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A review on Efficiency and Cost Effectiveness of Electro- and Bio-electro-Fenton processes: Application to the Treatment of Pharmaceutical Pollutants in Water

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List of abbreviations

Abbreviation	Definition
ADE	Air diffusion electrode
AO	Anodic oxidation
AOPs	Advanced oxidations processes
AOS	Average oxidation state
B-EF	Biological treatment first followed by EF
BDD	Boron doped diamond
Bio-EF	Biological treatment combined with EF
BOD ₁₄	Biological oxygen demand after 14 days
BOD ₅	Biological oxygen demand after 5 days
BOD _u	Ultimate biological oxygen demand
CE	Current efficiency
CF	Carbon felt
COD	Chemical oxygen demand
CV	Cyclic voltammetry
d	Day
DOC	Dissolved organic carbon
DSA	Dimensionally stable anode
EAOPs	Electrochemical advanced oxidation processes
EC	Energy consumption
EF	Electro-Fenton
EF-B	EF first followed by a biological treatment
GDE	Gas diffusion electrode
GF	Graphite felt
h	Hour
k _{app}	Apparent rate constant
K _{ow}	Octanol/water partition coefficient
MCE	Mineralization current efficiency
MF	Micro fluidic
min	Minute
MR	Macro reactor

NSAID	Nonsteroidal anti-inflammatory drugs
NTU	Nephelometric Turbidity Unit
Pt	Platinum
PTFE	Polytetrafluoroethylene
RPM	Rotation per minute
SBR	Sequence batch reactor
SEM	Scanning Electron Microcopy
SHE	Standard hydrogen electrode
TOC	Total organic carbon
UV	Ultraviolet
WWTP	Wastewater treatment plant

Abstract:

Nowadays, the treatment of wastewater is a worldwide concern due to the large impact on the environment and human health. Among different types of pollutant, pharmaceuticals are increasingly of emerging concern, as they are generally resistant to the conventional treatment methods and harmful to the environment. Advanced oxidation processes and especially electrochemical advanced oxidation processes (EAOPs) constitute an efficient way to eliminate this kind of pollutants. Among them, the electro-Fenton (EF) process is an environmentally friendly EAOP particularly efficient to remove persistent/toxic pollutant from the water. The main drawback of this method, however, is the relatively high cost due to the energy consumption when a complete mineralization of treated solutions is required. To reduce electrical energy consumption, the combination with a biological treatment was suggested as shown by several successful studies. This review is first addressing ways to improve the degradation efficiency and to reduce the cost of the EF process, with a focus on new types of reactors: especially geometrical modifications, change of the out streaming or the O₂ supply. The continuous process is then taken into consideration in order to enable scaling-up. Secondly, the combination of the EF process with a biological treatment for efficient removal of pharmaceuticals is overviewed with focus on the cost, the treatment efficiency and the order (pre- or post-) of treatment. The efficiency of such a system is clearly demonstrated.

Keywords: Electro-Fenton; Biological treatment; Combined Processes; Pharmaceuticals; Reactors; Scale-up.

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1. Introduction

Nowadays, the treatment of pharmaceuticals has become a hot topic as they are widely consumed all over the world. A strong increase in the consumption of pharmaceuticals has been observed in the last decade. In the US, IMS Health mentioned an increase of the sales from \$152,8 to \$280 billion which represents a 83% rise between 2000 and 2006 [1]. This increase can be explained by several factors such as: (i) population growth, (ii) population ageing, (iii) discovery of new properties of already existing drugs and (iv) decreasing price of drugs as patents expire [2]. As analytical chemistry techniques improve, especially in the limit of quantification, their presence was detected in natural water thus proving their non-effective elimination by wastewater treatment plants (WWTP), since concentrations between ng L^{-1} and $\mu\text{g L}^{-1}$ were usually found in natural waters [3,4]. Indeed, in addition to the industrial and hospital effluents, these products are also released to urban wastewater whole or partly degraded after human and veterinary uses [4,5]. Pharmaceutical compounds are not efficiently eliminated by WWTP or by natural elimination processes in the environment [6]. Elimination processes occurring in a conventional wastewater treatment plant are well-described in several review papers [7]. Pharmaceuticals can be eliminated from wastewater during the sewage treatment whether by transfer to another phase or by degradation. This process can occur by biological transformation or by abiotic degradation which involves reactions such as photolysis or hydrolysis. Several review papers provide a snapshot of the removal efficiency of some selected pharmaceutical molecules achieved in WWTPs [8–10]. As it can be seen from Table 1, it is difficult to draw a general conclusion on the persistence or on the removal efficiency of each compound as many molecules are showing significantly different removal levels in different WWTP. However, these review papers conclude that the removal efficiency depends on the properties of molecules and on the design and operating conditions of WWTPs. Some pharmaceuticals, such as metoprolol, diclofenac, etc. are hardly removed by

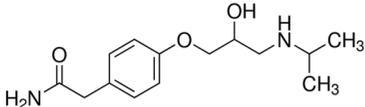
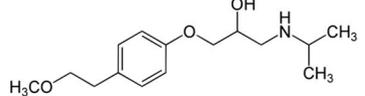
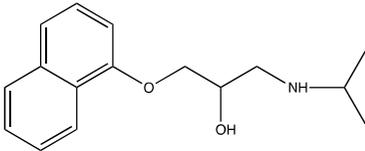
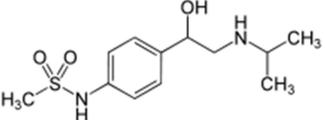
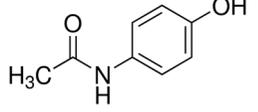
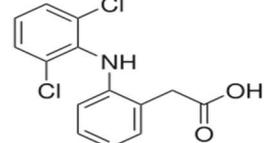
sewage treatment plants with a removal efficiency less than 40%. Other molecules such as atenolol, ketoprofen and trimethoprim are moderately removed (40-70%) whereas others (acetaminophen, naproxen, salicylic acid, etc.) are more efficiently removed (>70%). However, the percentage of removal is hardly ever equal to the degradation rate as some of the pollutants can adsorb themselves on the bacteria. This parameter can be evaluated thanks to $\log(K_{ow})$, where K_{ow} is the octanol/water partition coefficient (Table 1). To improve the removal rate, chlorination and UV irradiation are sometimes used after the biological treatment but the oxidizing power of both methods is not strong enough to degrade most of the pharmaceuticals, their metabolites or degradation products [1]. Other physical, physicochemical methods like coagulation-flocculation, activated carbon adsorption and membrane filtration can be used to remove those micropollutants, [8]. However these treatments are not eliminating the pollutants, they transfer them from one phase to another or produce the concentrates to be further treated by other methods. In order to degrade them, strong and non-selective oxidants are thus necessary.

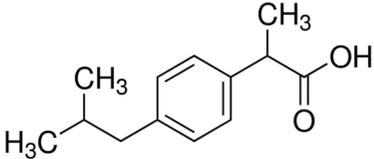
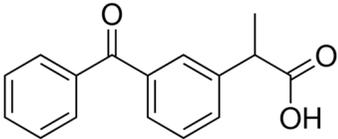
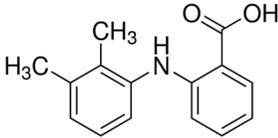
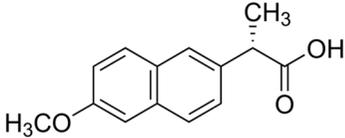
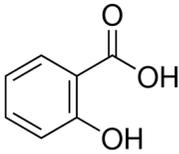
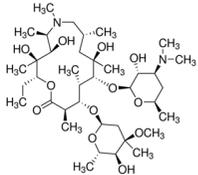
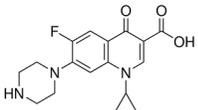
Alternatively the so-called advanced oxidation processes (AOPs) have been developed to destroy efficiently toxic and/or persistent organic pollutants [11,12]. Most of the AOPs are aqueous phase oxidation processes based on the generation of hydroxyl radicals, the second strongest oxidant after fluorine, which can destroy nearly any type of organic contaminants thanks to its very high oxidation power ($E^\circ = 2.8 \text{ V/SHE}$) [12–14]. Among different AOPs, electrochemical advanced oxidation processes (EAOPs) are of particular interest as they were shown to have a high removal efficiency and the capability to reach complete mineralization of the treated solutions [15–17]. These processes are environmentally friendly and generate a great amount of hydroxyl radicals under specific operating conditions [18]. The electro-Fenton (EF) process is one of the most popular EAOPs coupling the chemical Fenton's process to electrochemistry. It has been used successfully in the treatment of a lot of

