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Recent advances in electro-Fenton process and its emerging applications

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Abstract

The electro-Fenton (EF) process is a powerful electrochemical advanced oxidation process. Its development has progressed over the past three decades as a clean and effective technique for wastewater treatment. Even though conventional EF has been shown to be a powerful process for efficient degradation/mineralization of toxic and/or persistent organic pollutants; it still suffers from some downsides for industrial-scale development. Recently, research has focused on improving its effectiveness and relevance, mainly by modifying certain operating parameters; improvements in electrode material and reactor configuration, as well as coupling with other treatment methods. Therefore, this review evaluates the current state of the EF process and presents the most recent advances such as 3D-EF, chelate-EF, self-powered EF, pulsed current EF, bio-EF, sono-EF, sulfite-EF, pyrite-EF, and ferrate-EF in addition to its emerging applications like disinfection, generation of value-added products, and removal of emerging pollutants from water. The suitability of different modified or hybrid-EF processes is discussed based on their performance in H_2O_2 generation, degradation kinetics, mineralization efficiency and cost effectiveness. This review article is intended to be comprehensive, critical and of general interest, covering recent developments and advances in EF process with the aim of providing a powerful method for the treatment of wastewater polluted with biorecalcitrant pollutants.

Keywords: Electro-Fenton; Hydroxyl radicals; Electrochemical advanced oxidation; Emerging pollutants; Wastewater treatment; Coupled processes

Graphical Abstract

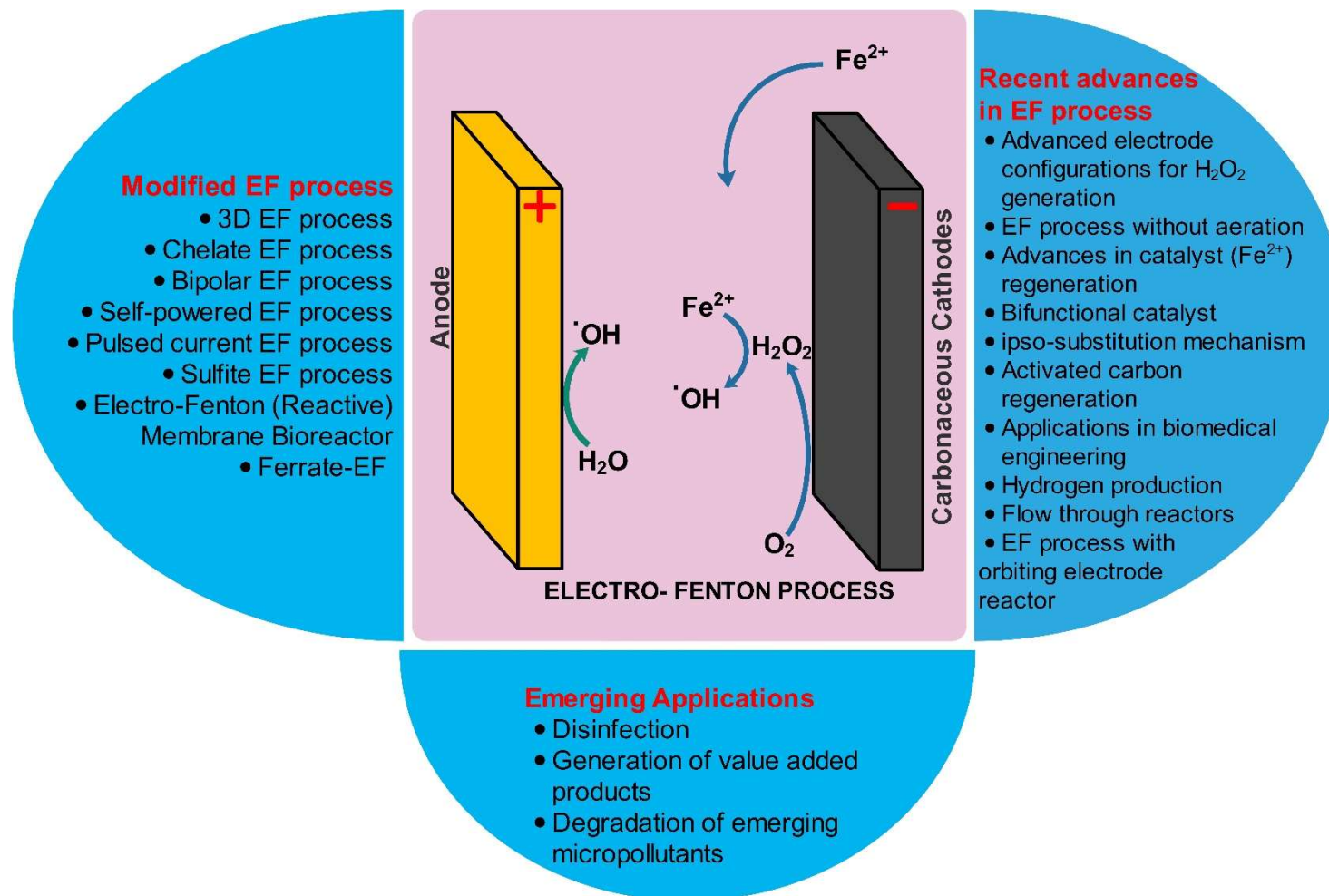


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List of abbreviations

AC: Activated carbon
AGU: Anhydroglucose
AOP(s): Advanced oxidation process(es)
AF: Anodic-Fenton
BEF: Bioelectro-Fenton
BDD: Boron-doped diamond
COD: Chemical oxygen demand
CNT: carbon nanotube
DSA: Dimensionally stable anode
EAOPs: Electrochemical advanced oxidation process(es)
EF: Electro-Fenton
FF: Fered-Fenton
GDE: Gas diffusion electrode
HER: Hydrogen evolution reaction
MCF(s): Microbial fuel cell(s)
MCE: Mineralization current efficiency
NADE: Natural air diffusion electrode
OER: Oxygen evolution reaction
•OH: Hydroxyl radical(s)
PC: Peroxi-coagulation
PEC: Photo-electro-catalysis
PFC(s): Photocatalytic fuel cell(s)
PEF: Photoelectro-Fenton
PFOA: Perfluorooctanoic acid
PMS: Peroxymonosulfate
POP(s): Persistent organic pollutant(s)
PS: persulfate
PV: Photovoltaic
RE: Renewable energy
Sono-EF: Sonolysis assisted EF

SPEF: Solar photoelectro-Fenton

SR: Sulfate radical

SR-AOPs: AOPs involving sulfate radical

TOC: Total organic carbon

1. Introduction

Recently, advanced oxidation processes (AOPs) have received much attention for the treatment of recalcitrant organic pollutants (Oturán & Aaron, 2014; Scaria et al., 2021). AOPs are effective for the complete removal of these compounds by mineralizing them, and improving biodegradability of the solution (Nidheesh et al., 2022) and reducing toxicity (Babu et al., 2019). Among the AOPs, Fenton reaction (Eq. 1) based processes have been greatly appreciated in their efficiencies in treating recalcitrant organic compounds. However, the slow ferrous regeneration rate in Fenton reaction resulted in higher ferrous ion requirements for the effective removal of pollutants, which ultimately resulted in higher sludge generation (Oturán & Aaron, 2014). This disadvantage of the conventional Fenton process was partially solved using heterogeneous catalysts (Nidheesh, 2015; Heidari et al., 2021) or chelating agents (Zhang & Zhou, 2019) or by adding external energy, such as electricity as in the electro-Fenton (EF) process, UV light as in the photo-Fenton process, and ultrasound as in the sono-Fenton process.



Since its beginning in 2000, EF process has gained much confidence in the researchers for its superior performance, simplicity and cost effectiveness (Oturán, 2000; Oturán et al., 2000; Brillas et al., 2009). Non-requirement of H_2O_2 in EF process attracted more researchers to work in this field as it reduces the complexity in handling H_2O_2 and its associated cost (Sirés & Brillas, 2012). EF process is able to generate H_2O_2 at the cathode surface by two-electron reduction of dissolved oxygen at acidic conditions (Eq. 2). Rapid cathodic reduction of ferric ions makes the process more active by the regeneration of Fe^{2+} (Eq. 3), and ultimately resulted in the optimal ferrous ion requirement of EF process as in the range of a few mg L^{-1} (Nidheesh et al., 2013; Zhou et al., 2018; Brillas & Garcia Segura, 2020).





