how this strategy can be implemented are as follows:

1) Ozone oxidation at acidic and/or near-neutral conditions mainly occurs through direct reactions of molecular ozone with organic substrates in a process commonly known as ozonolysis. Ozone preferentially attacks double bonds and can be applied to destroy the chromophores (i.e. N=N bonds) of dyes typically found in textile effluents, leading to complete decolorization. Moreover, effluents of agro-industrial origin (e.g. olive oil and table olives production, wine-making) contain polyphenolic compounds that are responsible for low biodegradability and can selectively be removed by ozonolysis (Karageorgos et al., 2006).
2) Integrating AOPs and biological processes has traditionally been employed for the treatment of effluents containing bioresistant and biodegradable fractions (Comninellis et al., 2008). Typically, a biological pre-treatment step is applied to

remove the biodegradable fraction followed by AOPs post-treatment as a final, polishing step. This is expected to reduce treatment costs considering that bioprocesses are less costly and more environmentally friendly than other treatment technologies. The concept of process integration does not exclude other scenarios, i.e. AOPs → biological treatment or biological treatment → AOPs → biological treatment depending on the effluent under consideration and the treatment objectives.

3) Integrating AOPs with separation processes may also prove beneficial for specific types of effluents containing e.g. lots of solids (e.g. agro-industrial effluents), volatile organics (e.g. effluents from electronic processing) and macromolecules. Solids must be removed first by filtration, sedimentation or coagulation, otherwise they can be dissolved during advanced oxidation and consequently increase the organic loading of the liquid phase. Moreover and in the case of photochemical AOPs, the increased effluent opacity may be detrimental to the process. In the case of polymer-processing effluents containing macromolecules of varying molecular size, an attractive option includes the application of ultrafiltration in between AOPs and biological post-treatment; chemical oxidation can easily break down large macromolecules to more biogenic oligomers and ultrafiltration can guarantee that only molecules of certain size, below the membrane's cut-off, are fed to the biological reactor.

4) No matter how complex the original effluent is, the fast propagation of radical-induced and other reactions will generate numerous transformation by-products through various reaction pathways. Although it is practically impossible to identify the full set of by-products even with the most sophisticated analytical techniques, the distribution of key compounds in the reaction mixture can be

determined, alongside gross parameters such as biodegradability and toxicity indices. The use of suitable catalysts such as transition metal oxides and noble metals in e.g. WAO processes may alter the relative distribution of by-products compared to the respective uncatalyzed process and favor the formation of more biodegradable and/or less toxic compounds. Moreover, catalysts will accelerate partial oxidation reactions, thus leading to effluent's mineralization(Quintanilla et al., 2006).

3. Heterogeneous semiconductor photocatalysis

Semiconductor photocatalysis based on titanium dioxide is, perhaps, the most widely investigated AOP for the destruction and mineralization of a wide range of organic contaminants and microorganisms(Carp et al., 2004). TiO_2 photocatalyst exhibits several advantages including low cost, availability at various crystalline forms and particle characteristics, lack of toxicity and photochemical stability. A major shortcoming has to do with its wide band gap energy of about 3 eV, which means that only ultraviolet radiation can be used for its photo-activation. This limits the use of zero-cost natural sunlight since solar radiation reaching the surface of the earth contains only about 3-5% UV radiation. In this respect, it is of great interest to find ways to extend the absorbance wavelength range of TiO_2 to the visible region without the decrease of photocatalytic activity. During the last years, studies have focused on the improvement of TiO_2 photocatalytic efficiency by several methods such as generating defect structures, doping with metallic or non-metallic elements or modifying the TiO_2 surface with noble metals or other semiconductors(Pelaez et al., 2012).

Another strategy is the development of new materials that can predominantly be activated in the visible region; silver orthophosphate (Ag_3PO_4) is a low band-gap photocatalyst that has attracted enormous attention in the past few years due to its great potential in harvesting solar energy for environmental purification and oxygen evolution. More importantly, this novel photocatalyst can achieve a quantum efficiency of up to 90% at wavelengths >420 nm, thus implying a very low electron-hole recombination rate(Yi et al., 2010). A drawback of silver orthophosphate is its insufficient long-term stability since it is photochemically decomposed in the absence of a sacrificial agent. This can be overcome covering the surface of Ag_3PO_4 with metallic silver nanoparticles which create localized surface plasmon resonance effects and/or synthesizing various Ag_3PO_4-based composites.