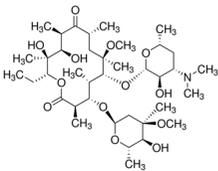
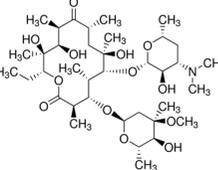
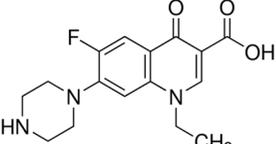
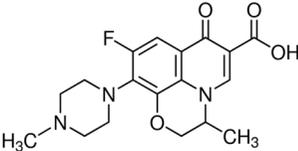
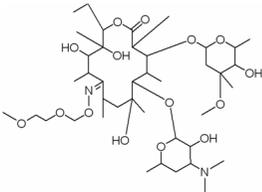
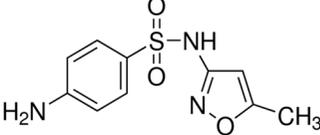
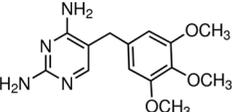
pharmaceutical active ingredients and real wastewaters [19–24]. However EAOPs becomes generally expensive when the objective is the quasi-complete mineralization of treated solutions because this operation needs longer electrolysis time leading to a significant amount of electrical energy consumption [25–27]. To reduce the operating cost and to make a cost-effective process, the combination of an EAOP with a biological treatment can be an appropriate solution by reducing the electrolysis time and by achieving the mineralization by a biological treatment [28,29].

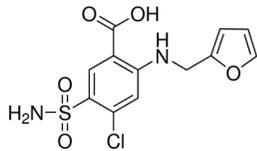
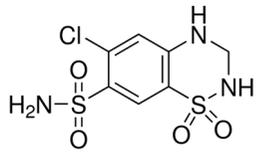
Therefore the purpose of this review paper is first to give an overview of the newest knowledge concerning the EF process and the reactor configurations and then to provide an overview on its applications to the treatment of pharmaceutical compounds. Then, the feasibility and the cost-effectiveness of the combined process bio-electro-Fenton (bio-EF) will be discussed and the whole literature about this topic will be provided.

Table 1: Occurrence and typical removal of common pharmaceuticals in WWTP

Pharmaceutical family	Molecule	Chemical Structure	Occurrence in hospital effluent ($\mu\text{g L}^{-1}$)	Occurrence in urban effluent ($\mu\text{g L}^{-1}$)	Removal in a typical WWTP (%)	Log (Kow)	Ref
β -blocker	Atenolol		0.1-200 ^a	0.15-35 ^{a*} 2.405 ^{**} : 0.99-8.38 ^b 0.1-33.1 ^d	8 \pm 5 ^c 63.4 \pm 24.4 ^d	0.16	[3,5-7,21]
	Metoprolol		0.4-27 ^a	0.025-7 ^a 0.266:0.014-0.703 ^b 0.002-1.52 ^d	10 \pm 15 ^c 37.6 \pm 26.4 ^d	1.88	[3,5-7,21]
	Propranolol		0.2-6 ^a	0.12-9 ^a 0.223:0.004-0.473 ^b	95 ^c	3.48	[3,6,7,21]
	Sotalol			0.18-3.5 ^a 1.012:0.129-3.2 ^b		0.24	[3,7,21]
	Diclofenac				1.34:0.1-4.11 ^c <0.001-94.2 ^d	36 \pm 18 ^c 35.8 \pm 23 ^d	4.51
NSAID ^f	Ibuprofen		0.07-150 ^a	0.01-350 ^a 14.6:0.170-83.5 ^c <0.004-8.56 ^d	75 \pm 30 ^c 91.4 \pm 8.1 ^d	3.97	[3,5,6,21]

	Ketoprofen			0.007-3 ^a 1.03: 0.08-5.7 ^c <0.004-8.56 ^d	39±22 ^c 51.7±23.5 ^d	3.12	[3,5,6,21]
	Mefenamic Acid			0.02-25 ^a 1.73:0.136-3.2 ^c <0.017-1.27 ^d	30±20 ^c 36.00-34.2 ^d		[5,8,9]
	Naproxen		0.6-10 ^a	0.018-27 ^a 26.4: 1.79-611 ^c <0.002-52.9 ^d	77±17 ^c 75.5±18.5 ^d	3.18	[3,5,6,21]
	Acetaminophen			1.57-56.9 ^d	99.8±0.5 ^d	0.46	[5,21]
	Salicylic Acid			0.1-75 ^a 212: 16-606 ^c 0.58-63.7 ^d	98±1 ^c 96.6±4.1 ^d		[5,8,9]
Antibiotic	Azithromycin			0.26 ^c	45 ^c		[9]
	Ciprofloxacin		0.03-150 ^a	0.007-6 ^a 0.413: 0.18-0.571 ^c	73±30 ^c		[5,9]

Clarithromycin		0.647 ^c	43 ^c	3.16	[6,21]
Erythromycin		5-80 ^a	0.045-3 ^a 0.108:0.07-0.141 ^c 0.14-10 ^d	30.2±30.1 ^d	[5,8,9]
Norfloxacin		0.03-45 ^a	0.01-1 ^a 0.438: 0.343-0.515 ^c	83±3 ^c	[5,9]
Ofloxacin		0.35-35 ^a	0.01-1 ^a	-0.39	[3,21]
Roxythromycin			0.01-1 ^a 0.0620: 0.0250- 0.117 ^c	37.5±7.5 ^c	[5,9]
Sulfamethoxazole			0.003-6 ^a 0.342: 0.02-1.25 ^c <0.003-0.98 ^d	58±22 ^c 64.6±20.4 ^d	[5,8,9]
Trimethoprim			0.02-7 ^a 0.449: 0.08-13 ^c 0.06-6.80 ^d	46.8±26.3 ^d	0.91 [3,5,6,21]

	Furosemide		0.01473 ^e	2.03	[30]
Diuretic	Hydrochlorothiazide		0.001735 ^e	-0.07	[30]

a: [5]

b: The occurrence of molecules was evaluated in fourteen rural and urban WWTP located in France [10].

c: [9]

d: [8]

e: Occurrence in a Spanish hospital effluent, measure of 25 pharmaceuticals during 5 days in June 2013 [30]

f: Non-steroidal anti-inflammatory drugs

*: minimum value-maximum value

** : mean value

2. Electrochemical advanced oxidation processes

2.1 Mechanisms involved in EAOPs

The most popular and commonly used EAOPs are anodic oxidation (AO), also called (electro-oxidation) and electro-Fenton (EF) processes. These processes belong to AOPs and are based on direct (AO) or indirect (EF) catalytic generation of $\cdot\text{OH}$ in the solution to be treated. Once generated in situ, these strong oxidizing agents will react on organic contaminants to oxidize them until their total or partial mineralization (Eqs. (1) and (2)).



These types of processes have been well-described by several reviews [12,13,16,31–33].

2.1.1 Direct oxidation (AO)

In this process the oxidation takes place at the surface of the anode. Heterogeneous hydroxyl radicals are obtained at the anode surface from the oxidation of water according to the following reaction (Eq. (3)) [34].



where M represents the anode material and $\text{M}(\cdot\text{OH})$ is the hydroxyl radical adsorbed on the anode (M) surface.

For this kind of oxidation, two different types of transfer can limit the process: mass transfer or charge transfer. Mass transfer is done by migration (driven by the electrical field), by diffusion (driven by chemical potential gradient) and by convection. It can be expressed with the Nernst-Planck equation. As it is experimentally difficult to distinguish these three processes, the mass transfer process is generally approached in a semi-empirical way under specific conditions as expressed in Eq. (4). These conditions are, i) the solution is conductive

enough (use of a supporting electrolyte), ii) the solution is well-mixed and iii) the applied potential (or current) is high enough to oxidize efficiently the substrate.

$$J_{\text{anode}} = k_m A (C_{\text{bulk}} - C_{\text{elec}}) \quad (4)$$

with J_{anode} , the current density (mol s^{-1}), k_m , the mass transfer coefficient (m s^{-1}), C_{bulk} , the concentration of pollutant in the bulk (mol m^{-3}), A , the surface of the electrode (m^2) and C_{elec} , the concentration of pollutant at the electrode surface (mol m^{-3}).