Versatile applications of EF process were tested in various environmental matrices. EF process is found as an alternative solution for reducing arsenic toxicity in drinking water by oxidizing arsenite to arsenate (Nidheesh et al., 2020) and for removing ammoniacal nitrogen (Menon et al., 2021). Treatment efficiency of EF process for reducing organic load from complex wastewater and real industrial effluents like landfill leachate (Oturán et al., 2015), textile wastewater (Nidheesh et al., 2014), pharmaceutical wastewater (Olvera-Vargas et al., 2021a; Ganzenko et al., 2020), municipal wastewater treatment plant effluents (Valro et al., 2017), mixed industrial wastewater (Popat et al., 2019) as well as mine water (Olvera-Vargas et al., 2021b) were recently reported. Apart from the treatment of water and wastewater, superior performance of EF process was reported for treating soil-washing effluents (Ganiyu et al. 2020; Liu et al., 2020a; Trellu et al., 2019) and sludge (Burgos-Castillo et al., 2018; Olvera-Vargas et al., 2019a); as well as recovering nutrients from sludge (Burgos-Castillo et al., 2018).

2. Electro-Fenton related processes

Based on the nature of modifications, EF related processes can be divided into two categories: (1) modified EF processes and (2) hybrid-EF processes (**Fig. 1**). In modified EF process, a slight modification for conventional EF process were done either to improve the efficiency of the process or to reduce the cost. Peroxi-coagulation (PC), ferred-Fenton (FF) and anodic-Fenton (AF) are the best examples of such modified processes. In PC process, sacrificial anodes such as iron or stainless steel are used (instead of stable anodes in EF process) to generate ferrous ions in the electrolytic system (Nidheesh & Gandhimathi, 2012; Olvera-Vargas et al., 2019b). However, controlling ferrous ion generation is quite difficult and ultimately PC process is considered as the combination of electrocoagulation and EF process (Nidheesh & Gandhimathi, 2014; Kumar et al., 2018). pH regulation is needed at regular interval to improve

the mineralization efficiency of PC process (Nidheesh, 2018) as EF process predominates in the acidic conditions, while electrocoagulation process predominates in alkaline and neutral pH conditions (Venu et al., 2016). FF and AF processes are the modified versions of EF and PC process in which H_2O_2 is externally added to the system to improve the efficiency (Nidheesh et al., 2018).

In hybrid-EF process, additional energy is added to the EF system to improve the performance. Sono-EF (SEF) and photo-EF (PEF) processes are the best examples for hybrid-EF processes. The addition of ultrasound or UV light improves the EF treatment efficiency by generation of additional radical from the decomposition of H_2O_2 and the acoustic cavitation phenomenon (in the case of SEF), by improving the ferrous ion regeneration rate and reducing the passivation of electrode (in the case of SEF) by the continuous cleaning with ultrasound energy (Oturán et al., 2008; Nidheesh et al., 2018). The bio-EF process (BEF) is another version of a hybrid-EF process in which energy generated from bioelectrochemical process such as the use of microbial fuel cells as input energy in the EF process. Another type of BEF process consists of sequential coupling between EF and biological degradation, in which the EF process can constitute a pre-treatment or post-treatment step (Olvera-Vargas et al., 2016a, Ganzenko et al., 2018).

A few research groups reviewed the advancements of EF process (**Table SI-1**) and most of the review articles are focused on the EF process, modified EF process and hybrid-EF process, which are not much focused on this review. However, there are several other applications of the EF process tested recently like, activated carbon regeneration, disinfection, production of value-added products and treatment of emerging contaminants. This review article focuses on such applications of EF and related processes. Furthermore, other modifications for EF process like, chelate-EF process, 3D-EF process, self-powered EF process, sulfite EF process etc. and

recent advances like the use of bifunctional catalyst, cathode modifications, flow-through reactors etc. are included in this review.

3 Advantages and inconvenient of conventional EF process

In recent years, the EF process has been considered as one of the most frequently used EAOPs approaches (Ganiyu et al., 2018). A recent study highlighted the cost effectiveness (considering operating costs such as sludge management, chemical use and electricity consumption) of EF process compared to ozonation, H₂O₂ photolysis, Fenton and photo-Fenton at laboratory scale (Mousset et al., 2021). The accumulated oxygen-equivalent criterion was newly introduced and it showcased the superiority of EF with only 0.0004 and 0.0012 kg-O₂ of dose to reach 50% and 99% of mineralization, respectively (Mousset et al., 2021). Nevertheless, some advantages and drawbacks of the EF process should be still considered. Among the advantages, following can be indicated (Sirés & Brillas, 2021):

- i) Low quantity and cheaper catalyst source,
- ii) In-situ production of both H₂O₂ and Fe²⁺ to produce •OH in solution increases the effectiveness of the process,
- iii) Use of low-cost cathodic materials to produce H₂O₂ by O₂ reduction reaction, especially carbon-based materials,
- iv) Suitable for treating different water matrices because of the significant amount of homogenous •OH originated from Fenton reaction
- v) Design and construction of the electrochemical reactors can be optimized to efficiently feed the O₂ to the cathode surface, increasing its concentration in the effluent,

- vi) Novel cathodic carbon-materials can be synthesized to enhance their electro-activity and selectivity to produce H_2O_2 ,
- vii) Easy post-treatment separation and reusability of the treated effluents
- viii) Easy automation and operability as well as lower energy requirements when coupled to renewable energies, such as solar or eolic (Ganiyu et al., [2020](#))
- ix) EF can be combined to efficient anodic production of heterogeneous $\bullet OH$ in undivided cell by using non-active anodes, such as BDD,
- x) EF can be upgraded to PEF by using photoactive anodic materials, which are exposed to artificial or natural irradiation (Divyapria et al., [2021](#)) or combined to others processes such as biological treatment (Olvera-Vargas et al., [2016b](#)),

On the other hand, important drawbacks limit the applicability of conventional EF process, such as:

- i) Fe^{3+} complexes formed are difficult to be eliminated at the end of the process,
- ii) EF process is optimal in acidic pH conditions (i.e., pH 2.8 – 3.5) and requires a final neutralization step to obtain environmentally tolerable effluents from the environmental point of view,
- iii) H_2 evolution at the cathode, limiting the H_2O_2 generation efficiency,
- iv) $pH \geq 4.5$ promotes the precipitation of Fe^{3+} as ferric hydroxide (loss of catalyst),
- v) Non-recyclability of the catalyst used, making the technique unsuitable for continuous experimental process

Although the EF process must accomplish several tasks to real applicability, this electrochemical technology continues to be more efficient than anodic oxidation (Ganiyu et al., [2021a](#)), and its efficiency can be significantly improved with the development of hybrid-EF processes.

4. Recent advances in EF process

4.1. Advanced electrode configurations for H₂O₂ generation

Electrochemical cathodic H₂O₂ generation is one of the key factors controlling the efficiency of Fenton-based EAOPs (Ganiyu et al., 2021b). The rate and quantities of H₂O₂ electro-generation during electrolysis are affected by the cathode material used and cathodic configuration (Zhou et al., 2021). Conventional aeration suffers from O₂ mass transport and limitation owing to its lower water solubility (Petrucci et al., 2016). As such, different reactor designs and cathode-aeration configurations have been studied to allow greater H₂O₂ generation and higher O₂ mass transfer, respectively.

Higher O₂ mass transfer and H₂O₂ production rate can be achieved by the gas pressure or turbulent state of the solution through the cathode and/or innovative reactor designs. The cathode designs include gas diffusion and rotating cylinder electrodes, which pressurize the system and create turbulence, thus improving the mass transfer of the O₂. Li et al. (2020a) using electrode aeration, thereby providing gas directly inside the electrode (**Fig. 2a**) This design allows easier transport of gas inside the electrode to form gas-liquid-solid interfaces with a higher O₂ mass transfer and utilization. A natural air diffusion electrode with superhydrophobic three-phase interface was recently used for fast production of H₂O₂ (101.67 mg h⁻¹ cm⁻²) with high oxygen utilization efficiency (44.5% – 64.9%) (Zhang et al., 2020a). The cathode matrix and diffuse layer allow air to naturally diffuse into the reduction reaction interface.

Several reactor designs such as high-pressure reactor (Scialdone et al., 2015), filter-press flow-cell (Pérez et al., 2018), jet-type vertical/horizontal flow-reactor (Yu et al., 2020) and pressurized jet aerators (**Fig. 2b**) (Pérez et al., 2018) have been reported to produce high quantity of H₂O₂ with high O₂ mass transfer rate via super-saturation of pressurized O₂, supply

of clean air and super-saturation of O₂ at ambient pressure, respectively. For example, the H₂O₂ production rates of 9.2 mg h⁻¹ cm⁻² (jet aerators) (Pérez et al., 2017) and 101.67 mg h⁻¹ cm⁻² (natural air diffusion electrode) (Zhang et al., 2020a) were reported, which is much higher compared to conventional aeration using graphite cathode (2.45 mg h⁻¹ cm⁻²) (Xia et al., 2015).

4.2. EF process without aeration

As already mentioned in other sections, cathodic material is a key factor in the effective electro-generation of H₂O₂ in EF process. It influences on the H₂O₂ yield, current efficiency, and parallel reactions. At the same time, the performance of the cathode determines the energy requirements and cost. From the pioneering studies related to the EF approach (Brillas et al., 2009), it is evident that the gas diffusion electrode (GDE) favors the gas diffusion process and can accelerate oxygen reduction (Wang et al., 2020). Nevertheless, gas diffusion via GDE depends on the O₂ supply (pure O₂ or air) and electrochemical reactor design, occurring important deficiencies, such as H₂O₂ yield and production rate, low oxygen utilization rate and higher energy consumption. Then, the highly efficient and economic O₂ supply methodologies to the cathode remain a challenge for the effective application of GDE (Zhang et al., 2021a).

