Perspective

Sustainable-by-Design Approach of Active Catalysts to Produce Reactive Oxygen Species in Water Matrices

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Abstract: An overview of the latest advances in the design of active catalysts with the ability to promote (photo) Fenton processes in water from a Green Chemistry perspective is discussed herein. A critical evaluation of the most relevant advances has been disclosed, and a brief perspective is presented about what is needed to fill the gap of knowledge in this field.

1. Introduction

The definition of Contaminants of Emerging Concern (CECs) refers to the chemicals that can be found in surface waters and may cause ecological or human health threats and are not currently regulated. CECs in wastewater include pharmaceuticals and personal care products, surfactants, and pesticides, which are usually recalcitrant to the conventional types of wastewater treatment. Thus, the development of new technologies to effectively remove those contaminants from water has become more and more urgent in recent decades. In this context, Advanced Oxidation Processes (AOPs) are regarded as the most effective strategy to fulfil this purpose through the generation of reactive oxygen species (ROS), an extremely powerful oxidant species. Among AOPs, great attention has been devoted to Fenton processes, based on the dismutation reaction of hydrogen peroxide catalyzed by iron ions (namely Fe^{2+} and Fe^{3+}) to produce hydroxyl radicals ($HO^\bullet$) and other reactive radicals ($HOO^\bullet$, $O_2^{\bullet-}$), even though these processes are actually way more complex, with many other reactions involved; some of these reactions lead to the formation of either radical or non-radical, powerful oxidizing species [1] capable of degrading organic pollutants in water, and other parasite reactions consuming H_2O_2 or active radicals (radical scavenging reactions), thus lowering the global efficiency of the process.

However, the possibility of applying the Fenton process using H_2O_2 coupled with an iron salt (usually $FeSO_4$) to a plant scale suffers from major limitations affecting the pre- and post-treatment steps. The use of iron salt as an active catalyst demands the use of a strong mineral acid (namely H_2SO_4) to obtain a strongly acidic pH and prevent iron precipitation as hydroxides during the treatment. And as a result, a consequent post-treatment neutralization step is required before any other subsequent treatment or disposal of the treated wastewater. Another inconvenience is also set by the high running costs of the plant, mostly due to the expenses related to collecting, treatment and disposal of the iron-containing sludges obtained from the neutralization after the AOP, and the market price of hydrogen peroxide used as oxidant [2,3].

To overcome these drawbacks, alternative modified Fenton processes have been designed, mainly varying the oxidant, catalyst, and strategies provided to the system. For this purpose, variants based on the Fenton reaction, including electro-Fenton, heterogeneous Fenton, and Fenton-like, each possibly coupled with light irradiation for the analogue photo Fenton-type process, have been developed and investigated in the literature mostly for the removal of target compounds or for the treatment of real wastewaters.

Homogeneous catalysts studied in (photo) Fenton-like processes include iron complexes with high solubility in water (regardless of pH conditions). Moreover, this solution has been also proved to enhance the effectiveness of the treatment in degradation of aqueous contaminants by allowing the formation of powerful oxidant species containing iron in high oxidation states (Fe (IV) and Fe (V)) through a ligand to metal charge transfer (LMCT) mechanism, making Fenton-like and photo Fenton-like processes the most promising technologies for the removal of most contaminants of emerging concern from wastewaters. Notwithstanding their effectiveness and despite the great efforts spent in their optimization, mostly devoted to achieving the highest mineralization of selected target molecules, there is still a large lack of knowledge concerning the development of the catalysts and the technologies for these processes to make them feasible at a large scale and improve their sustainability in accordance with the 12 principles of Green Chemistry [4] and the Safe and Sustainable by Design (SSbD) principles recently published by the European Commission [5].

Within this context and from this perspective, a critical discussion of the classic Fenton and the Fenton-type technologies from the Green Chemistry (Table 1) and the Safe and Sustainable by Design (Table 2) point of view is addressed, aiming to disclose what has been done and what is still needed to fill the gap towards the sustainable approach in designing catalysts active in producing reactive oxygen species in aqueous environment.

Table 1. The 12 principles of Green Chemistry and their subsequent advancements in Fenton catalysts development application.