4. Sulphate radical AOP

Whereas typical Advanced Oxidation Processes (AOP), are all based on the oxidation of organics by OH-radicals (*OH), more recently, the use of sulphate radical (SO_4^{*-}) based oxidation processes (SR-AOP) has gained attention as an innovative alternative for typical AOP processes. Since the pioneering paper in this field by Anipsitakis and Dionysiou(Anipsitakis and Dionysiou, 2003), a renewed scientific interest in these technologies resulted in several papers describing the use of various sulphate radical generation methods and the effectiveness of the treatment for the degradation of a myriad of different organic pollutants.

Some distinct advantages of SR-AOP processes are supporting their application. First, the redox potential of SO_4^{*-} is in the range between 2.5 – 3.1 V (Devi et al., 2016) and hence they are capable to effectively oxidize a wide range of organics. An important property is that the reactivity of SO_4^{*-} is pH independent whereas the efficiency of organics removal by *OH decreases with increasing pH (e.g., the optimal pH for the

Fenton reaction is around pH=3): at neutral pH, SO_4*^- is significantly more reactive than *OH (Anipsitakis and Dionysiou, 2003). This is definitely an important benefit of SR-AOP, since the use of additional chemicals to adapt the pH of the wastewater can avoided. Especially in the case of high flow rates or heavily buffered wastewater this can be problematic. Because of the longer lifetime (3-4 x 10^{-5} s) of SO_4*^- in water and the very fast reaction rates, the probability of a reaction with organic pollutants is higher than for *OH (Ghanbari et al., 2016). It was confirmed in various papers that SO_4*^- induced degradation leads to a better mineralization rate than *OH for several types of pollutants. An additional factor playing a role here is the self-scavenging effect is less significant for SO_4*^-, allowing to create higher radical concentrations in water and hence improve the reaction kinetics for heavily loaded wastewater. A final important feature is that owing to the better selectivity of SO_4*^- compared to *OH, SO_4*^- can be employed to attack specific functional groups that are responsible for the molecular ecotoxicity characteristics of the pollutant(Lutze et al., 2015).

SO_4*^- radicals are generated via the activation of a precursor molecule. Used precursors are peroxymonosulphate (PMS, HSO_5^-) and persulphate (PS, $S_2O_8^{2-}$). PS is available as a salt such as $Na_2S_2O_8$ or $K_2S_2O_8$, whereas PMS is only stable in the form of a triple salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), which is commercialized under the brand names Oxone or Caroat. Various activation methods have been described, such as adding a metal catalyst (Fe, Cu, Co,…)(Oh et al., 2016), increasing the temperature (thermal activation)(Ji et al., 2015), via UV-light(Guan et al., 2011) or by ultrasound(Ferkous et al., 2017).

Whereas promising results have already been achieved, the number of publications dealing with SR-AOP is still much lower that for classical AOPs, and various aspects still need to be investigated to fully understand the degradation mechanisms occurring:

- The type of dominant radicals ($SO_4{}^{*-}$ or *OH) produced depends largely on the process conditions, wastewater composition and activation method used, and has a large influence on the occurring degradation mechanisms. Although quenching studies have been performed in some initial studies, the interaction of the radicals with different types of organics is still unclear;
- It was previously hypothesised that, owing to the better selectivity of $SO_4{}^{*-}$ compared to *OH, $SO_4{}^{*-}$ can be employed to attack specific functional groups that are responsible for the molecular ecotoxicity characteristics of the pollutant. Clarity how the toxicity of the formed byproducts of SR-AOP compared to classical AOP still needs to be assessed for different classes of target pollutants. Since SR-AOP makes use of sulphur containing precursor chemicals, the residual sulphates could have an impact on the receiving water bodies;
- The information currently available is almost uniquely based on labscale batch experimental work. The behaviour of the system in continuous mode is still unclear. Also the scale-up of the process, hereby also including testing the robustness of SR-AOP for pollutant degradation in real wastewater with time-varying composition;
- Currently, toxic metals like Co rank amongst the most efficient activation methods for $SO_4{}^{*-}$ production. To avoid a rigorous and costly removal of these metal ions from the wastewater after the SR-AOP, they cannot be used as homogeneous catalysts. Research is still lacking on the behaviour (stability, leaching, fouling problems, …) of these metals when used in immobilized form as heterogeneous

catalysts. The further development of immobilised catalysts is another point to be looked after in this respect.