Limiting currents are reached when $C_{\text{elec}} = 0$, meaning that the applied potential (or current) is high enough. That is why in the literature J_{anode} is generally expressed as in Eq. (5).

$$J_{\text{anode}} = k_m A C_{\text{bulk}} \quad (5)$$

In contrast, when the process is controlled by the current density, this latter can be expressed by the Butler-Volmer equation (Eq. (6)).

$$J_{\text{anode}} = k A C_{\text{elec}} \quad (6)$$

where k is the heterogeneous rate constant which depends on the difference of potential (m s^{-1}) applied to the cell, C_{elec} is the concentration of the substrate at the electrode surface (mol m^{-3}).

During the anodic oxidation, if the current density applied (J_{appl}) is higher than J_{lim} , then the process is controlled by the mass transfer; on the opposite, if $J_{\text{appl}} < J_{\text{lim}}$ then the process is controlled by the charge transfer [35].

Two different behaviors can occur depending on the anode material [13]. Active anodes promote the formation of higher states oxides or superoxides (MO) (Eq. (7)) [36].



This type of anodes forms chemisorbed radicals which limit the reaction at the surface of the anode as there is a strong interaction between the radicals and the anode surface. The most

common anodes of this type are Pt and mixed metal or (DSA, dimensionally stable anode).

On the opposite, the non-active anodes enable the formation of physisorbed radicals with a quite weak interaction between hydroxyl radical ($\bullet\text{OH}$) and the anode surface (M) (Eq. (3)). Hydroxyl radicals thus formed are able to react in the diffusion layer and can conduct to complete mineralization of organics. The most representative non-active anodes are BDD, tin or lead oxides and sub-stoichiometric titanium oxides.

AO process can also imply indirect (or mediated) oxidation occurring in the bulk of the solution thanks to the formation, at the electrode surface, of a mediator (an oxidizing species). Once migrated to the bulk solution, these oxidizing agents can participate in the oxidation of organic pollutants. Usually it concerns active chlorine species and peroxy anions. For instance, the relatively strong oxidants such as hypochlorous acid/hypochlorite anion (formed in chloride medium), peroxydisulfate anion (formed from sulfate medium) and peroxyphosphate anion (formed in phosphate medium) can be created [32] at the anode surface and contribute to the oxidation process in the bulk solution.

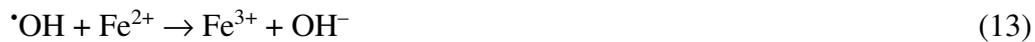
2.1.2 Indirect electro-oxidation: Electro-Fenton (EF) process

EF process is an indirect EAOP since hydroxyl radicals are not generated directly from charge transfer at the electrode level but in the solution from the well-known Fenton's reaction (Eq. (8)) [37,38]. In the Fenton's process, homogeneous hydroxyl radicals ($\bullet\text{OH}$) are generated from Fenton's reagent, a mixture of H_2O_2 and Fe^{2+} , added externally to the solution to be treated. In contrast, for the EF process, the Fenton's reagent is electrochemically produced at the cathode. H_2O_2 is formed by a 2-electron reduction of dissolved O_2 (Eq. (9)) and Fe^{2+} by a single electron reduction of ferric cation (Eq. (10)). At the anode, water is oxidized to O_2 (Eq. (11)) and, depending on the anode material, adsorbed hydroxyl radicals can be formed (Eq. (3)).



The Fenton's process is a major step forward as it is easy to implement and uses relatively inexpensive and harmless chemicals [12,39]. It was first applied in 1960 for the treatment of organic pollutants [40], since then a large application to the treatment of effluents was reported, such as the discoloring effluents of dye industries [41] or the treatment of different kind of wastewaters [42].

Despite its interesting use in the treatment of effluents contaminated by organic pollutant, this process suffers from some drawbacks such as needing high amounts of Fenton's reagent to generate enough quantity of $\cdot\text{OH}$. The introduction of a high amount of H_2O_2 and Fe^{2+} implies economic aspect and also the formation of ferric hydroxide sludge needing a supplementary processing. Moreover this situation favors the rate of wasting reactions (Eq. (12) and (13)) resulting in low efficiency.



The EF process, developed and popularized by Oturan's and Brillas' group at the beginning of the 21st century has been designed to avoid the disadvantages of the classical Fenton's process by coupling between electrochemistry and Fenton's chemistry [31,43]. Electrochemistry offers an amazing help in this respect [15]. Indeed, in contrast to the classical Fenton's process, in the EF process the Fenton's reagent is in situ generated (H_2O_2) or regenerated (Fe^{2+}): H_2O_2 is generated on a suitable cathode by a 2-electron reduction of dissolved O_2 (Eq.

(9)) and regeneration of Fe^{2+} from Fe^{3+} formed in Fenton reaction (Eq. (10)). The electrocatalytic regeneration of ferrous iron allows the use of a catalytic amount of this ion as catalyst thus avoiding the ferric hydroxide sludge formation and also preventing the waste Eq. (13) [12,13]. Therefore, the use of EF process instead of Fenton's process allows the following advantages: (i) minimizing reagent cost by in situ generation of Fenton's reagent, (ii) avoiding risks related to transportation and storage of H_2O_2 , (iii) avoiding (or minimizing) reactions wasting $\cdot\text{OH}$ (Eqs. (12) and (13)) because H_2O_2 and Fe^{2+} concentrations are quite low since they are consumed as soon as they are formed, (iv) eliminating sludge formation and (v) generally providing high removal rate of organics due to the electrochemical regeneration of Fe^{2+} which catalyzes Fenton's reaction [16,17,44,45].

The use of an appropriate cathode material is essential in the EF process; it should be able to generate efficiently H_2O_2 and have a low catalytic activity for its reduction. Moreover the cathode must have high overpotential for H_2 evolution since the process is optimal at acid medium [44]. These characteristics are generally satisfied by carbonaceous materials that are often used in EF process such as three-dimensional carbon materials (carbon felt, graphite felt, carbon sponge, activated carbon fiber) [46–50] and carbon-PTFE- O_2 gas diffusion cathode [51]. Other carbonaceous materials like graphite, reticulated vitreous carbon and carbon nanotubes have also been tested. More recently BDD and Ni foam have been also shown to be able to produce H_2O_2 [49,50,52,53].

On the other hand, the nature of the anode is also very important in EF process. In the case of the use of a non-active anode, $\text{M}(\cdot\text{OH})$ are produced on the anode surface [54]. In this case EF process also includes AO process since homogeneous ($\cdot\text{OH}$) and heterogeneous $\text{M}(\cdot\text{OH})$ are produced simultaneously in the bulk solution and on the anode surface, respectively, thus enhancing strongly the oxidation power of the process [55]. The best non-active anode material known is the BDD. However, its high cost can constitute an obstacle to its scale up

for large-scale applications. Therefore, research is done on the use of ceramic electrodes based on sub-stoichiometric titanium oxides (Ti_nO_{2n-1}) [56,57]. Recent studies have shown that this new anode material is able to provide results close to that of BDD in AO and EF processes [58,59].

During the EF treatment, numerous reactions are involved and the mass transfer constitutes an important parameter in the degradation of pollutant as some reactants have to reach the surface of the electrode (O_2 , Fe^{3+}) when others have to reach the bulk from the electrode surface (H_2O_2 , Fe^{2+}). For instance, the oxygen required for the formation of H_2O_2 (Eq. (9)) has to be transferred from the gas phase to the aqueous phase and then needs to be adsorbed onto the electrode surface before its reduction process [13]. The required dissolved oxygen concentration is reached usually by aeration. If oxygen is not provided at an adequate rate, it becomes a limiting factor, controlling H_2O_2 generation rate and consequently the EF process. As the diffusivity of oxygen in the gas phase is significantly higher than in the liquid phase, it is considered that the gas phase offers no transfer resistance. Thus, it can be suggested that the overall oxygen transfer rate (OTR) is controlled by the liquid phase, expressed as follows (Eq. (14)):

$$OTR = k_L a (C_{bulk, O_2}^* - C_{bulk, O_2}) \quad (14)$$

where OTR is the oxygen mass transfer rate ($mol\ m^{-3}\ s^{-1}$), $k_L a$ is defined as the volumetric oxygen mass transfer coefficient (s^{-1}), C_{bulk, O_2}^* and C_{bulk, O_2} are the equilibrium concentration and the oxygen concentration in the bulk ($mol\ m^{-3}$), respectively.