In this sense, two strategies have been developed: i) improvements on the cathodic materials composition and properties and ii) the use of passive O₂ diffusion from air, using O₂ dissolved in the effluents. In the former case, significant advances have been achieved thanks to the nanotechnology to modify, synthesize or enhance the properties of GDE to transport the gas via its structure or accelerating the O₂ transformation to H₂O₂ with higher production efficiencies. However, the passive O₂ diffusion from air to GDE is limited by the mass transport of O₂ in solution to the cathode and its solubility in water, in the latter case.

Obviously, the improvement on the O₂ diffusion or alternative methodologies to produce H₂O₂ will enhance the performance of EF approach. Therefore, in the last few years, Du et al. (2020)

and Wang et al., (2021a) have reported significant insights on the innovative strategies to enhance both H_2O_2 production and its utilization efficiency using natural air diffusion electrode (NADE) (**Fig. SI-1**). For example, H_2O_2 production on NADE reached 158% and 188% when 0.2 and 1.2 A were applied (Zhang et al., 2021a), respectively, with the total energy consumption of only 7.2% and 25.4% compared to the conventional GDE. These results clearly demonstrated that NADE was superior to a conventional air electrode due to the ultra-high oxygen mass transfer efficiency and non-requirement of external aeration, which significantly reduce energy consumption.

4.3. Advances in Fenton's reagent regeneration using multifunctional catalysts

Homogeneous EF is highly efficient in eliminating organic compounds (Arellano et al., 2020a; Mousset et al., 2020) however, it represents some drawbacks. The low solubility of Fe(III) in aqueous solution involves operation in acidic conditions (pH around 3) during electrolysis implying the precipitation of ferric sludge before the disposal of treated wastewater. Moreover, the catalyst recyclability from the sludge is then limited. Heterogeneous EF has therefore been subsequently proposed (Ganiyu et al., 2018).

Iron oxide-based cathode materials (e.g., magnetite, hematite, goethite, ferrihydrite) have been widely considered to favor the Fenton reaction (Ortiz de la Plata et al., 2010). These catalysts allow an increase in the Fe(II)/Fe(III) redox cycles, but this may decrease in the meantime due to the selectivity toward the electro-generation of H_2O_2 from oxygen reduction. Recently, sulfur-doped iron materials (e.g., FeS_2) offer promising regeneration rates of Fe(II) catalysts, while promoting the H_2O_2 electro-generation (Tian et al., 2020a). Therefore, these bifunctional catalysts permit enhanced degradation kinetics and mineralization of organic pollutants in wastewater (**Fig. 3a**). Other promising multifunctional catalysts such as nitrogen-doped graphene (Du et al., 2021a), carbon nanotubes-doped iron (Su et al., 2019) and nitrogen-doped

iron materials (Cao et al., 2020) have been proposed to enhance these processes. For example, FeOx nanoparticles embedded in N-doped hierarchically porous carbon (FeOx/NHPC) allow enhanced H₂O₂ electro-generation and Fe(II) regeneration, leading to higher EF treatment efficiency (**Fig. 3b**) (Cao et al., 2020).

Though promising, further long-term stability and cost effectiveness studies of these catalysts will be required for testing the viability at industrial-scale. Moreover, the influence of those catalysts on alkalization rate at the cathode surface should be carried out to avoid cathode passivation, when dealing with real wastewater containing magnesium and/or calcium and carbonates (Adnan et al., 2022).

4.4. Degradation of perhalogenated organics: ipso-substitution

All AOPs, particularly EF process, rely on the generation of [•]OH, whose reactivity is quasi non-selective towards organic molecules (Mousset et al., 2018). Three modes of [•]OH action were typically proposed, since several decades: (1) electron transfer reactions, (2) hydrogen atom abstraction, (3) electrophilic addition to an unsaturated bond (Oturán & Aaron, 2014). More recently, the efficiency of AOPs towards the degradation of perhalogenated organic compounds (C_xX_y), especially those with fluorine-carbon (C-F) bonds, was questioned (Mousset et al., 2018). Moreover, they have no unsaturated bonds and hydrogen atoms, while there is no possibility of direct electron transfer. Therefore, reduction processes were more favored to treat these oxidized contaminants. An additional mechanism of [•]OH (fourth mode) attack, namely ipso-substitution (**Fig. SI-2**), was recently demonstrated with the degradation and mineralization of carbon tetrachloride by the EF process in combination or not with anodic oxidation using BDD anode (Mousset et al., 2018).

This new mode further justifies the use of EAOPs to remove per- and polyfluoroalkyl substances, particularly perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid.

These fluoropolymer-based molecules are persistent and represent environmental and human health risk. Updated guidelines arouse interest in proposing complementary advanced physicochemical treatment (Trojanowicz et al., 2018), including EF process (**Fig. 3c-e**). PFOA decay rate constant of 1.15 h^{-1} as well as 90% of degradation rate could be obtained at -0.4 V/SCE of cathodic potential using EF (**Fig. 3c**) (Liu et al., 2015). An increase of PFOA removal efficiency has been even noticed when BDD anode was coupled to EF (93% of TOC removal after 4 h electrolysis) (**Fig. 3d**) (Wang et al., 2019). 91% of PFOA mineralization could be reached in 2 h with solar photo-electro-Fenton (SPEF) like technology (**Fig. 3e**) (Wang et al., 2021b). This latter combination improved the removal efficiency of EF due to synergistic effect of light towards H_2O_2 decomposition into $\cdot\text{OH}$ and Fe(II) regeneration. These promising lab-scale research further needs confirmation with real matrices at pilot scale and at actual concentrations found in the water bodies (ng L^{-1} to $\mu\text{g L}^{-1}$ range). Caution should be taken with the by-products, especially the release of F^- ions, whose concentration need to respect regulations.

4.5. Activated carbon regeneration: application to effluents with low pollutant concentration

Activated carbon (AC) is a widely used adsorbent. Once the material reaches its maximum adsorption capacity, an optimal treatment aims at allowing (i) desorption of pollutants and regeneration of AC for reuse and (ii) degradation and/or mineralization of desorbed pollutants for avoiding any environmental contamination.

The EF process recently appeared as a promising technique for achieving both objectives (Trellu et al., 2018). The concept is based on the use of AC as cathode during the regeneration step. Electrochemically-enhanced desorption is ascribed to electrostatic interactions between the cathodic material and negatively charged compounds (Xiao & Hill, 2019). Local alkaline

pH conditions at the cathode favor the presence of negatively charged organic compounds under deprotonated form (**Fig. 4**). Oxidant species can also participate to the regeneration of the material by oxidation of adsorbed pollutants into more hydrophilic by-products (Trellu et al., 2018; Xiao & Hill, 2019). Oxidation of organic compounds in the bulk solution is also an important phenomenon that enhance pollutant desorption by the continuous shift of adsorption equilibrium (Trellu et al., 2021) (**Fig. 4**). The role of these different pathways strongly depends on the nature of the AC material (fiber, monolith, packed bed of grains, chemical composition, pore size distribution), which has an influence on reactivity of the material (e.g., H_2O_2 production), ohmic drops within the material (particularly for thick AC filters) and mass transport conditions during the electrochemical desorption.

It was reported that the EF process allows for near complete degradation and mineralization (91%) of desorbed pollutants using AC fibers cathode and phenol as pollutant. Moreover, oxidation of the AC surface might be avoided by a protection effect from cathodic polarization (Banuelos et al., 2015). Therefore, it is possible to reuse AC for several cycles with low effect on the adsorption capacity (Trellu et al., 2018). This application of the EF process allows for achieving high current efficiency, since adsorption represents a pre-concentration step that reduces mass transport limitations. For example, a MCE of 35% and an energy consumption of 0.2 kWh per gram of TOC removal were reported by Trellu et al. (2018). A crucial challenge is now related to the process scale-up and its implementation in continuous operation mode.

4.6. Hydrogen production

Decarbonization strategies are being considered to limit global warming, including an energy transition plan and electrification of society, which is the forecast to lead to the advent of the hydrogen economy. Hydrogen could become the energy vector of the future, replacing

combustion engines to decrease toxic emissions (Kumar et al., 2020). Although the hydrogen production is not a complete eco-sustainable process, it could reach lower prices if it is coupled to renewable energies and water treatment processes. This process is relevant because it favors the green hydrogen production systems, while that, significant innovations could be generated when anodic reactions could receive more relevance, for example:

- i) Cathodic H₂ production coupled to direct or mediated oxidation of organic pollutants or wastewater by using divided reactors (Santos et al., 2020a). Therefore, H₂ evolution would become a value-added side-reaction. Other sources of green H₂ production, not addressed here, are biofuel cells, photoelectrochemical cells and so on,
- ii) Cathodic H₂ production coupled to H₂O₂ electro-generation at a large O₂-overpotential anode like BDD, as in EF approach.