#	Principle	Future Developments
1.	Prevent Waste	Project clean syntheses for catalyst preparation; Design self-degradable or bio-degradable catalysts; No sludges production.
2.	Atom Economy	All reactants should be included in the catalyst; Effective catalyst to minimize H_2O_2 and catalyst addition.
3.	Less Hazardous Chemical Syntheses	Nonharmful chemicals should be used within catalyst preparation and application.
4.	Design Safer Chemicals	Design non-toxic and eco-compatible catalyst, activable by nonthreatening visible light.
5.	Safer Solvents and Auxiliaries	Solvents and auxiliaries should be avoided or innocuous when used within catalyst preparation and application.
6.	Design for Energy Efficiency	Catalyst should be photo-activable under visible light (or monochromatic) and low energy radiation.
7.	Use of Renewable Feedstocks	Precursors used for catalyst preparation should derive from renewable feedstocks.
8.	Reduce Derivatives	Direct and few-steps synthetic pathway should be designed for catalyst preparation.
9.	Catalysis	Effective catalyst should be employed to achieve lowest catalyst loadings within wastewater treatment.
10.	Design for Degradation	Design self-degradable or bio-degradable catalyst.
11.	Real-time Analysis for Pollution and Prevention	Real-time monitoring of influent and effluent to dose oxidant and catalyst loadings accordingly and obtain optimal wastewater purification.
12.	Inherently Safer Chemistry for Accident Prevention	Catalyst activable by visible irradiation would prevent unhealthy expositions to high-energy radiation sources (e.g., UV) and the cogenerated by-products (e.g., chlorite and bromate, trihalomethanes).

Table 2. The eight principles of Safe and Sustainable by Design and their application to Fenton-like catalyst development.

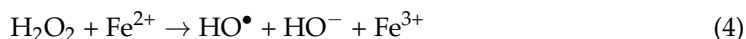| SSbD Principle (Based on)	
1. Material efficiency	All reactants should be included in the catalyst; Effective catalyst to minimize H_2O_2 and catalyst addition.
2. Minimize hazardous chemicals	Nonharmful chemicals should be used within catalyst preparation and application.
3. Design for energy efficiency	Catalyst should be photo-activable under visible light (or monochromatic) and low energy radiation.
4. Use renewable sources	Precursors used for catalyst preparation should derive from renewable feedstocks.
5. Prevent hazardous emissions	Effective catalyst to achieve complete mineralization of hazardous pollutants.
6. Reduce exposure to hazardous substances	Design safe synthetic routes for the catalyst preparation, involving non-hazardous reagents.
7. Design for end-of-life	Design self-degradable or bio-degradable catalyst.
8. Consider the whole life cycle	The GC and SSbD principles should be applied through the entire life cycle of the catalyst preparation.

2. Critical Discussion

A critical evaluation from the Green Chemistry point of view of the classic Fenton process, as it has been proposed in the literature so far, highlights how it fails in respecting many principles of Green Chemistry.

In particular, the addition of concentrated strong mineral acids to the wastewater to be treated, raises concerns about using hazardous chemicals (3rd, 5th, 8th and 12th principles); moreover, the required neutralization post-treatment step, leading to the formation of sludges, does not meet the 1st principle. Another critical point is related to the large amount of hydrogen peroxide required to carry out these processes which disattends the 2nd Principle, raises the operative costs due to the very expensive H_2O_2 and has high environmental impacts associated with the process, as proved in the few Life Cycle Assessment (LCA) studies of Fenton processes reported in the literature [6,7]. Thus, it is noteworthy that the same issues affecting the practicability of Fenton on a large scale, also impair its sustainability.