It is worthy to note that the oxygen mass transfer has been well studied for water and wastewater treatment systems but not in EF process. The value of $k_L a$ depends mainly on the configuration of the reactors, on the air flow rate, on the airflow diffuser which will influence the bubbles size and on the hydrodynamics in the reactors.

The transfer from the bulk to the anode (pollutants) and the transfer from the cathode to the bulk (H_2O_2 and Fe^{2+}) are key points for the efficiency of the process. That is why, understanding the controlling parameter is important. As it was explained previously for the AO (Eqs. (4) – (6)), the expression of the current density in EF follows the same behavior. But, the system is more complex as for the EF, the oxidation of pollutants can occur on the anode surface (AO) and in the bulk (involving both homogeneously generated $\cdot\text{OH}$ from Fenton reaction and mediated oxidation from oxidants formed at the anode).

There are several operating parameters involved in EF process efficiency which have now long been studied [12,13,60,61]. The principal parameters are: solution pH, current applied, catalyst nature and concentration, supporting electrolyte (nature and concentration), electrode gap, oxygen (or air) supply rate and temperature.

The pH is a very important parameter of this process, it is usually recommended to work at a pH around 3 [62]. The acidic medium is required for the formation of H_2O_2 (Eq. (9)), however pH values lower than 2 lead to the transformation of H_2O_2 to peroxonium (H_2O_3^+) which is less reactive toward Fe^{2+} in the formation of $\cdot\text{OH}$ via Fenton reaction and at higher pH this compound decomposes into water and oxygen [63–65]. Moreover, at pH above 4, Fe^{3+} precipitates as $\text{Fe}(\text{OH})_3$ and at pH below 1, Fe^{2+} forms complexes with H_2O_2 [66].

The current is another key factor in EF process since the rate of electrochemical reactions is promoting the generation of $\cdot\text{OH}$ (Eqs. (9), (10) and consequently Eq. (8)) and $\text{M}(\text{OH})$ (Eq. (3)). Therefore this parameter influences significantly the oxidation and/or mineralization efficiency of the process [12,67]. But a too high current promotes competitive reactions consuming electrical energy in side reactions (reduction of water to H_2 or its oxidation to O_2) or wasting $\cdot\text{OH}/\text{M}(\cdot\text{OH})$ (recombination or oxidation reactions) in the electrolytic cell [13,16,68]. The current value determines also the type of limitation for the system whether by the mass transfer or by the charge transfer as explained previously. Usually this parameter is

experimentally determined for each compound/equipment before treatment.

Another highly important parameter is the nature or concentration of the catalyst. Among different catalysts tested for EF process, it was evidenced that iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) is one of the best since it is not harmful, has low cost and requires low concentration [13]. With regard to the Fe^{2+} concentration, the optimal value depends on the cathode used; optimal values about 0.1 – 0.2 mM for carbon-felt cathode and 0.5 mM for gas diffusion cathode were reported many times in literature [12,13,16]. High Fe^{2+} concentration is generally avoided since it promotes the wasting reaction given in Eq. (13) [12,54]. This factor is also usually experimentally adjusted. Meanwhile the $\text{Cu}^{2+}/\text{Cu}^+$ couple was also investigated as catalyst in the EF process and contradictory results have been published. For instance a recent study, demonstrated that copper could be more efficient and more cost-effective than iron with a higher TOC removal rate [69]. But, other researchers highlighted that iron catalyst provides a better mineralization efficiency than copper ions [70].

Airflow and air diffuser are also important parameters that influence significantly both oxygen transfer and hydrodynamic conditions in the reactors. In the case of low oxygen flow rate the solution cannot be saturated in O_2 and oxygen transfer can become the limiting step affecting the efficiency of H_2O_2 production rate and accordingly $\bullet\text{OH}$ generation rate through Fenton's reaction.

In addition, temperature is an influent parameter that impacts all the process. It affects the kinetics of chemical and electrochemical reactions and mass transfer parameters (diffusion coefficient, etc.). In general, temperatures ranging between 20 and 30 °C are applied in the literature [71] since higher temperatures decrease O_2 solubility as well as promote H_2O_2 decomposition. For the nature of the electrolyte, good conductivity ions must be used. Indeed, Ghoneim et al. [72] performed an experiment comparing the efficiency of the EF with three different electrolytes: Na_2SO_4 , NaCl and KCl . The better efficiency of Na_2SO_4 have been

explained by the higher conductivity of SO_4^{2-} compared to Cl^- [73]. They also obtained a higher degradation rate using KCl than NaCl explained again with the greater conductivity of K^+ compared to Na^+ . On the other hand, the degradation of methyl parathion by EF with sodium sulfate was slower than with NaClO_4 or NaNO_3 because of the formation of sulfato-complexes with iron [74,75]. The electrolyte allows to increase the solution conductivity by avoiding an ohmic potential drop responsible for a higher energetical consumption. Meanwhile it was demonstrated that a too high concentration of Na_2SO_4 can produce a great decrease in the TOC abatement which can be due to the side reaction [76,77].

2.2 Reactor configuration

Recent ways of enhancing efficiency and decreasing the costs in EAOPs consist in choosing a specific reactor configuration to enhance mass transfer and current efficiency. The reactor configuration is a key point for the efficiency of the degradation by electro-Fenton. Some review papers have given an overview of the different cell configurations used until 2012 [13,60]. Most of the studies have been performed at lab-scale with undivided cell reactors with volumes lower than 300 mL. Another system, quite similar to the previous one (undivided cell), is the use of divided cells with two or three electrodes. The undivided system has the advantage of lower operating costs due to the possible use of a lower cell voltage in comparison with the divided cells. Moreover the latter has the advantage of avoiding H_2O_2 to reach the anode and to be oxidized there (Eq. (15)) thus preventing the following side reaction [13].



Two other systems used to a lesser extent were the filter press reactors operating in batch and recirculation mode [78] and the bubble reactor operating in continuous mode [79]. However, in the last 5 years, new reactor configurations or enhanced configurations of formerly used

reactors were developed that allows having a greater efficiency and/or lower costs [61]. Therefore, the aim of this section is to give an overview of those new studies which are sum-up in Table 2. Some of these configurations are also illustrated in Fig. 1. The novelties include: i) the way of mixing in order to favor mass transport and transfer to the anode, ii) the manner in which the oxygen is transferred to the solution, iii) the shape and distance between electrodes and their number, iv) the shape and the volume of the cell and v) the type of out streaming.

2.2.1 Geometric parameters

Recent research has most specifically focused on geometric changes in electrodes. Among them, Su et al. [80] studied the impact of using plate or rod electrodes for aniline removal (Fig. 1). The experimental conditions are described in Table 2. They found out that the plate electrodes have a better aniline degradation rate than the rod electrodes for added $[H_2O_2] > 29$ mM. This phenomenon is explained as the distance between the electrodes is lower (1.5 cm) for plate electrodes while it is significantly higher (5.5 cm) for rod electrodes. This allows the plate electrode system to have a lower electrical resistance and thus a better electrical efficiency. On the contrary, in the case of lower $[H_2O_2]$ added to the solution, the rod electrode cell is more efficient at degrading the pollutant [80]. The area of the working electrodes is 900 cm^2 and 600 cm^2 for the plate electrode reactor and of 433 cm^2 and 36 cm^2 for the rod electrode reactor. Thus, the effect observed can also be partly explained by the difference on the surface of the electrodes.

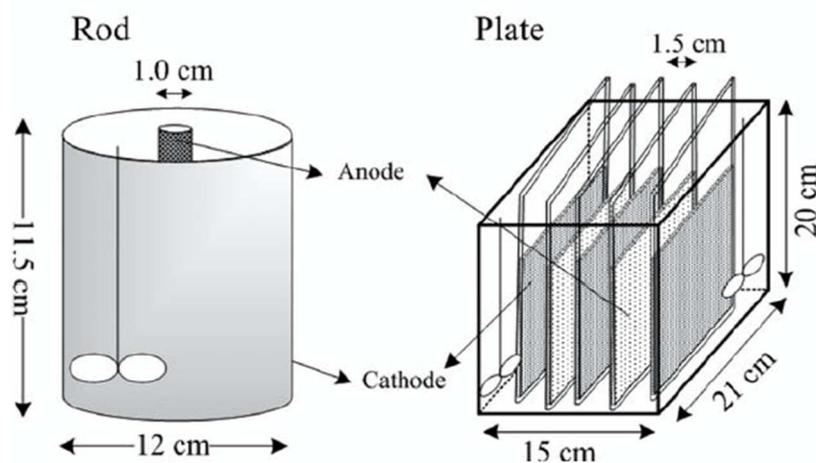


Fig. 1: Reactors with rod and plate electrodes. Reprinted with permission from ref [80]. Copyright 2012, American Institute of Chemical Engineers.