Since the hydrogen production and EF usually need electrode materials having different electronic structures to satisfy the requirement of different reactions, the combination of the two reactions has been scarcely done. Therefore, it is a great challenge to couple both the processes for an efficient production of hydrogen and the green degradation of organic pollutants.

Wang et al. (2021a) developed an electrolyzer using CoP/C cathode for H₂ production and CoFeP/C anode for methylene blue degradation (**Fig. SI-3**). This process need about +1.68 V, which was the result of coupling H₂ evolution reaction (HER) and EF, increasing greatly the energy utilization than the water splitting. The potential distribution on the electrode and the H⁺ concentration gradient in the reactor were evaluated by numerical simulation, optimizing the electrode shape and determining the influence of diffusion transport on the reaction. On the other hand, the HER over-potential decreased 3.3 mV at 10 mA cm⁻², while the EF was

improved in 2-folds, in terms of efficiency, by using a flow-reactor, demonstrating the potential of flow-reactor for various applications.

4.7. Flow-through reactors in EF process

The electrochemical reactions take place on the electrode surface, on which the electrons and mass transfer of pollutants is important for efficiently removing pollutants. Recent works have found that flow-through EF reactors have more obvious advantages than traditional batch reactors in terms of H_2O_2 production and pollutant degradation (Moraleta et al., 2020). In the former case, the solution flows through electrodes, enhancing the mass-transfer and current efficiency, and thus promoting the degradation of pollutants (Ma et al., 2016). Gao et al. (2015) used a flow-through EF reactor with carbon nanotube (CNT) membrane stack as the cathode to treat oxalic acid solution, demonstrating that the degradation efficiency for oxalic acid was 4-folds than the combined degradation efficiency of anodic oxidation and Fenton process. Image of the 4 layered membrane stack and role of each layer is provided in **Fig. SI-4**.

The commonly used anodes in flow-through reactor are perforated Ti sheet (Liu et al., 2020b), dimensionally stable anode (DSA) (Ma et al., 2016) and BDD (Moraleta et al., 2020). Trellu et al. (2020) synthesized a sub-stoichiometric titanium oxide reactive electrochemical membrane anode with a mineralization efficiency of 67% for paracetamol. Carbon felt and carbon nanotubes are commonly used as cathodes. Liu's research group focused on the cathode modification for flow-through reactor, including Au nanoclusters CNT, and FeOCl modified CNT (Li et al., 2020b). After 120 min treatment, the degradation efficiency of 0.04 mM tetracycline was 92.1% at the rate constant of 0.056 min^{-1} .

Flow-through EF process has been widely used to treat heavy metals, dyes, antibiotics and domestic sewage (Jiao et al., 2020b; Zhang et al., 2018). Zhou's group built a novel stacked flow-through EF reactor to treat domestic sewage (Ren et al., 2019), fulfilling the sulfadiazine

removal and disinfection in domestic sewage simultaneously with a very low energy consumption (0.21 kWh m^{-3}) due to higher H_2O_2 yield ($4.41 \text{ mg h}^{-1}\text{m}^{-2}$).

4.8. EF process with orbiting electrodes reactor

As previously stated, the electrochemical reactor design is a key factor to improve the efficiency of the EF processes as well as the possibility to scale up the treatment technology. For this reason, different groups have investigated different alternatives for the electrochemical devices. Among the most interesting contributions, Zahrani and Ayati ([2020a](#), [2020b](#)) have reported the use of a nanocatalyst in a novel reactor with orbiting electrodes. In this case, the performance of EF process was significantly improved by using the heterogeneous approach. The EF reactor was constructed with cylindrical plexiglass with graphite electrodes, in which 4 anodes were placed around the main container, and 4 cathodes were putted in the middle using a rotating mechanical stirrer. The orbital speed of the electrodes in the center was adjusted. The described arrangement allows to decrease the effects of the mass transport due to the agitation flow in one direction as well as to reduce the diffusion layer. The results clearly evidenced that the treatment of organic compounds was suitable over a wide range of pH, and is able to eliminate 90% of organics without adjusting the pH of the effluent. The authors also showed the reusability of zeolites-based nanocatalyst, and the lower energy requirements due to the use of orbiting electrodes, allowing to develop an eco-friendly EF system. It is important to remark that orbiting electrodes enhanced the diffusion of the in-situ generated $\cdot\text{OH}$ and H_2O_2 , favoring an efficient elimination of the organics.

5. Modified EF Processes

5.1. Three dimensional EF (3D-EF) process

Two-dimensional electrode commonly used in EF process has disadvantages such as slow mass-transfer rate, small treatment capacity and low current efficiency. To overcome these drawbacks, the so-called 3D-EF (Robles et al., 2020a) has been developed, in which a number of particles are filled in between the traditional two-dimensional electrodes. The particles are polarized to form countless microelectrodes, (that is, the end of the particle facing the cathode is positively charged and the other end facing the anode is negatively charged) which further leads to additional electrochemical redox reactions in the system. The 3D electrode activates H_2O_2 to generate $\cdot\text{OH}$, thereby achieving efficient degradation of organic pollutants. The 3D-EF increases the specific surface area of the working electrode, shorts the pollutant transfer distance, which improves the mass-transfer efficiency and current efficiency.

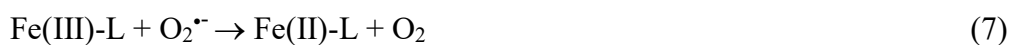
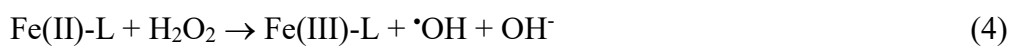
At present, the manufacture of 3D electrodes with high catalytic activity, including the common activated carbon, foamed nickel, foamed iron, iron-carbon and, so on, is a research hotspot. Ghanbarlou et al. (2020) synthesized a nitrogen-doped graphene-iron based electrocatalyst and used it as a 3D electrode, confirming that nitrogen doping improved the oxygen reduction activity, and the presence of iron promoted heterogeneous EF reactions. To reduce the catalyst dosage and to improve the treatment efficiency, Du et al. (2020b) synthesized $\text{Fe}/\text{Fe}_3\text{C}@PC$ catalyst, in which the micro-electrolysis of Fe^0 and porous carbon were the key to improve the activity though the catalyst dosage was only one tenth of that reported in literature.

The 3D-EF process has broad application prospects in wastewater treatment to remove dyes, pesticides, antibiotics, landfill leaches and so on. For example, Lu (2021) used an aged-refuse bioreactor combined with 3D-EF to treat aged landfill leachate, achieving the removal rate of 96.2%, 94.3%, 99.2% and 93.6% of COD, $\text{NH}_3\text{-N}$, total phosphorus and color, respectively.

5.2 Chelate-EF process

As mentioned in the previous sections, EF has been typically performed at pH 3 using Fe(II) or Fe(III) salts dissolved in the solution/wastewater. The pH limitation to acidic values is related to the speciation of Fe(III) ions in the solution, which precipitate at pH values higher than 4 due to progressive Fe(III) hydrolysis entailing the formation insoluble species. The acidic operating pH of EF is an important limitation representing additional treatment costs related to acidification/neutralization steps, as well as Fe sludge management, even if very less amount is generated.

In order to expand the operational pH to near-neutral values, chelating agents have been used (Zhang & Zhou, 2019; Krishnan et al., 2022). Such compounds possess the ability to form stable Fe-complexes in solution over a wide pH range, since the stability constants of such coordination compounds are higher than those of Fe-hydroxide species. In addition to the stability of Fe-complex in a wide pH interval, their Fenton-like reactions with H₂O₂ are generally faster than the conventional Fenton reaction, which accelerates the degradation of organic pollutants (Deng et al., 2018). Such behavior is explained by the greater ability of Fe-complexes to facilitate electron transfer from Fe²⁺ due to the presence of the ligand, which tends to lower the standard reduction potential of the complex. Fe-complexes produce •OH and other oxidizing species through a Fenton-like mechanism, which can be represented by the general reactions depicted in Eqs. 4-7.



Different organic and inorganic compounds have been used as chelating agents in neutral pH as can be seen in **Table SI-2**. The most common organic compounds include aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA) and ethylenediamine-N,N'-disuccinic acid (EDDS), while polyphosphates have been the most used inorganic ligands (Deng et al., 2018; Krishnan et al., 2022). The advantage of inorganic ligands like polyphosphates is that they do not act as $\bullet\text{OH}$ scavengers unlike organic chelates (EDTA and EDDS) (Deng et al., 2020). Finally, the reduction of Fe(III)-complexes to regenerate Fe(II)-complexes involves several mechanisms (**Fig. SI-5**), that are determined by the chemical properties of the ligands such as orbital hybridization, spin state of the metal ions and functional groups. Such mechanisms include electrochemical reduction at the cathode surface by direct electron transfer or through introduced atomic H^* , and chemical reduction in the bulk solution (Liu et al., 2020c).