- The mechanisms that are responsible for the synergistic effects that are observed when coupling SR-AOP with typical AOPs still need to be elucidated. Here again the type of radicals involved will play a predominant role.

5. Electrochemical Advanced Oxidation Processes

For decades, electrochemical technology has looked for new applications in the remediation of environmental issues, following the great success obtained in the development of efficient industrial processes(Sarkka et al., 2015). In particular, treatment of water and wastewater has been always an important target, trying to combine the "green label" which may be easily associated to electrochemical processes (chemicals-free because only electrons are required, no waste production, operation at room temperature and atmospheric pressure) with their great ability to deplete pollutants in an efficient way (Bebelis et al., 2013; Oturan and J.J., 2013; Rodrigo et al., 2014; Sirés et al., 2014).

Pioneering works can be found in the literature more than forty years ago (Keenan and Stuart, 1976; Poon and Brueckner, 1975) and, in a certain way, they could considered as the consequence of trying to apply the experience and knowledge gained on organic electrosynthesis (Beck, 1973; Lund, 1971; Zwierzchowskanowakowska, 1976) to the removal of organics in aqueous wastes. In fact, these first approaches to the use of the electrochemical technology in the treatment of wastewater were almost exclusively based on the so-called "anodic oxidation", which may be defined as the electrochemical treatment of a waste in which only oxidation mechanisms associated to the direct electrolysis of pollutant (or to their chemical oxidation by oxidants produced on the anode surface) are looked for. At that early moment, results were not promising at all. Low mineralization efficiencies were an outstanding drawback and the search for efficient electrodes for this particular application was a real challenge (Canizares et al., 1999; Comninellis and Pulgarin, 1991; Vlyssides and Israilides, 1997) . For several years, platinum and graphite carbon-based electrodes focused the interest, as a consequence of their wide use in other electrochemical applications, even as different as electro-analysis. Then, the development of metal oxide electrodes based on the DSA® becomes the target, trying to reproduce in a certain way their success obtained in the chlor-alkali industry with the application of these electrodes to the production of chlorine (Comninellis and Pulgarin, 1993; Chiang et al., 1995; Polcaro et al., 1999; Pulgarin et al., 1994). However, because of very different reasons, processes developed lack the required efficiency to be competitive, in particular when they were compared to other oxidation processes, such as the advanced oxidation processes(Sires and Brillas, 2012). Fenton, ozonation and irradiated technologies clearly overcame the results that electrochemical technology could yield in that moment. In addition, despite oxidation of water to oxygen could be explained through the formation of hydroxyl radicals, there were no evidences of the role of these hydroxyl radicals in the oxidation of organics. Hence, in that moment, electrochemical technologies could not be properly considered as advanced oxidation processes, which, in fact, it was not a real problem, but it prevented the efficient promotion and or marketing of the technology to potential end-users. Opposite, many evidences of other mechanisms were found, such as the mediated oxidation by chlorine or the direct oxidation(Radjenovic and Sedlak, 2015). For the first case, the production of the very hazardous and undesired organo-chlorinated intermediates was a clear and very negative evidence (Comninellis and Nerini, 1995). For the second, the formation of polymers on the surface of the electrodes, which in turn produces a sort of passivation was a clear indicator and prevented the efficient use of the technology (Iniesta et al., 2001).

In the late 90s, the application of diamond coatings for this environmental remediation purpose was first proposed (Foti et al., 1999; Fryda et al., 2000; Fryda et al., 1999; Gandini et al., 1999). Pioneering results were astonishing, in particular when mineralization efficiencies were compared to those obtained with the previously studied electrodes (Canizares et al., 2005; Canizares et al., 2008; Rodrigo et al., 2001). In addition, by different techniques it was demonstrated for the first time that, with diamond anodes, hydroxyl radicals played a very important role on the oxidation of organics and hence that, in this case, electrochemical technology was a real advanced oxidation technology (Marselli et al., 2003). Moreover, not only the formation of hydroxyl radicals was observed but, the formation of many oxidant species such as peroxosulphates, peroxophosphates, peroxocarbonates and ozone, among others(Canizares et al., 2009b), which produced a real “oxidant cocktail” which helped to understand the outstanding efficiencies obtained, only limited by the low concentration of pollutants as they clearly fit to a first order kinetic (Canizares et al., 2007). This kinetic could be explained both in terms of the mediated oxidation by the “oxidant cocktail” and in terms of the pseudo-direct electrochemical oxidation not on the surface but in their nearness (in a so-called “reaction cage”) by a layer of hydroxyl radicals formed on the surface of the diamond which explains the almost-perfect fitting of results to a diffusion controlled process.