Another idea is to create a reactor composed of two gas diffusion electrodes (GDE): cathodes placed in parallel with two anodes, the two GDEs being in the center of the cell [81]. This configuration enables a greater production of H_2O_2 , and thus allows forming more hydroxyl radicals according to the Fenton's reaction (Eq. (8)). Authors compared this system (reactor 1) with the reactor composed of one anode and one cathode in the same position (reactor 2) and with the reactor composed of one anode and one cathode positioned vertically (reactor 3), the latter one being the mostly used configuration. As shown in Table 2, the reactor with two GDE cathodes is more efficient in terms of production of H_2O_2 and current efficiency compared to the other reactors. This reactor was also more cost-effective with a much lower energy consumption [81] with the same current intensity. The higher efficiency can be explained by the higher working area in this reactor as it is equipped with two more electrodes although the additional manufacturing costs are not taken into account in the cost calculation. The parallel configuration of the electrodes in reactor 1 can explain the lower energy consumption. Indeed, this configuration reduces by two the current intensity which results in a lower voltage for the cell and thus in a lower energy consumption compared with reactor 2

where the current is not divided. The surfaces of the electrodes facing each other in reactor 3 are smaller causing a lower conductance and thus an increase of the cell voltage.

Another cell geometry has been proposed by Lei et al. [82]: the trickle-bed reactor (Fig. 2) to enhance the efficiency of the electro-Fenton process. This system is made of several pieces which constitute the fixed part of the packed bed of the reactor using the downward movement of a liquid and the upward movement of gas. Details about the reactor configuration and the treatment conditions are given in Table 2. The air and the solution are both mixed before entering the cell. This configuration enables to dissolve the oxygen first in the liquid allowing the easy transfer of oxygen to the electrode surface and therefore enhancing the production of hydrogen peroxide. They found out that this system is as efficient as GDE but avoids electrolyte leakage and gas bubbles which makes its application at a larger scale possible [82].

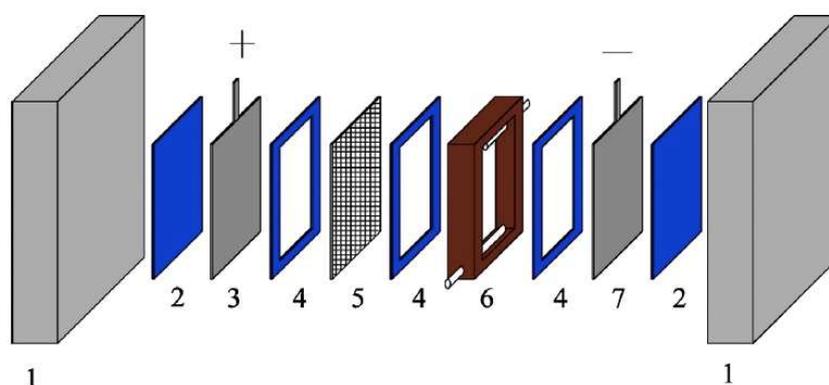


Fig. 2: Scheme of the trickle bed reactor. 1: Cell body, 2: Gasket, 3: Ti/PbO₂ anode, 4: Gasket ring, 5: Nylon diaphragm, 6: Cathode frame for loading graphite chips and 7: Nickel plate. Reprinted with permission from ref. [82] Copyright 2013, Elsevier

Finally, Xu et al. [83] suggest the use of tubular membranes for both anode and cathode (Fig. 3). The electrodes and the experimental conditions used are detailed in Table 2. The reactor has the advantage of enhancing the mass transfer without needing any aeration. Using cyclic voltammetry (CV) analysis, the authors showed that the tubular anode exhibits better catalytic

activity than the plate electrode. Indeed, the CV curves area for the tubular anode is 1.58-fold greater than that of plate anode. This greater catalytic activity can be explained by the presence of micro-porosity which provides a larger surface area for the tubular anode. The micro-porosity also enhances the dispersion and dissolution of oxygen present in the solution. In a plate electrode, the electrolyte flows along the electrode and some pollutant will bypass the electrode surface without undergoing degradation [84]. By flowing toward the electrode (and not along it), the mass-transfer to the electrode is enhanced. This is demonstrated with computational fluid dynamics [85] and by chronoamperometry measurements where the current density is greater for the tubular membrane; 1.71 and 3.43 mAcm⁻² after a test time of 20 sec for the plate and porous electrode respectively [86]. Finally, the authors demonstrated that their system does not require aeration by measuring the amount of H₂O₂ and hydroxyl radicals produced with and without aeration (Table 2) [83].

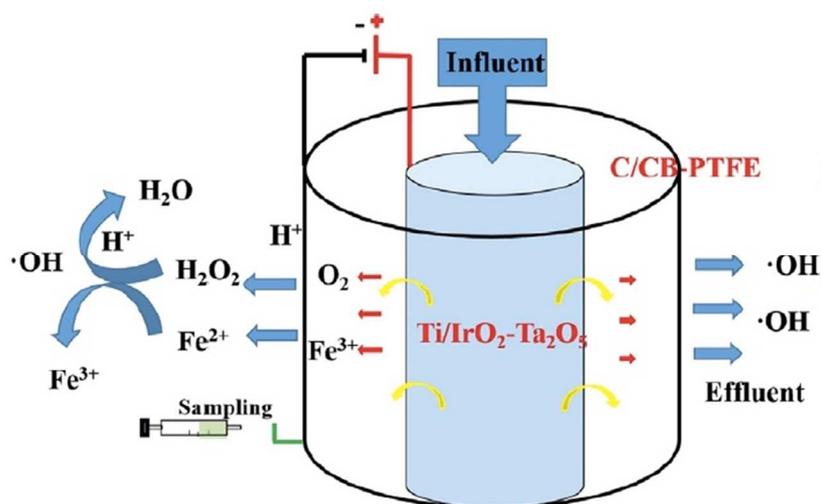


Fig. 3: Scheme of the dual tubular membranes EF reactor. Reprinted with permission from ref. [83]. Copyright 2016, Elsevier.

Another tubular system was recently created. It is based on two driving forces: i) the transmembrane pressure and ii) the current. The authors demonstrated the efficiency of their

system, described in Table 2 (A) by the higher H₂O₂ production of their system by finding optimums current and transmembrane pressure [87].

2.2.2 Out streaming

As in the study on tubular membranes, research was done on the effect of the direction of the flow whether parallel to the electrodes (flow-by) or perpendicular to them (flow-through or vertical-flow). Two recent studies analyzed the degradation of methylene blue and tartrazine, respectively, in both different operating conditions. The single compartment system working on methylene blue is composed of perforated DSA (dimensionally stable anode) electrode as the anode and a modified graphite felt as a cathode (Fig. 4) [88]. The second multiple cell reactor, used to degrade tartrazine, is equipped with PbO₂ anodes and modified graphite felt mesh cathodes [89]. Results obtained showed the superiority of the flow-through reactor over the flow-by reactor in the same conditions (Table 2). This result can be explained by the enhancement of the mass transport in the vertical-flow compared to the parallel flow [90,91]. The higher efficiency is related to the greater accumulation of H₂O₂ in the flow-through (57.8 mg L⁻¹) than in the flow-by system (51.9 mg L⁻¹) [88].