In addition to their ability to form stable Fe-complexes in solution at near-neutral pH values and accelerate the Fenton reaction, some organic ligands have also been used as reductants to enhance Fe^{2+} regeneration. In the case of EF, the cathodic electrochemical reduction of Fe^{3+} to Fe^{2+} is a major feature ensuring continuous Fe^{2+} regeneration. However, some efforts have been made to boost such important catalyst regenerative process including the use of electrode surface functional groups or mediators to enhance Fe^{3+} reduction (Liu et al., 2021).

5.3. Self-powered EF process

The developments of self-powered EF process aims at (i) decreasing operating costs, (ii) decreasing environmental footprint of the process and (iii) promoting the application of the process in areas with limited access to the electricity grid (Ganiyu et al., 2020; Ganiyu & Martínez-Huitle, 2020).

The first approach is to use conventional renewable energy (RE) sources such as solar photovoltaic (PV) energy or wind turbines as power source. RE can be used for directly powering the EF process. Solar PV cells have been the most widely used (Ganiyu et al., 2020). The main advantage of this configuration is its ease of implementation (Garcia-Segura & Brillas, 2014). However, the level of current supply is difficult to control since it depends on solar irradiation. The implementation of batteries is required for avoiding such intermittent energy supply (Zhang et al., 2016). However, these batteries must be able to provide the required energy of the EF installation (in terms of capacity and power) and they represent an additional cost to take into consideration. Besides, the use of triboelectric nanogenerators has been recently proposed as a new energy source for powering EF process (Tian et al., 2020b).

Another approach is based on the production of energy directly from the reactor, without external power supply. These reactors are based on the development of microbial fuel cells (MFCs) or photocatalytic fuel cells (PFCs). For MFCs, the anode is used as final electron acceptor by microorganisms, which can participate to biodegradation of organic compounds (Santoro et al., 2017). The EF process is usually implemented in the cathode chamber where H_2O_2 is electrochemically generated and subsequently activated to $\cdot\text{OH}$ through Fenton or Fenton-like reactions. Photo-active anodes are used for implementation of PFCs (instead of bioanodes for MFCs) (He et al., 2022). When it is irradiated by a UV or visible light source, these photo-active anodes allow for the release of electrons by photo-excitation as well as the oxidation of organic compounds by reactive oxygen species generated from excited holes formed by photo-excitation (Ganiyu et al., 2020). Implementation of the EF process in the cathode chamber allows for improving the removal of organic compounds in the so-called PFC-EF process (Zhao et al., 2017). The main current limitation of these so-called MFC/PFC-EF processes is the low current density and power density that can be obtained. Thus, much slower degradation kinetic is usually reported for MFC/PFC-EF processes, compared to conventional

EF process. For example, it was reported 95% decolorization of Rhodamine blue and 90% TOC removal in 12 h of treatment by MFC-EF process (Zhuang et al., 2010). Some studies have also reported the use of MFCs and PFCs for generating electricity and powering ex-situ the EF process (Zhu & Logan, 2013).

5.4. Pulsed current EF process

The concept is based on the implementation of “on-off” cycles for powering the EF process. The objective is to maintain process effectiveness, while decreasing energy consumption. For example, similar COD removal was obtained by Thanapimmetha et al. (2017) when using pulsed current with a 2.5 kHz pulse frequency (and 25% “on” mode), compared to constant DC supply (Thanapimmetha et al., 2017). However, the process is different from conventional EF treatment, since a sacrificial iron anode was used as iron source and H_2O_2 was externally added.

Arellano et al. (2020b) recently proposed a slightly different approach based on the use of bi-electrical current. Two different currents were applied sequentially during the treatment. Two modes were compared: 600 mA during 30 min - 50 mA during 60 min (600, 50) and *vice versa* (50, 600). Similar TOC removal rate was obtained in both cases, but energy consumption was much lower in the first case (600, 50). In fact, at 600 mA, the formation of $\cdot\text{OH}$ in the bulk solution reached a maximum after 30 min of electrolysis and then continuously decreased with time, most probably because of parasitic reactions.

Farhat et al. (2018) have also shown the suitability of an intermittent current supply for the oxidation of organics at a BDD anode. In this study, the current was switched on during 5 min and switched off during 15 min. When sodium sulfate was used as electrolyte, they observed that the target pollutant (diatrizoate) was also degraded within 15 min without current supply. For a similar degradation yield (90%), the use of such intermittent current supply allowed for

decreasing energy consumption by 36%. These results were explained by the role of electrochemically activated sulfate in radical chain reactions after switching off the current.

5.5. EF with reactive membrane bioreactor

Carbon-based membranes have also been used in membrane bioreactors (MBR) to control membrane fouling (caused by organic compounds) through $\cdot\text{OH}$ radicals formed by EF process. For this, two approaches have been explored. In the first case, two electrodes are placed inside the MBR, including a carbonaceous cathode producing H_2O_2 , which decomposes in the presence of Fe^{2+} in the solution. In this system, $\cdot\text{OH}$ assist the degradation of organic matter by the microorganisms, which also contribute to the decrease of membrane fouling (Jia et al., 2015). Since the electrodes are in contact with the wastewater mixed with activated sludge, $\cdot\text{OH}$ also induce cell damage and modifications to the microbial communities with beneficial effects for pollutant removal.

In the second approach, the filtration unit also serves as an EF cell that functions as an anti-fouling system. For this purpose, carbon-based membranes such as carbon nanotube hollow fiber membranes loaded with Fe^{2+} ions were used as both cathode and filtration materials (Trellu et al., 2020). Such EF-MBR reported by Yang et al. (2020) achieved 93% and 88% of COD and NH_4^+ removal, respectively, in 100 days at a hydraulic retention time of 8 h. During the EF membrane recovery phase, the initial transmembrane pressure was retrieved due to the efficient fouling control effect entailed by $\cdot\text{OH}$ produced by the EF reactions.

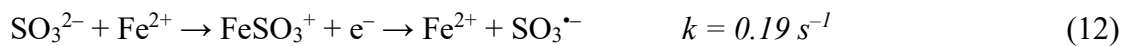
6. Coupling with other processes

The efficiency of the EF process can be significantly enhanced by coupling with other wastewater treatment techniques. Most of these technologies are performed simultaneously

with EF with the aim of enhancing the regeneration of Fenton's reagent or concurrent production of additional reactive species.

6.1. Coupling of EF with sulfite/sulfate radical

EF-sulfite and EF-SR-AOPs involve simultaneous activation of sulfite and peroxide precursors (persulfate (PS) and peroxomonopersulfate (PMS)) during EF process by the same catalyst used in the EF process and partial activation at electrode surface. The mechanisms of reactive species generation in these coupled technologies are summarized in Eqs. (8–13) (Ganiyu et al., 2021b).



EF and photoelectro-Fenton (PEF) coupled with PMS was reported for the treatment of real washing machine wastewater (Ghanbari & Martínez-Huitle, 2019). Fe_3O_4 nanoparticles used for simultaneous activation of H_2O_2 and PMS to $\bullet\text{OH}$ and/or $\text{SO}_4^{\bullet-}$ and $\text{SO}_5^{\bullet-}$. UV light accelerated the process efficiency by generating more reactive species via PMS activation and Fe^{2+} regeneration, achieving 97.1% TOC removal efficiency at optimum conditions. EF-sulfite process using FeC (Song et al., 2021) also exhibited enhanced degradation of carbamazepine compared to EF. Reactive species $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ were generated by FeC/ Fe^{3+} catalytic and/or electrocatalytic activation of SO_3^{2-} and H_2O_2 . EF-sulfite using pyrite modified carbon felt (FeS_2/CF) was reported for the degradation of anthracene over pH 3 – 9 (Chu et al.,

2020). Enhanced degradation of anthracene was achieved by FeS₂/CF (85.9%) compared to anodic oxidation with CF alone (34.0%), and EF (75.3%) at pH 3 and 10 mA cm⁻².

6.2. Coupling with photoelectrocatalysis

Photoelectrochemical–EF is a self-powered system where electricity generated by photocatalytic fuel cells (PFCs) is utilized to power EF process (Ganiyu et al., 2020). PFCs involve photo-excitation of electrons at the photoactive anode surfaces, creating excited holes that interacts with H₂O/OH⁻ to produce [•]OH/O₂^{•-} and excited electrons that reduces O₂ to H₂O₂ (Bai et al., 2016). PECs–EF coupled photocatalysis using photoanode/cathode and EF was reported to degrade various classes of pollutants (Mousset & Dionysiou, 2020).

