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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, AOPs 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 paper, including hybrid processes, heterogeneous semiconductor photocatalysis, sulphate-radical oxidation and electrochemical advanced oxidation for water/wastewater treatment. Moreover, the use of photoelectrochemical processes for energy production is discussed. The work ends with some perspectives that can be of interest for the ongoing and future research.

1. Introduction

Nowadays, there is a growing concern about how to minimize the impact of wastewater discharges into the environment. For decades, the improvement in the removal of pollution by simple coagulation and biological processes has 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 fulfill the gap 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 (Klavarioti et al., 2009).

This lack of efficiency of the conventional treatment technologies justified the initial interest of the scientific community for other novel processes and the search of operating conditions capable of improving their applicability and efficiency. The so-called Advanced Oxidation Processes (AOPs) constitute a family of similar but not identical technologies that are based predominantly (but not exclusively) on the production of very reactive hydroxyl radicals (Comninellis et al., 2008a). AOPs include heterogeneous and homogeneous photocatalysis, Fenton and Fenton-like processes, ozonation, the use of ultrasound, microwaves and γ-irradiation, electrochemical processes and wet oxidation processes. One of their main advantages compared to conventional technologies is that they effectively degrade recalcitrant components without generating a secondary waste stream as is the case for e.g., membrane processes. Moreover, in most cases the formation of hazardous species in the effluent is limited. This is a specifically important benefit over competing technologies such as for instance chlorine oxidation of organics, during which a considerable amount of organo-chlorinated species is formed (Pablos et al., 2013).

From the turn of the century till now, the number of processes has increased drastically with the development of hybrid synergistic technologies based on the combination of various AOPs. These combinations have helped to overcome the occurrence of refractory species and also to improve significantly the performance of AOPs.

However, despite this great advancement, there is still slot for more research. It is generally accepted that degradation rates by AOPs can adversely be affected by several factors including the complexity of the water matrix, the type and concentration of the

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contaminant, the type and concentration of the oxidants and catalysts, and the reactor configuration. Hence, AOPs cannot be considered mature yet and there are many new fields of research and development, among which hybrid processes, heterogeneous semiconductor photocatalysis, novel oxidants such as sulphate-radicals and novel advanced electrochemical oxidation technologies that are worthy 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 in the right direction towards increasing the oxidative capacity of the process due to (i) the increased production of reactive oxygen species (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 zero stands for a simpler cumulative effect.

$$S = \frac{k_{combined} - \sum_1^n k_i}{k_{combined}} \tag{1}$$

Combination of AOPs typically results in a synergistic effect, because of the wider spectrum of oxidants involved in the processes. However, although not very common, in few cases coupling AOPs may result in antagonistic effects, thus leading to decreased degradation rates; for example, this may happen if excessive amounts of ROS, that may behave as self-scavengers, are produced.

Anyhow, by properly combining AOPs, there are different ways in which selectivity can be improved. Bearing in mind that (i) the selectivity of AOPs is in general low since the hydroxyl radical (i.e., the dominant oxidizing species) oxidizes a wide spectrum of organic species, and (ii) a lot of wastewater, and in particular those originating from industrial processes, 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 in the water. Some examples of how this can be achieved are listed below:

1) Ozone oxidation at acidic and/or near-neutral conditions mainly occurs through the direct reactions of molecular ozone with organic substances in a process commonly known as ozonolysis. Ozone preferentially attacks double bonds and can, e.g., be applied to destroy the chromophores (i.e. N=N bonds) of dyes typically encountered in textile effluents, leading to complete decolorization. Moreover, wastewater originating from agro-industrial origin, such as olive oil, table olives production and wine-making) contains polyphenolic compounds that are responsible for a low biodegradability and can selectively be removed by ozonolysis (Karageorgos et al., 2006).
2) A combination of AOPs and biological processes has traditionally been employed for the treatment of effluents containing bio-resistant and biodegradable fractions (Comninellis et al., 2008b). Typically, a biological pre-treatment step is applied to remove the biodegradable fraction of the organic contaminants followed by an AOP post-treatment as a final polishing step. This is expected to reduce treatment costs considering that biological processes are less costly than other treatment technologies. The concept of process integration does not exclude other scenarios, in which AOPs are applied as a pre-treatment step, which is required when the influent wastewater contains toxic or inhibitory components that may hamper the proper operation of the biological treatment (Van Aken et al., 2015). Also, the application of AOP as both a pre-treatment and a post-treatment step is feasible.
3) Integrating AOPs with separation processes may also prove beneficial for specific types of effluents such as those containing a high concentration 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 to avoid that they are dissolved during AOP, hence increasing the organic loading of the liquid phase and accordingly the oxidant consumption. Moreover, in the case of photochemical AOPs, the increased effluent opacity will be detrimental for the penetration depth of the light and hence for the overall process efficiency. In the case of polymer-processing effluents containing macromolecules of varying molecular size, an attractive option is the application of ultrafiltration in between AOP and biological post-treatment: chemical oxidation easily breaks down large macromolecules to more biogenic oligomers and ultrafiltration guarantees that only molecules having a 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 a wide variety of transformation by-products through various reaction pathways. 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 a more complete effluent's mineralization (Quintanilla et al., 2006). It must be noted that applying the currently available state-of-the-art analytical techniques, it is practically impossible to identify the full spectrum of by-products. Therefore, the distribution of major key components in the reaction medium and effect based parameters such as biodegradability and toxicity indices are generally used.

3. New semiconductor materials for solar-driven photocatalysis

Semiconductor photocatalysis based on TiO_2 is, perhaps, the most widely investigated AOP for the degradation and mineralization of a wide range of organic contaminants and even microorganisms (Carp et al., 2004). TiO_2 photocatalysts exhibit several advantages including low cost, availability in various crystalline forms and particle characteristics, absence of toxicity and photochemical stability. A major shortcoming is related to its wide band gap energy of about 3 eV, meaning that only near-ultraviolet (UV) radiation (~300–400 nm) 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 lowering its photocatalytic activity. Therefore, various recent studies have been dedicated to improving the TiO_2 photocatalytic efficiency by applying different strategies including the generation of 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 are predominantly activated in the visible region. E.g., silver orthophosphate (Ag_3PO_4) is a low band-gap photocatalyst that has