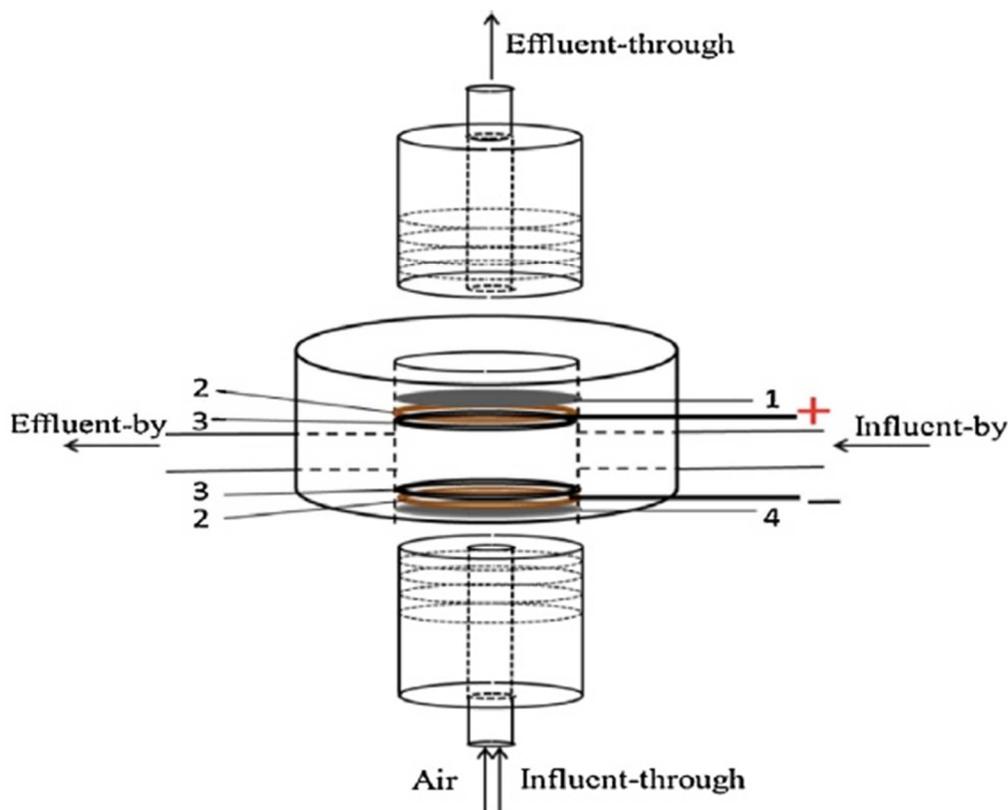


Fig. 4: Scheme of the flow-through reactor containing 1: a perforated DSA anode, 2: the titanium ring, 3: the insulating rubber ring and 4: the modified graphite felt cathode. Reprinted with permission from ref. [88]. Copyright 2016, Elsevier.

Concerning the multiple flow through the reactor (Fig. 5), made of maximum 10 compartments, both operating conditions were able to remove totally the 0.4 mM tartrazine from the aqueous solution; however the vertical flow was more efficient as can be seen from the TOC removal values (Table 2). By comparing the electrical energy consumption per kg TOC removed for a different number of compartments, the authors showed the cost-efficient choice to be the 8 compartment reactor [89]. The higher mineralization efficiency and the lower energy consumption can be explained by the enhancement of the mass transfer of O₂ and pollutant thanks to the flow-through configuration. This better transfer provides a higher current efficiency and thus a lower energy consumption [92]. Recently another stack electrode system was proposed by Hu et al. in which it was demonstrated that by putting closer the

electrodes, they could increase the COD abatement and the energetical consumption. The specific energy consumption was of 50 and 30 kWh (kgCOD)⁻¹ for 1 pair of electrode separated by 10 and 2 mm respectively after 6 h [93].

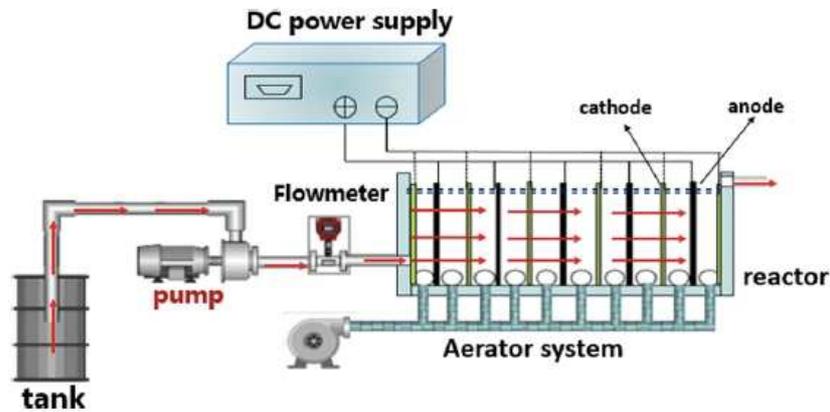


Fig. 5: Scheme of the 10-compartment reactor. Reprinted with permission from ref. [89]. Copyright 2016, Elsevier.

2.2.3 Special way of supplying O₂

Recently an interesting idea appeared in numerous publications: a special way of providing oxygen to the system without supplying an air or oxygen flow rate. This system is based on the use of two parallel rotating cathodes with an anode in the middle (Fig. 6) [94]. The operating parameters related to this reactor are described in Table 2. This system enables to bring oxygen without blowing air or O₂ in the solution making it more cost-effective and providing a good mass transfer between the solution and the electrode surface as demonstrated by comparing with the same electrodes but without rotating cathodes and providing O₂ (Table 2) [94].

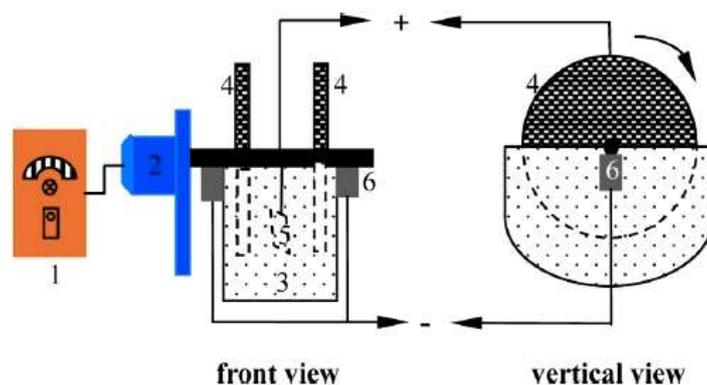


Fig. 6: Scheme of the reactor with two parallel rotating cathodes with 1: speed controller, 2: motor, 3: electrolytic cell, 4: rotating graphite felt disk cathode, 5: Pt anode and 6: carbon brush. Reprinted with permission from ref. [94]. Copyright 2018, American Chemical Society.

Another two-compartment reactor avoiding the use of oxygen is based on the catalytic generation of H_2O_2 (Eq. (16)) thanks to Pd/C particles. The design of this novel reactor is based on the work reported by Liu et al. [95] reporting an electrolytic system able to generate different pH environment without adding any chemicals by using water electrolysis to create O_2 and H_2 . A low pH was first used to produce H_2O_2 and then a high pH was employed to neutralize the treated solution before its release to the natural water stream [95]. The characteristics of the reactor are described in Table 2. The first compartment enables the formation of H_2 , O_2 and H^+ by water electrolysis, of H_2O_2 (Eq. (16)) leading to hydroxyl radicals from the Fenton's reaction.



The second compartment accumulates OH^- which is utilized to neutralize the solution when needed. The main advantage of this system is to avoid chemicals to set the solution pH and to obtain a neutral solution after treatment that can be directed directly to a bioreactor. To illustrate the efficiency of their reactor, the authors compared the production of H_2O_2 and its accumulation to some values reported in the literature and concluded that it could produce more H_2O_2 than carbon fiber or carbon nanotubes cathodes but less than a GDE cathode. This

reactor presents some drawbacks such as a high voltage required due to the electrical resistance of the salt bridge and the high price of the catalyst; however it was shown to be reusable [96]. In order to overcome such drawbacks another system was created by Zhang et al.. Their system produced O_2 and an acidic medium thanks to the use of a second anode where water is oxidized in O_2 and H^+ . This system is promising by avoiding the use of O_2 and the use of expensive material such as Pd [97].

One of the latest study on a new way of providing O_2 was proposed by Perez et al., [98] which consisted of a combination of a flow-through system and a Venturi-based jet aerator (Fig. 7) which allows an efficient production of H_2O_2 and a very good oxygen supply with low energy costs. This system is based on the Venturi effect as in the thinner part of the tube a depression is created which sucks the air into the system leading to a higher liquid velocity which enables to break the oxygen gas bubbles and thus helps their dissolution in water. This system is compared to a similar reactor using GDE cathode and a flow-by cell system. The reactor with Venture-based jet aerator can produce $960 \text{ mg } H_2O_2 \text{ L}^{-1}$ whereas the reactor with GDE cathode produces $700 \text{ mg } H_2O_2 \text{ L}^{-1}$ (Table 2). It is also showed that the efficiency of such an aeration is higher by comparing the same reactor without oxygen supply or with air sparging to the jet aerator. The concentration of H_2O_2 obtained at a current density of 75 mA cm^{-2} after 30 min, is very low for no oxygen supply and, 8 and $400 \text{ mg } H_2O_2 \text{ L}^{-1}$ for air sparging and jet aerator, respectively [98].