PEC-PEF using Pt-decorated TiO₂ photoanode and air diffusion PTFE cathode was reported to enhance degradation efficiency of organic pollutants and textile dye with TOC removal efficiency following the sequence PEC (80%) < EF (87%) < PEC-PEF (97%) (Almeida et al., 2015). Nordin et al. (2017) utilized PFC-EF for the degradation of Reactive Black 5 using ZnO/Zn photoanode, which achieved 84.6% dye removal efficiency with 15.37 mW cm⁻² power output.

6.3. Coupling with ultrasound (sono-EF)

Sonolysis utilize ultrasound irradiation to generate [•]OH via water pyrolysis. Sonolysis/ultrasound assisted EF (sono-EF) involves sonication of EF system. Therefore, additional H₂O₂ and [•]OH are generated by sonolysis (Eqs. (14 and 15)) in addition to [•]OH of formed through Fenton reaction (Menon et al., 2021).



Accelerated destruction of 4,6-dinitro-*o*-cresol and 2,4-dichlorophenoxyacetic acid was achieved by sono-EF compared to EF, whereas no improvement was observed for the degradation dye azobenzene (Oturán et al., 2008). Enhanced degradation of 4-chlorophenol was reported for sono-EF, achieving >99.9% removal compared to 83% and 1.85% obtained with EF and sonolysis alone (Nazari et al., 2018).

6.4. Bioelectro-Fenton process

BEF process couples MFCs with EF. There are two configurations of BEF in literature: i) MFCs–in-situ EF, where EF operates at the cathode chamber of the MFCs and (ii) MFCs–ex-situ EF, where external EF reactor is powered by MFCs (Ganiyu & Martínez-Huitle, 2020; Ganiyu et al., 2020). Enhanced medicinal herbs wastewater remediation was reported in a continuous flow BEF equipped with Fe@Fe₂O₃/graphite plate cathode, achieving up to 93% COD removal (Birjandi et al., 2020). Coal gasification wastewater was treated by BEF using FeVO₄/CF cathode with maximum power output of 849.7 mW m⁻³ and 91.5% TOC removal efficiency obtained at pH 7 (Xu et al., 2018). A second type BEF consists of sequential coupling between EF (as pre-or post-treatment step) and biological degradation (Olvera-Vargas et al., 2016a, 2016b; Ganzenko et al., 2018).

6.5. Ferrate-EF process

Recently, a new and promising hybrid process by a coupling between EF and ferrate was described (El Kateb et al., 2021). This coupling is based on selective oxidation of organics by ferrate and strong mineralization power of the EF. The use of ferrate as a pre-oxidation step followed by EF treatment led to an effective removal of paracetamol as well as the acute toxicity of treated solution. The recycling of iron from ferrate oxidation step as catalyst for EF process constitutes an interesting future of this coupling. Thus, the coupling of EF with a pre-

oxidation by ferrate appears as a promising combination for an effective treatment of wastewater contaminated by persistent organic pollutants.

6.6. Synergy effect of EF coupled AOPs processes

The synergy effects of PEF and SPEF occur as a result of regeneration of Fe^{2+} (one of the components of Fenton's reagent) beside production of $\cdot\text{OH}$, which can catalyze the Fenton reaction (Brillas et al., 2009). Light irradiation used in PEF and SPEF also enhance the mineralization of organic complex (Garcia-Segura & Brillas, 2014). Sono-EF generate H_2O_2 leading then to the formation of $\cdot\text{OH}$, which also accelerates the Fenton reaction (Menon et al., 2021). Photo-electrocatalysis coupled with EF (PEC-EF) and PFCs-EF combine generation of additional oxidants via both photocatalysis and photoelectro-Fenton processes to compliment the EF process. The synergy effect of EF-sulfite/SR-AOPs is due to the production of additional oxidants as well as in-situ regulation of pH (sulfite and peroxymonosulfate lowers the pH of solution to acidic range at which EF is optimum) (Song et al., 2021).

6.7. Economic prospect and challenges of coupled processes

PEF, PFCs-EF, PEC-EF and sono-EF have high operating cost compared to EF alone, which includes maintenance and energy consumption of UV-lamp or ultrasound use for the irradiation/ultrasonication. However, using natural sunlight (solar energy) source as in SPEF process minimize the energy and operating cost of PEF, thus SPEF and solar powered PFCs-EF/PECs-EFs are technically and economically more effective compared to EF alone. For example, energy consumption during PEF and SPEF treatment of Acid Blue dye solution 29 at 50 mA cm^{-2} was 257 and 57 kWh (kg TOC^{-1}), respectively, demonstrating the effectiveness of SPEF (Salazar et al., 2019).

7. Emerging Applications of EF process

7.1. Disinfection

Electrochemical disinfection is an emerging field in electrochemical treatment of water and wastewater and is found to be a cost effective alternative for conventional chlorination or ozonation (Martínez-Huitle & Brillas, 2021; Srivastava et al., 2021). Inactivation of *Escherichia coli*, somatic coliphages, heterotrophic bacteria, enterococci, *Clostridium perfringens* spores, eukaryotes (amoebae, flagellates, ciliates and metazoa) (Anfruns-Estrada et al., 2017), *helminth eggs* (HE) (Robles et al., 2020b), antibiotic-resistant bacteria and antibiotic resistance genes (Chen et al., 2020) by EF process was reported recently. Lysis of cell walls by the attack of oxidants generated via electrochemical reactions is the main disinfection mechanism proposed. Reactive oxidant species inactivate the microorganisms via direct attack of cellular membrane, by reducing cells viability and by attacking intracellular biomolecules after diffused into the cells (Valero et al., 2017). Apart from the attack of reactive oxidant species, electric field is also able to inactivate the microorganism via oxidation effect of intracellular coenzyme A (Matsunaga et al., 2000) or by causing permanent pores generation on microbial cells, imparting irreversible permeability by destabilizing cytoplasmic membrane, and by destructing chemical gradients (Kourdali et al., 2018).

Even though, EF process is very effective for the disinfection of microorganisms, its application for the disinfection of drinking water supply is not advisable due to (a) inefficiency of EF process for providing residual protection of drinking water during water supply due to the short lifespan of $\cdot\text{OH}$, (b) addition of salt is required to improve the conductivity of water (for enhancing EF process performance) and further treatment is needed for removing these added salts and (c) increased cost of treatment. However, this process is an alternative to disinfection of real wastewater (including municipal wastewater) as the wastewater contains adequate salts and the EF process is able to disinfect the wastewater while removing the pollutants.

7.2. Generation of value-added products

EF oxidation is able to produce biofuels and biochemicals from lignin (Zhang et al., 2021b), glucose from cellobiose (Keller et al., 2021), and renewable biopolymers from potato starch (Dang et al., 2019); as well as able to recover phosphorous from sludge (Burgos-Castillo et al., 2018). Lignin degradation during EF treatment resulted in the generation of 23 by-products and at the optimal operating conditions, which aimed for the optimal production of long-chain fatty acids yielded 138.41 mg g⁻¹ of palmitic acid and 112.31 mg g⁻¹ of octadecanoic acid (Zhang et al., 2021b). Chelate-EF process is able to produce thermally stable biomaterial from potato starch and the produced materials have carbonyl and carboxyl contents of 0.81 per 100 anhydroglucose units (AGU) and 0.79 per 100 AGU, respectively (Dang et al., 2019). The biomaterial produced from potato starch have higher viscosity and the production was controlled by molar ratios of iron-citrate complex to H₂O₂.

Controlling of Fenton oxidation is a challenge for improving the yield of required value-added product. Non-selective attack of [•]OH is the main hurdle to optimize the production of targeted compound. For example, glucose produced from cellobiose further undergoes oxidation and converted to organic acids, aldehydes or may be mineralized (Keller et al., 2021). Keller and co-workers coupled EF process with layer-by-layer nanofiltration process to improve the yield of glucose. The used membrane system is able to retain 80-90% of iron and cellobiose, (which enhances the effective oxidation of cellobiose), while allowing glucose to permeate through the membrane. Thus, EF process is able to produce glucose from cellobiose near to its highest possible production (25%) after coupling with nanofiltration units.

7.3. Degradation of emerging micropollutants

Treatment of emerging micropollutants from water medium is a great challenge due to its recalcitrant nature, toxicity and imperceptible concentration. These chemicals are not included

in regulatory standards and their limiting concentration in any environmental matrices, and their effect on ecology and human health are still not very clear. Their presence in water treatment plant (Tran & Gin, 2017) and wastewater treatment plant (Mailler et al., 2016) reveals the inability of conventional water and wastewater treatment process to treat such pollutants and AOPs are found as an essential treatment units required for treating such toxic compounds (Scaria et al., 2021).