Recently, the use of alternative oxidants, which are potentially cheaper and more sustainable, in place of the most common H_2O_2 to drive Fenton processes has been evaluated as a possible solution to reduce the costs and environmental impacts associated with the provisioning of hydrogen peroxide. In this context, some pioneering studies have been published reporting promising results regarding the degradation of target pollutants. Among others, the use of sodium hypochlorite as an oxidant has been demonstrated to provide a cheaper alternative compared to hydrogen peroxide at the expense of a slightly lower efficiency in the treatment of simulated wastewater containing a mixture of aromatic compounds (89% vs. 72% COD removal in the optimized conditions) [8]. However, the environmental impacts associated with the production of NaClO on an industrial scale are considerably higher than those associated with the industrial production of H_2O_2 according to the Ecoinvent database (Ecoinvent 3.8). As another option, three different reagents (sodium sulfite, SO_3^{2-}, potassium metabisulfite, $S_2O_5^{2-}$, and sodium persulfate, $S_2O_8^{2-}$) were tested, and their efficiency in the degradation of phenol as a target compound was compared with that of hydrogen peroxide. Within this study, authors demonstrated that sulfite and metabisulfite can be effectively activated by Fe-TAML (tetra amido macrocyclic ligand) which contributes toward the degradation of phenol. However, further studies should be performed to evaluate the environmental impacts associated with the use of these oxidants.

Additionally, electrochemical systems able to produce both H_2O_2 and Fe^{2+} ions in situ, known as electro-Fenton, have been developed. In detail, electro-Fenton implies the continuous electro-generation of H_2O_2 inside the reactor through to the cathodic

reduction of dissolved O_2 (Equation (1)) and of ferrous ions (Fe^{2+}) by oxidative dissolution of sacrificial anode of metallic iron (Fe^0) (Equation (2)), and the regeneration of Fe^{2+} by cathodic reduction of Fe^{3+} (Equation (3)) obtained from the reaction of H_2O_2 with Fe^{2+} (Equation (4)).

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^0 \rightarrow Fe^{2+} + 2\,e^- \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + HO^- + Fe^{3+} \tag{4}$$

This strategy cleverly avoids the disadvantages of the H_2O_2 supply and limits the drawbacks related to the addition of the iron salt catalyst being steadily produced in solution at low concentrations [9,10]. Indeed, by providing iron ions at concentrations below the solubility limit, the acidification step can be avoided. However, the feasibility of electro-Fenton for real scale applications is limited due to its costs related to high energy consumptions [11] (6th Principle). For example, in 2020 electro-Fenton has been tested for the degradation of chloroquine as a target pollutant [12]. However, to accomplish the complete removal of the chloroquine drug, the optimized operational conditions required (pH = 3.0, O_2 flow rate of 80 mL/min and a current density of 60 mA/cm^2 for 5 h of treatment time) are hardly feasible on a plant scale. For this reason, in 2021 a new study was published reporting the possibility of applying electro-Fenton on a bench scale for the degradation of clofibric acid [13]. Reported results showed that the scaled-up treatment was efficient and cost effective thanks to a clever reactor design in the scaling-up process. Thus, authors took a first step forward towards a more realistic application of electro-Fenton on a real plant scale, even though the proposed process certainly needs further optimization to become a feasible and competitive technology.

With the aim of working at a circumneutral pH, in recent decades the development of modified Fenton processes has drawn much attention from scientists and engineers, mainly looking for strategies for catalyst modifications. Among them, heterogeneous iron-based materials and homogeneous iron complexes have been deeply investigated. First, heterogeneous systems proposed in the literature include catalytic systems based on bulk catalysts containing metallic iron or iron oxides, as hematite, goethite or magnetite [14–16]. Interestingly, a naturally occurring iron-containing mineral was applied as a heterogeneous catalyst for the degradation of a recalcitrant cationic dye, the crystal violet [17]. Moreover, the same catalyst was also tested in the treatment of real textile wastewater.

More recently, zero valent iron nanoparticles (nZVI) have been employed as novel heterogeneous catalysts for modified Fenton and photo Fenton [18,19]. During the last decade, a nanoscale zero-valent iron (nZVI) catalytic system has been extensively investigated and shown high potential in removing organic contaminants in wastewater, combining absorption and redox activities, thanks to its unique structure made of a core–shell of the Fe$^{(0)}$ core and iron oxide external layer. Heterogeneous catalytic systems allow the avoidance of the acidification and post-treatment neutralization steps, thus preventing the formation of sludges (1st principle) and the risks associated with the use of concentrated mineral acids (3rd, 5th and 12th principles).