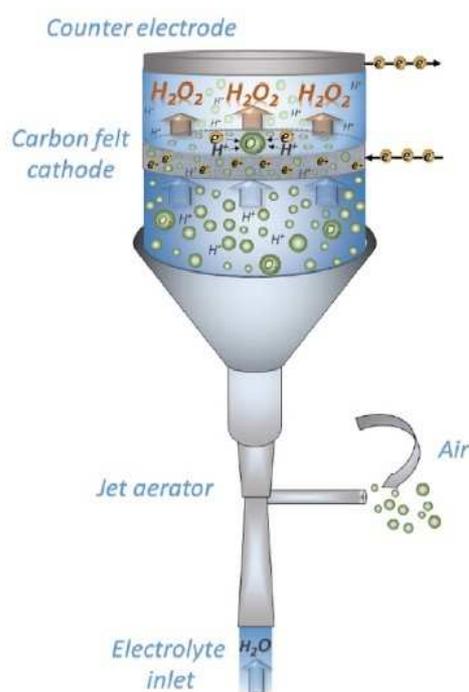


Fig. 7: Scheme of the jet-cell reactor. Reprinted with permission from ref. [98]. Copyright 2016, Elsevier.

2.2.4 Micro-fluidic

A different type of reactor was recently used for electro-Fenton processes: microfluidic reactors [99–101]. It was first used by Scialdone et al. (2013) who studied the capacities of this type of reactor compared to a conventional undivided macro reactor. The two different reactors are described in Table 2. The micro-reactor had the following advantages: i) no use of electrolyte as there is a very small transfer resistance due to the size of the system, ii) no need of gaseous stream as oxygen is provided by water oxidation at the anode. The use of a graphite cathode provides a cheap and easy to handle system. The chemical oxygen demand (COD) is used as comparison parameter. As can be seen in Table 2, the abatement is more than two times higher for the microfluidic reactor compared to the macro reactor. The better efficiency of the micro reactor is explained by a comparison of H_2O_2 production which is 0.6 mM and 6 mM for the macro and microreactor, respectively. Besides, the calculated current efficiency (CE) values also highlight better performance of the microreactor (8% for the macro-reactor against 33% for the micro-reactor at 10 A m^{-2}). This fact can be explained by

high solubility of O₂ in micro conditions: it is formed by water oxidation at the anode and dissolved close to its maximum solubility. As the system is small, the O₂ is present at a high concentration at the cathode (both electrodes being close to each other) and leads to the formation of a higher concentration of H₂O₂ [101]. However, the very small size of the channels could be problematic since they can be plugged when real effluents with organic and mineral particles are treated. The group of Scialdone investigated also the performances of the different advanced oxidation processes for a microfluidic treatment and concluded that combining EF and electro-oxidation could significantly be enhanced by microfluidic [100]. The last study on microfluidic system applied to EF dealt with the use of micro-reactor cells in series. They concluded that using three EF reactors in series was not useful compared to the use of one micro-reactor as the EC value increases much more than the TOC abatement rate for the reactors in series [99].

2.2.5 Energetical consumption

In order to compare the systems, the energetical treatment costs were estimated when possible for the different systems. The EC were of 0.5 and 20 Wh gTOC⁻¹ for the system with rotating cathodes [94] and the two cathodes in the center [81] respectively. This can suggest that the rotating cathode is a more cost-effective system. Meanwhile this treatment is done in batch so to well-evaluate the real cost of the treatment, experiments in continuous mode are required. In two other systems the EC could be evaluated but the formula was modified (Eq. (17)) in order to take into account the continuous mode.

$$EC = (E * I) / ((TOC_0 - TOC(t)) * D) \quad (17)$$

With E, the cell voltage in Volt, I the current in Ampere, TOC₀, the TOC initial, TOC(t), the TOC at the steady state, D the flow rate in L h⁻¹.

Using the formula, the flow-through multiple system [89] is consuming 140 kWh (g TOC)⁻¹

whereas the flow through single system [88] is consuming 4 Wh (g TOC)⁻¹ so 35 times less. Meanwhile an important point have to be underlined, the amount of treated pollutant which is of 20 mg per h for the single system against 240 mg per h pour the pilot. So the gap is reduced by taking this point into account. Nevertheless the consumption is higher in the pilot which can be explained by the scale up of the treatment as the single system is done in 150 mL. However, it is at this step impossible to compare experiments done on the different reactor configurations (different pollutants, different initial TOC configuration, different flow mode, etc.). Much more researches are needed on this aspect and the EC should be estimated for each configuration and considered as a key parameter.

Table 2: New cell configurations and the conditions of treatment

Name of the reactor	Volume	Distance between electrodes	Number of electrodes	Nature of the electrodes	Type of out streaming	Stirring	Active aeration	Efficiency	References
Trickle bed reactor Fig. 2	Active dimensions of the electrode: 42 cm ³		2 cathodes 1 anode	- Cathode frame for loading graphite chips - Ni cathode plate - Ti/PbO ₂ anode	Recirculation flow or continuous mode	By the flow and aeration	Air flow rate of 0.1 m ³ h ⁻¹	Solution of X-3B 123 mg L ⁻¹ mineralized at 87% in 3 h at 4,5 V (10 mA cm ⁻²)	[82]
Plate electrodes Fig. 1	5L (reactor)	1.5 cm	3 cathodes 2 anodes	- Cathodes: Ti coated with stainless steel - Anodes: Ti coated with IrO ₂ /RuO ₂	Batch mode	Yes with a stirrer	No	At 58 mM of H ₂ O ₂ , 1.07 mM of Fe ²⁺ , 22.5 mM of aniline initial concentration the percentage of removal of aniline were 87.2 and 77.2 % for plate and rod electrodes respectively after 1 h After 120 min of treatment, the TOC removal was 57.9% and 39.1% for the flow-through and flow-by system respectively with 50 mA, a pH of 3, a flow rate of 7 mLmin ⁻¹ , 0.3 mM of Fe ²⁺ and an initial concentration of pollutant 50 mg L ⁻¹	[80]
Flow through single system Fig. 4	150 mL (reactor)	0.8 cm	1 anode 1 cathode	Cathode: modified graphite felt Anode: perforated DSA	Continuous	By the flow and aeration	Pumped air at 50 mL min ⁻¹	TOC removal vertical-flow system: 65%, the parallel-flow system 52% at pH 3, voltage 4.0 V, flow rate 40 mL min ⁻¹ , Fe ²⁺ of 0.4 mM tartrazine.	[88]
Flow through multiple system Fig. 5	2 L (reactor)	2 cm	4 anodes 5 cathodes (8 compartments)	Cathode: graphite felt mesh Anode: PbO ₂ /Ti mesh	Continuous	By the flow and aeration	Aeration rate: 80 mL min ⁻¹	TOC removal vertical-flow system: 65%, the parallel-flow system 52% at pH 3, voltage 4.0 V, flow rate 40 mL min ⁻¹ , Fe ²⁺ of 0.4 mM tartrazine.	[89]
Micro-fluidic (MF)	Height of the filter press 120 μm (MF) ^a 50 mL for the macro-reactor (MR) ^b	120 μm (MF) 1 cm (MR)	1 anode 1 cathode (MR) and a polytetrafluoroethylene spacer in addition for MF	Anode: Ti/IrO ₂ Ta ₂ O ₅ Cathode: graphite (MF) Cathode: carbon felt (MR)	Flow mode with a single passage (MF) batch mode (MR)	No (MF) Yes, with a magnetic stirrer (MR)	No (MF) Yes, 0.35 L min ⁻¹ of compressed air (MR)	50 mL of 0.43 mM of Acid Orange 7 and 0.5 mM of FeSO ₄ , 0.035 M of Na ₂ SO ₄ (only MR) at a pH of 3 in 500 min: COD abatement was of 75 % (MF) and of 30 % (MR) under 20 and 100 A/m ² respectively for MF and MR.	[101]