EF process is found to be effective for treating various types of emerging pollutants (**Table SI-3**). Higher pollutant degradation and mineralization efficiency of EF process for wide range of pollutants including cefazolin (Heidari et al., 2021), monolinuron (Diaw et al., 2020), clopyralid (Santos et al., 2020b), sulfamethazine (Sopaj et al., 2020), and chloroquine (Midassi et al., 2020) indicates the adequacy of EF process for treating emerging pollutants. EF process using BDD anode was found more effective than EF process using Pt anode (Oturán et al., 2013) and even than anodic oxidation process. Ability of BDD to generate persulfate and sulfate radicals from electrolyte containing sulfate ions (Divyapriya & Nidheesh, 2021) in addition to $\cdot\text{OH}$ generation via Fenton reaction and anodic oxidation of water, enhanced the efficiency of EF process significantly (Midassi et al., 2020). The enhancement in treatment efficiency of EF process, further improved by coupling with other process such as anodic photo-electrochemical oxidation (Orimolade et al., 2020; Titchou et al., 2022), photo-EF (Ye et al., 2020; Espinosa-Barrera et al., 2021) and sono-EF (Hasani et al., 2020). For example, cefixime removal efficiency of EF process and sonication was reported as 81.7% and 9%, respectively, against 97.5% removal efficiency of sono-EF process (Hasani et al., 2020).

Biodegradability enhancement and toxicity reduction are the main advantages of EF process for the treatment of emerging pollutants. EF treatment of a complex pharmaceutical mixture containing 13 pharmaceutical compounds resulted in a strong biodegradability enhancement within 3 h of treatment (Ganzenko et al., 2020). This enhanced biodegradability is mainly due

to the formation of intermediates and by-products during EF treatment as mentioned in **Table SI-3**. Toxicity test using *Escherichia coli* and *Staphylococcus aureus* for the synthetic wastewater containing cefixime antibiotic and sono-EF treated wastewater indicated the toxicity reduction during EAOPs treatment (Hasani et al., 2020). Similar results were observed by Orimolade et al. (2020), with *Vibrio fischeri* growth inhibition test. However, intermediate and by-products generated during EF treatment may be more toxic than parent compound(s). This behavior was observed for the treatment of pharmaceutical mixture (Ganzenko et al., 2020) where the biomass took more time to acclimatize with EF treated solution. Therefore, toxicity must be removed after EF treatment of emerging pollutants and before further biological treatment or disposal process.

8. Conclusions and perspectives

Since the publication of pioneer works in the early 2000s, the EF process has continued to develop and become one of the most powerful EAOPs for removing biorecalcitrant organic/inorganic pollutants from water/wastewater. First, concerning electrode materials, the use of non-active anodes in an EF undivided cell, such as BDD or sub-stoichiometric TiO₂, enhanced significantly the efficiency of the EF process by generating supplementary •OH at the anode surface. Although carbon-felt and GDE remain the main cathode materials, modified carbonaceous electrodes have been developed to enhance H₂O₂ generation, or incorporate iron oxides as catalysts into the cathode surface for heterogeneous EF. In fact, some of the main disadvantages of the process (acidic pH around 3 and loss of the catalyst in treated effluent) have been overcome by using solid catalysts in heterogeneous EF. Second, several EF variations have been developed to increase the efficiency and its applicability, such as 3D-EF, chelate-EF, self-powered EF, pulsed-current EF, etc. Third, different hybrid processes like sono-EF, photo-EF, bio-EF, and ferrate-EF have been proposed to reduce treatment costs or enhance the mineralization power of the process.

At the current state, the EF process stands out as a promising sustainable technique for the treatment of toxic/persistent organic/inorganic pollutants in contaminated water. Currently, bench-scale studies have considerably progressed, including optimization of operating parameters and reactor design. The next challenge is mainly related to the development of large-scale applications for smart water solutions to guarantee sustainability in the water sector, which is the premise of the Sustainable Development Goal 6 from United Nations: clean water and sanitation. To achieve such objective, the design of suitable reactors (with low cost and sustainable electrode materials) assessed with real wastewaters, and the integration with other treatment processes, are required. For field scale applications, the main challenge remains in the development of more efficient, stable and cost-effective electrodes materials along with suitable reactor design. Development of cost effective and stable anodes to replace BDD and TiOx, and new composite cathodes which incorporating iron as catalyst and allowing high H₂O₂ generation seems to be the main challenges to overcome. Further cost comparison studies, including energy consumption, will be required at large scale to better evaluate the cost effectiveness of the emerging EF-based technologies.

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Figure captions

Figure 1. Schematic diagram of EF and related processes

Figure 2: (a) Inside-electrode aeration and (b) jet aerator: 1. Funnel-like piece 2. Support Plate 3. Gasket 4. CF electrode 5. Feeder 6. Support 7. Methacrylate spacer 8. IrO₂-based anode. (a): Reprinted with permission from (Lie et al., [2020](#)). Copyright 2021, Elsevier and (Perez et al., [2018](#)). Copyright 2018, Elsevier, respectively.

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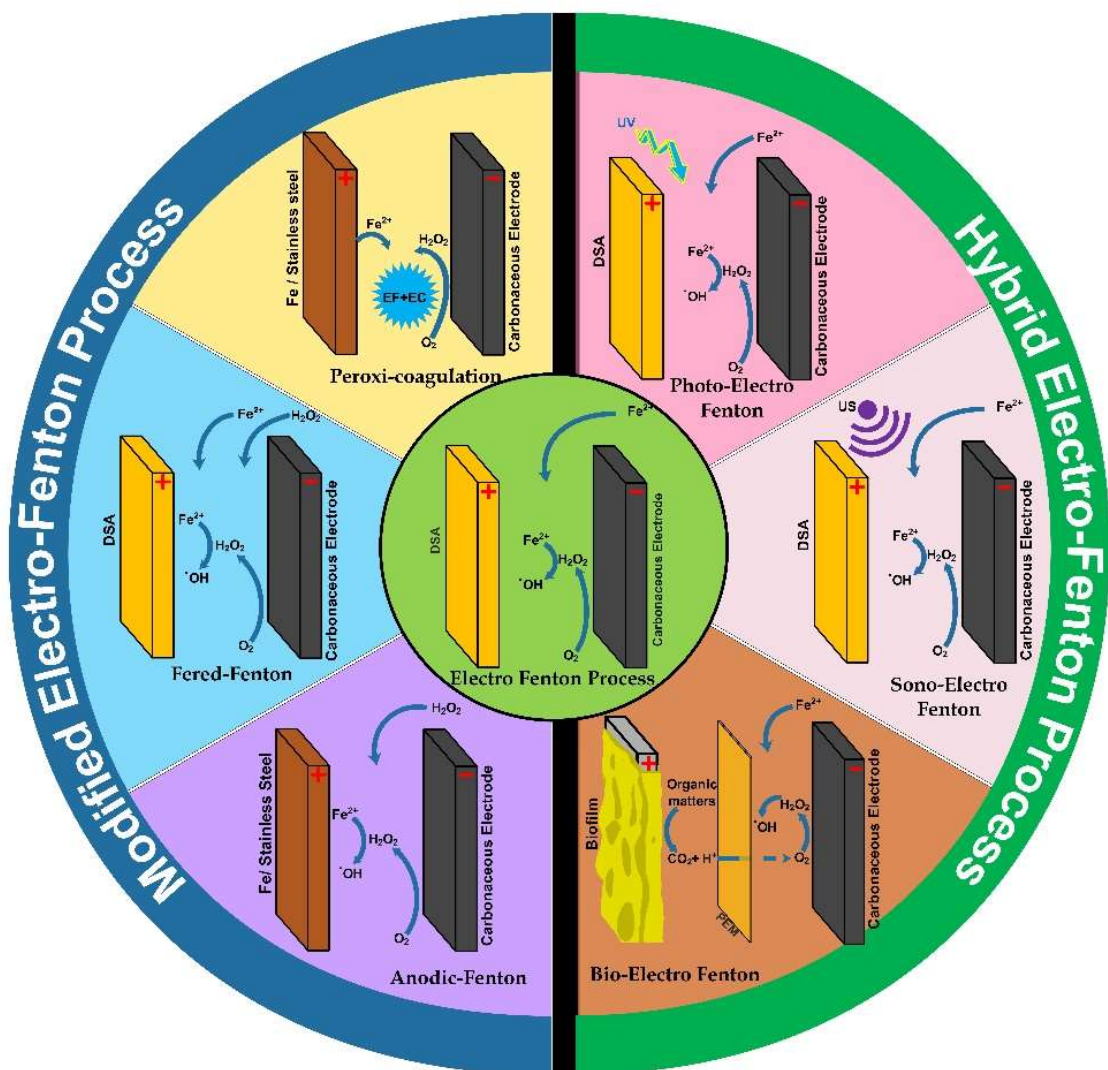