To overcome the diffusional limitations, two approaches have been faced during the last decades: the improvement in the mass transport through the promotion of turbulence and the activation of the oxidants produced on the surface of the anode from their molecular to the radical form. From the kinetic point of view, radical sulfate is known to be more powerful oxidant than its precursor, the peroxodisulphate, with kinetic constants that are several log-units above in the case of the radicalary species and the same applies for all peroxospecies and for many other oxidants such as chlorine. This activation can be obtained by the interaction of the molecular oxidant with UV light or high frequency US and even, sometimes by interactions with other oxidants in the bulk (Souza et al., 2013). For this reason, the combination or irradiation and electrochemical technologies is becoming a very interesting topic of research with very promising applications(Cotillas et al., 2016), although it does not always lead to improvement in the efficiency, in particular when the amount of oxidants contained in the system is large.

In addition to the limitation found at low pollutant concentration in the anodic oxidation with diamond anodes, the high resistivity of this surface brings up other important limitation. Despite being doped with boron (or less frequently with nitrogen or fluoride), the conductivity of diamond electrodes is much lower than that of other typical electrodes used in electrolysis and hence the cell voltage and the ohmic loses are greater. This means that a great amount of work has to be done in order to face this important problem and for this reason, and also because of the mass transfer limitations, the cell design is taking a big importance nowadays, trying to improve throughout electrochemical engineering what it could not be improved with the material itself with special mechanical designs that try to minimize the interelectrodic gap, maximize the turbulence with promoters, reduce the ohmic loses with special current feeders, etc.(Souza et al., 2016)

Likewise, scale-up has not always been faced in the right way, sometimes because of the economic difficulties and sometimes because the lab-scale is still ill defined and hence scale up studies are not worth. There are many manuscripts, which despite claiming the evaluation of the scale-up, are not focused on a real scale up (evaluating the effects of the flow dynamic, materials, construction details, etc.) but they are simply based on the use of a larger volume of the value typically used in most lab-scale studied. In fact, here we find a great challenge for the application of this type of EAOP and a topic in which the improvement in the efficiency is still very reachable.

Another different approach to apply electrochemical technology as advanced oxidation processes comes with the electrochemical production of hydrogen peroxide, which is known to be easily and efficiently obtained by cathodic reduction of oxygen on the cathode surface during electrolysis of wastewater. This approach was also faced at the turn of the millennium (Brillas et al., 1997; Oturan et al., 1999; Pratap and Lemley, 1994). Here, the type of cathode plays a very important role, not only the material but also the mechanical design and GDE (gas diffusion electrode) becomes a very important choice will allows to obtain very high efficiencies. Other approaches are being tried nowadays, such as the jet flow cell in which significant amounts of hydrogen peroxide can be reached with a permeable cathode in which an oversaturated oxygen aqueous solution is passed through (Perez et al., 2016).

The great advantage associated to the cathodic production of hydrogen peroxide is that it can be easily combined with the anodic oxidation and, hence, efficiencies over 100% (theoretically up to 200%) in the removal of COD can be obtained. The main drawback is that hydrogen peroxide is not a good oxidant itself and need to be activated. It is just the same problem than that found when dosing it in chemical oxidation processes and, obviously, the same activation pathways can be proposed in order to obtain an efficient technology: the fenton and/or irradiation approaches (Martinez-Huitle and Brillas, 2009). Regarding the first, initially, the most intuitive way to produce the iron catalyst required to generate an electro-fenton process is by the electrochemical oxidation of an iron plate(Boye et al., 2003). However, this is not properly an electro-Fenton process but a peroxi-coagulation because the amounts of iron produced are huge and coagulation becomes a much more important process than the oxidation itself. Opposite, the addition of small amounts of iron precursors (ferric chloride, goethite, Mohr salt, etc.) is the right way to produce the Fenton reagent in the electrochemical cell and many inputs are to be considered such as the comparative specific surface area of the anode and cathode, cell potential and pH (Brillas and Martínez-Huitle, 2015; Edelahi et al., 2003; Oturan, 2000; Sires and Brillas, 2012). The key point in the efficient reduction of the iron (III) preventing its transformation into non soluble species. Regarding the second approach, as for the anodic oxidation, combination with UV light irradiation and US is a very important hot topic that may help to define real applications (Boye et al., 2003; Diagne et al., 2009; Fdil et al., 2003; Moreira et al., 2013; Oturan et al., 2012; Sires et al., 2006). Use of solar light is a well-characterized aspect and help to prevent unnecessary raises of costs (Garcia-Segura et al., 2014; Moreira et al., 2013; Salazar et al., 2011). In any case, stirred tank cells are the most commonly studied reactors and, as the process is not expected to undergo diffusional limitations, stirring rate is not a very relevant input. However, even with the very large amount of works published in the last decade, there are still some important missing points to be discovered in this technology. Here, the most difficult point in the scale up is the cathodic production of hydrogen peroxide, because of the difficulties that have to be faced in order to have large electrode plenty of triple phase boundaries where oxygen can be efficiently transformed into hydrogen peroxide(Garcia-Segura et al., 2014; Garcia et al., 2013).