Notwithstanding the undeniable advantages of heterogeneous systems, mainly the possibility to carry out the process avoiding pH modifications and the recovery of the catalyst, heterogeneous catalysts may undergo iron particles leaching during the treatment; moreover, the suspended solid catalysts in the photo Fenton process encumber the incoming radiation, making the irradiation less effective (6th principle). A possible solution could be the development of suitable supporting materials for those powder catalysts; however, this would further enhance the costs and impacts related to the preparation of the catalyst. Finally, the toxicity for plants and animals of such materials should be addressed, especially taking into account that they would realistically reach the ecosphere after the treatment.

Alternative strategies to run Fenton-type processes at a neutral or circumneutral pH involve the use of other non-ferrous transition metal redox couples (e.g., Cu^+/Cu^{2+}, Al^0/Al^{3+}, Cr^{3+}/Cr^{6+}) [20–22]. However, most of the proposed alternatives are heavy metals, thus their applicability for environmental applications is a concern.

As matter of fact, the most promising approach to perform Fenton-like and photo Fenton-like processes, without further acidification of the sample, which is to be treated, has been the development of novel iron-based catalysts soluble in a board range of pHs, mostly employing chelating agents to form stable complexes with iron. Noteworthy, the presence of a ligand-to-complex iron, beside the enhancement of the solubility of the catalyst, also improves the efficiency of the process overall. In fact, recent studies have demonstrated that the presence of the ligand generally speeds up the reaction between H_2O_2 and Fe^{III} and facilitates the formation of ferryl species ($[Fe^{IV}=O]^{2+}$) with high oxidizing power [23,24].

In this field, early studies from prof. Collins, who reported on the ability of TAMLs in the activation of hydrogen peroxide for green oxidation processes [25], paved the way for the design of new effective catalysts for this application. In order to form stable and soluble complexes with iron ions, chelating agents must have two or more functional groups, mainly carboxylic, hydroxyl, amide and amine groups, which can form bonds with the metal center. Ligands which have both two or more carboxylic groups and at least an amine group can be classified as amino polycarboxylic acids (APCAs) [26]. Among APCAs, the well-known ethylenediaminetetraacetic acid (EDTA) has drawn great attention from the scientific community, and is applied as a catalyst for the degradation of a wide number of contaminants, especially in photo Fenton-like processes [27–29], even though it actually has certain environmental concerns associated with each stage of its life cycle, from synthesis, to use, to end of life. Despite the consolidated synthetic protocol on an industrial scale (more than 55 ktonnes globally produced per year [30]), the synthesis of EDTA lacks of greenness for different reasons: the precursors used, especially ethylenediamine and formaldehyde [31], are harmful and toxic substances (see 3rd principle) derived from fossil resources (7th principle). Moreover, the use of EDTA as a ligand in this field raises some concern related to its concentration in the environment, which has been increasing due to its massive use and its persistence since it is poorly biodegradable (in contrast with the 10th and 11th principles of Green Chemistry). In fact, EDTA dissolved in groundwater is able to leach micronutrients from the soil, and remobilize toxic heavy metals from sediments, making them bioavailable and resulting in the eutrophication phenomena. For this reason, inspired by the 12 principles of Green Chemistry and the benign-by-design approach [32,33], the design of biodegradable (10th principle) and biomass-derived (7th principle) ligands of the new generation has to be pursued by the scientific community. To date, through following this approach, two alternative chelating agents of new generation have been employed as ligands in designing novel catalysts for (photo) Fenton-like processes, namely the ethylenediamine disuccinate and iminodisuccinate iron complexes, Fe-EDDS [34–37] and Fe-IDS [38–40], respectively. Both ligands can be obtained from maleic anhydride, a biomass-derived platform molecule (in accordance with 7th principle). However, the synthesis pathway from maleic anhydride for EDDS leads to a mixture of all four possible enantiomers, of which only one ([S,S]-EDDS) is readily biodegradable. The sole biodegradable enantiomer [S,S]-EDDS could be selectively obtained through the reaction between 1,2-dibromoethane and enantiopure aspartic acid, thus accomplishing the 10th and 12th principles but at the of expense of the 3rd, 4th and 12th principles due to the higher cost of the enantiopure aspartic acid and more dangerous precursor (the dihalomethane). To date, indeed, most studies recently published in the literature reported the use of the Fe-EDDS complex regardless of the stereochemistry (and thus, the biodegradability) of the ligand itself. In these studies, Fe-EDDS has been employed as a catalyst in the photo Fenton processes for a wide variety of applications, including the degradation of antibiotics in distilled water [37], of pharmaceuticals in hospital wastewaters [35,36], or for the treatment of industrial winery wastewaters [34]. Beyond the results in terms of pollutants removal, generally >90% are under optimized conditions which is achieved at the expense of quite