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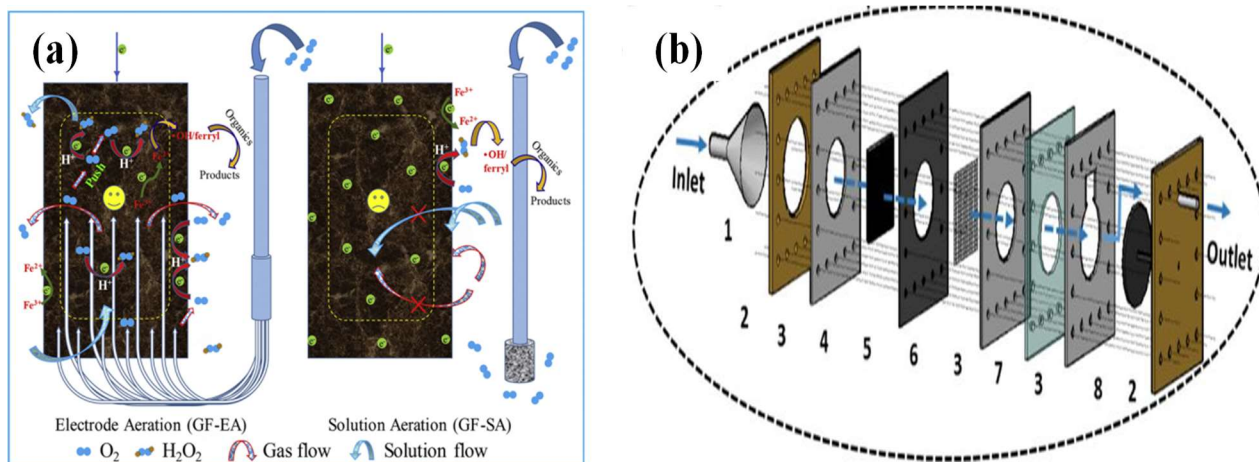


Figure 2: (a) Inside-electrode aeration and (b) jet aerator: 1. Funnel-like piece 2. Support Plate 3. Gasket 4. CF electrode 5. Feeder 6. Support 7. Methacrylate spacer 8. IrO_2 -based anode. (a): Reprinted with permission from (Lie et al., 2020). Copyright 2021, Elsevier and (Perez et al., 2018). Copyright 2018, Elsevier, respectively.

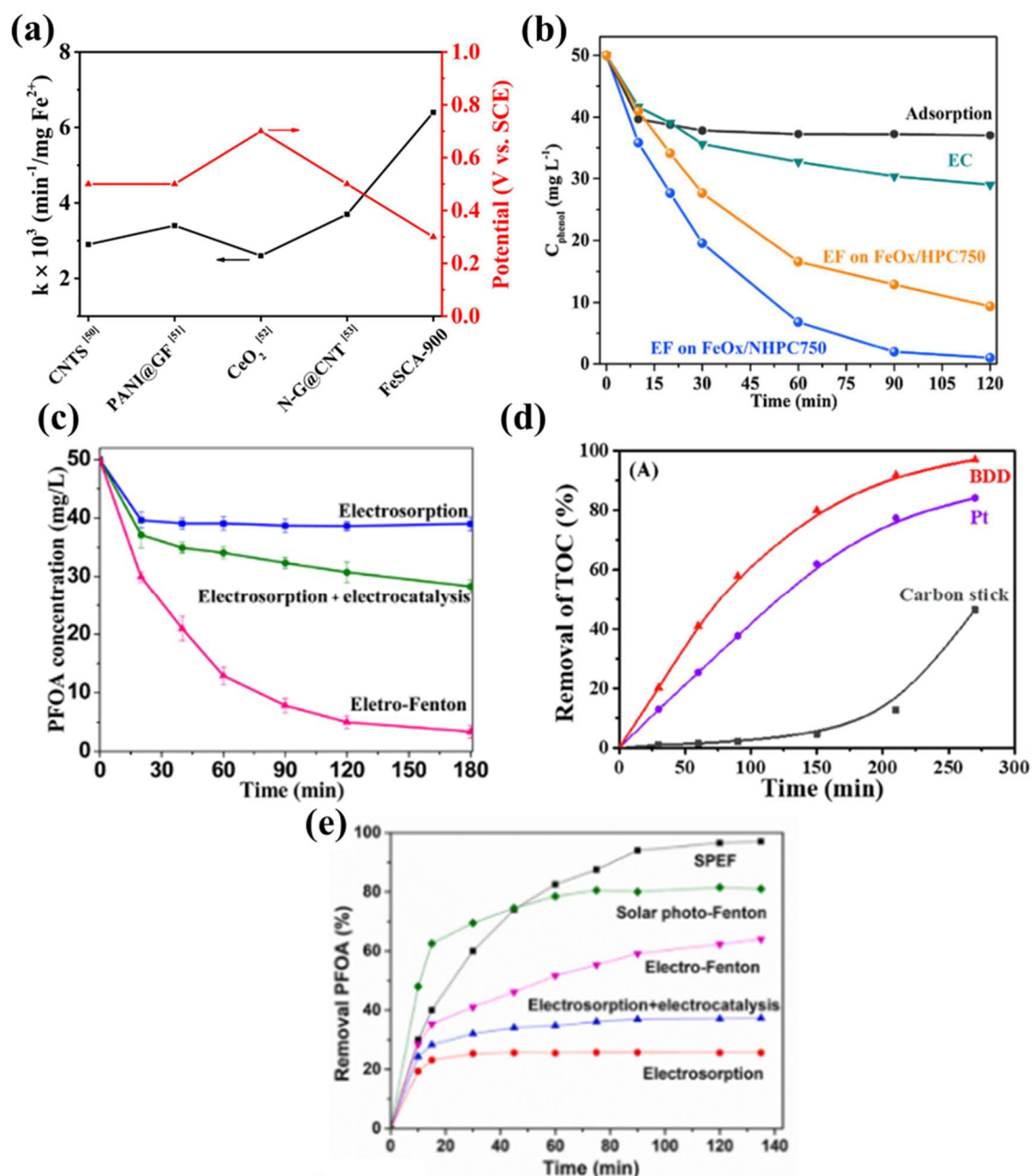


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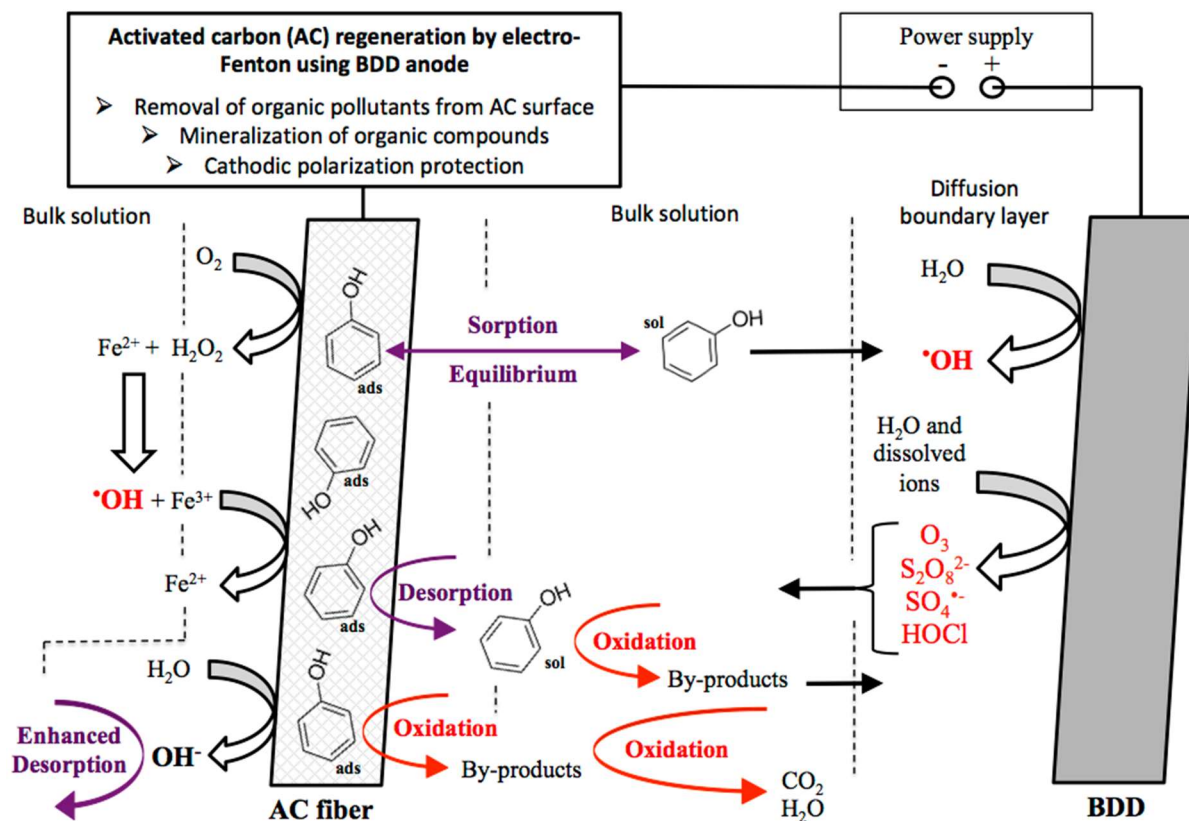


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