Regarding applications of both types of EAOP, it is interesting to observe how they started with the evaluation of the treatability of synthetic solutions that tried to simulate real industrial wastewater and, rarely, with real industrial effluents (Barrera-Diaz et al., 2014; Rodrigo et al., 2010). Phenolic species and dyes were a real challenge at the turn of the century, typically in wastes with an intermediate organic load (sometimes even higher than 10000 ppm of COD). Obviously, the costs found for the technology were very high, in particular when compared with biological processes but they were not far away from those of other non-electrochemical AOP (Canizares et al., 2009a; Saez et al., 2014) and, hence, they become an promising alternative for non-biodegradable wastes. Then, the search for new applications moved the target from these species to persistent pollutants, which typically are found in the environment at the ppb-level, but which in most studies were studied in the range of the ppm. Here, because of the lower concentration (and the previously commented first order kinetic), economic feasibility was even worse, although still comparable to those obtained with other AOP. Currently, there is a very important application which is still in evaluation: the disinfection (Lacasa et al., 2013). The huge amount of oxidants produced kill very efficiently the pathogens contained in water or wastewater and here the technology is very efficient.

Hence, a brilliant future is still expected for the advanced electrochemical oxidation processes which is a clear consequence of a very intensive work during more than four decades.

6. Perspectives and recommendations

After so many years of research on AOPs for wastewater treatment, the proof of concept is already available; what is really missing though is the next step from the purely academic (lab- or pilot-scale) research to large-scale, fully operational applications. It is the authors' strong belief that the major obstacle is the level of specific cost (i.e. monies per unit mass of contaminant removed or unit volume of effluent treated) associated with AOPs and in comparison with other more "conventional" treatment techniques. How can AOPs become more attractive cost-wise? Some thoughts are as follows:

1) AOPs should not do and cannot do the "full monty". AOPs must be forced to become selective in the sense that they must have a well-defined treatment target,

e.g. to remove micro-contaminants, to kill pathogens, to polish already treated industrial streams. Otherwise, precious and costly elements (oxidants, catalysts, energy) are wasted unnecessarily. In simple terms, battery treatment schemes must be considered, where AOPs need not have the first violin role.

2) The use of renewable energy sources is critical; in this sense, photochemical AOPs driven by sunlight have an obvious head start.
3) The field of AOPs can greatly benefit from advances in the area of materials science, where new materials with exciting properties are discovered. For instance, graphene materials have recently been tested with success as activators in sulfate-radical AOPs; this pinpoints the fact that AOPs for environmental applications is a topic lying at the interface of science and engineering and different disciplines must join forces to tackle the problem in a successful way.
4) Waste valorization is a relatively new and rather unexploited concept that could reduce treatment costs. The example of red mud, a residue from bauxite processing, containing iron oxides, titania and alumina is characteristic as this material can potentially serve as an AOP catalyst.
5) Public awareness must be enhanced and perceptions must be changed to digest that there is no such thing like “zero-cost” technology. Therefore, the best one can opt for is “low-tech, low-cost” technologies.

Overall, the complete replacement of existing treatment technologies by AOPs does not look promising from an economic point of view; this said, combination of AOPs with conventional wastewater treatment systems is conceptually feasible; this can happen in a sustainable manner if proper design, process optimization and smart thinking are applied.

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