high catalyst loading (H_2O_2/Fe-EDDS molar ratios ranging from 10 to 50). It is noteworthy that these studies demonstrated that Fe-EDDS-catalyzed-photo-Fenton-like processes can also be effectively activated under solar irradiation in place of the most common but more energy-demanding UV-C irradiation. This remarkable result allows avoidance of issues related to the UV-C generally used to activate this kind of photocatalysts, e.g., the unhealthy expositions to high-energy radiation sources and the cogeneration of by-products (e.g., chlorite and bromate, trihalomethanes). On the other hand, iminodisuccinate (IDS), a pentadentate ligand also obtainable from biomass-derived maleic anhydride through a simple reaction with NaOH and aqueous ammonia, shows complete biodegradability within 28 days according to the OECD standards regardless of its stereochemistry. This ligand has been employed in the development of an iron-based homogeneous catalyst for photo Fenton-like processes for the first time for the treatment of highly refractory olive mill industrial wastewaters [38] and more recently for the treatment of greywaters aiming for the reuse [41], and for the removal of pharmaceuticals [42] as well as the disinfection of urban wastewaters [43]. In these studies, the biomass-derived, and biodegradable Fe-IDS catalyst was effectively employed as a catalyst in both UV-C and solar-activated photo Fenton-like processes without significative activity loss, thus proving the possibility of carrying out the process with solar irradiation. However, except for the first study, in which the H_2O_2/Fe-IDS molar ratio under optimized conditions was 250 [38], for this catalyst the molar ratios of the oxidant to Fe-L in the optimized conditions ranged from 10 to 20, suggesting either a poor efficiency of the catalyst or non-optimized experimental conditions used. As a matter of fact, an ideal catalyst for photo Fenton-like processes should provide high efficiency, which can be evaluated measuring its Turn Over Frequency (TOF) value [44], so that low concentrations of the catalyst need to be added to the system; moreover, another desirable feature of the catalyst should be the possibility of being photo-activated by visible or solar light irradiation instead of the more energy-demanding UV-C light, usually used to run photo Fenton processes. In fact, in this context, some research groups have been investigating the possibility of carrying out photo Fenton-like processes using low cost and low energy-demanding LEDs as a radiation source [29,45–47].

3. Conclusions and Future Perspectives

In this perspective article, a critical evaluation of the accordance of the main catalytic systems with Green Chemistry principles for different (photo) Fenton and (photo) Fenton-like processes has been disclosed. Even though nice work has been carried out in designing Fenton-type processes and effective catalysts for these kinds of processes, there is still a large gap of knowledge concerning the development of effective catalytic systems to make the application of these processes at a plant scale economically feasible and environmentally sustainable. With this aim, the scientific community should be actively involved in the design of new catalysts with high efficiency and low environmental impacts. This goal can be achieved with the synergistic contributions of different expertise and different tools combined in a holistic approach. The catalyst design should be supported with theorical studies involving DFT calculations to enhance the chelating strength of the organic ligand to be employed and the possibility of obtaining iron-based complexes photoactivable under visible, solar, or monochromatic irradiation. Catalytic activities evaluations (TOF calculation [44]) should be considered, and green metrics including E-factor [48], Process Mass Intensity, (PMI) [49], and life cycle assessment (LCA) methodologies should be employed to evaluate the sustainability of the new catalysts and their applications in advanced oxidation processes for wastewater treatment.

Conflicts of Interest: The author declares no conflicts of interest.

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