Reactor with 2 cathodes in the center	200 mL (reactor)	1.5 cm	2 anodes 2 cathodes	Anode: DSA with IrO ₂ Cathode: GDE (carbon black deposited on carbon fiber)	Batch mode	Yes, with a magnetic stirrer and aeration	Yes, air flow rate of 0.5 L min ⁻¹	H ₂ O ₂ was 566, 531 and 487 mg L ⁻¹ , the CE was 85.4, 75.8 and 70.2 % in 180 min and the energy consumption was 8.6, 14.7 and 24 kWh kg ⁻¹ H ₂ O ₂ for reactor 1, 2 and 3 respectively under 0.05 M of Na ₂ SO ₄ , at a current intensity of 100 mA and at a pH of 7.	[81]
Venturi-based jet aerator Fig. 7	1 L (reactor)	1.8 cm	1 anode 1 cathode	Anode: Ti with IrO ₂ Cathode: Modified Carbon felt	Flow mode	By the flow and aeration	Yes (jet aeration)	At 180 min and under 50 mA cm ⁻³ , 0.05 M Na ₂ SO ₄ , 960 and 700 mg H ₂ O ₂ dm ⁻³ for the Venturi reactor and the flow-by cell with GDE.	[98]
Tubular membrane Fig. 3	71 cm ³ (graphite electrode)	1.0 cm	1 anode 1 cathode	Anode: Ti/IrO ₂ -Ta ₂ O ₅ Cathode: carbon black-polytetrafluoroethylene modified graphite	Batch mode	By the flow	No	A solution of 85 mg L ⁻¹ of tricyclazole(TCZ), with 0.05 M of Na ₂ SO ₄ , 1.0 mM of Fe ³⁺ , pH of 3, membrane flux of 103 L m ⁻² h ⁻¹ and current density of 10 Am ⁻² have a TCZ degradation of around 80% in 30 min, a production of H ₂ O ₂ of 1586 and 1494 mg m ⁻² h ⁻¹ and a ·OH concentration of 85.2 and 88.3 μM after 20 min with and without aeration respectively.	[83]
Tubular membrane (A)	1.5 L (reactor) 5 L whole system	1 cm	1 anode 1 cathode	Anode: Ti/Ti ₄ O ₇ Cathode: graphite-based membrane	Batch mode	By the flow	Yes, air	A solution of 0.1 mM of paracetamol, 0.2 mM of Fe ²⁺ , 0.05 M of Na ₂ SO ₄ at pH 3, at 18 °C, pressure of 2 bars and pumped at 3.0 L min ⁻¹ was mineralized at a rate of 44% under 100 mA in 8 hours.	[87]
Two-compartment cell with Pd/C catalyst	2 reactors of 250 mL linked by a salt bridge		Compartment 1: 1 anode and 1 Cathode Compartment 2: 1 cathode	Pt flakes	Batch mode		No	Rhodamine B initial concentration (10 mg L ⁻¹) decreased to 1.6 mg L ⁻¹ after 60 min, with 1 mM of Fe ²⁺ using 50 mA for each cathode.	[96]
Reactor with rotating cathodes Fig. 6	100 mL (reactor)	1.5 cm	1 anode 2 cathodes	Anode: Pt or DSA Cathodes: graphite felt	Batch mode	Rotation of the cathodes	No	A solution of 50 mg L ⁻¹ of methyl orange, 0.05 M Na ₂ SO ₄ , 0.2 mM Fe ²⁺ , pH of 3, after 20 min the pollutant was degraded using 2.37 kWh m ⁻³ for the rotating cathodes at 10 rpm and in 30 min using 3 kWh m ⁻³ when using the rotation of the	[94]

cathodes and providing 0.2 L min^{-1} of O_2 .

a : MF, micro-fluidic reactor
b : MR, macro reactor

2.2.6 Hints for scale-up

The different parameters stated in this section are also very important in order to scale-up the process to treat real effluent at an industrial scale. The already published research and review articles gave some hints to scale-up the process concerning i) the size and organization of the electrodes, ii) the temperature, iii) the mixing, iv) the out streaming and v) the continuous mode. In order to treat larger volumes, the system must be larger. Regarding the electrodes, two options are possible; either using high surface electrodes or using a stack system. The use of bigger electrodes produces a non-uniform repartition of the current on the electrode surface which reduces the yield. By using stacking electrodes, the cost is higher so a compromise has to be reached. When stacking is used the electrode configuration is also important, the configuration will be either in monopolar or bipolar configuration. In monopolar connection, all anodes and cathodes are directly connected to the power supply which provides a lower operating cost because of lower cell potential. In bipolar connection, only both border electrodes are connected to the current supplier which results in a higher cell voltage but this configuration provides a better depletion of organic pollutants [61]. The parameter mixing is directly related to the mass transport and mass transfer phenomena. It can become a real problem during the scale-up and can decrease significantly the efficiency of the process. Martínez-Huitle et al. highlighted this fact, identifying a real lack of mass transport in big-sized mixed tank reactor compared to flow reactor [61]. For example, dos Santos et al. [102] compared COD removal at a mixed cell and at a flow-pass cell, at 25 °C, with a current of 15 mA cm⁻² and 20 mA cm⁻² obtaining 50.3% and 76.2% of COD removal with a BDD anode for the mixed cell and flow cell, respectively. To improve the mass transport of mixed tank reactors, a recirculation can be added; this will not only improve mass transport efficiency but will also drag gas bubbles which otherwise would accumulate increasing the Ohmic resistance of the bulk and finally rising the energy consumption [61]. The type of flow is also a key

point for the scaling-up as it is directly related to the efficiency of the process, as seen before, the flow-through reactor provides better performance than the flow-by reactor. Radjenovic et al. proposed the combination of this type of reactor with three-dimensional electrodes in order to obtain the better cell system for a large scale treatment [103]. Computational fluid dynamics are recommended to optimize the flow system, especially at the entrance and at the exit of the cell where turbulences often happen. Nonetheless, only a few numbers of studies were reported on this tool [104–107]. Temperature belongs to the influent parameters in the reactor design, but it is often not studied as at bench scale there is no need to cool the system. However, at large scale applications, this parameter has to be taken into account and a cooling system should be involved.

For industrial application levels, the continuous mode has to be reached to enable the treatment of large amounts of wastewater. The stability of the electrodes is to be considered as this can directly pollute the solution or can decrease the efficiency of the process. Some studies evaluated the steady efficiency through several cycles [108–110] or by inspecting the electrode surface thanks to Scanning Electron Microscopy (SEM) after the treatment [111]. Most of the works describing a continuous electro-Fenton process are given in Table 3. Most of the experiments summarized in this table are carried out in heterogeneous system which avoids the formation of sludge and requires of a filtration post-treatment to eliminate or recover the catalyst [13]. Iron alginate gel beads are often used as solid catalysts aiming at degrading for example 81% of Lissamine Green B [111], 90% of Imidacloprid [112] and 99% of Azure B [108] (Table 3). The economic aspect of these reactors is often left aside, only a few studies considered it. With 20 A, 50 mL of industrial effluent is degraded consuming $0.14 \text{ kWh}(\text{gTOC})^{-1}$ [113], with 5 V, 0.15 L of Lissamine Green B is partly mineralized (COD removal of 86%) costing $15.75 \text{ kWh}(\text{kg dye})^{-1}$ [109], with 3.5 V, 3 L of Rhodamine B is treated reaching 98% of dye removal consuming $50 \text{ wh}(\text{gdye})^{-1}$ [114] and with 0.14 A, 1 L of

C. I. Acid red and blue are degraded using $0.024 \text{ kWh (gCOD)}^{-1}$ [115] (Table 3). However, only a few articles reported the continuous mode; more work has to be done and especially treatments with real wastewaters need to be studied. Industrial water from a chemical firm and a pulp and paper company [113], landfill leachate [116] and real wastewater from Mexico [117] are successfully degraded by EF in continuous mode. Thus the TOC removal is 80 and 60% for the chemical firm and the pulp and paper company, respectively, the COD removal is 60% for the landfill and a 92.3% discoloration is obtained for the water from Mexico (Table 3). In synthetic effluents, the concentration of pollutants is indeed higher than in real wastewaters, the interaction of different pollutants together and the effect of mineral ions as well as the effect of natural substances such as humic acids, are not yet evaluated.

Table 3: EF applied to continuous system

EF system reactor configuration	Pollutants	Solution	Current / Voltage	Residence time	TOC removal	Pollutant degradation rate	COD removal	Energy consumption	Ref
Cylindrical plexiglas reactor, two electrodes placed at the center of the reactor separated by 10 mm Anode: graphite Cathode: modified graphite electrode using multi-walled carbon nanotubes with cationic surfactant	C.I. Acid Red 14 (a) C.I. Acid Blue 92 (b)	0.05 mM Fe ³⁺ , flow rate: 0.33 L h ⁻¹ *, pH: 3*, effective volume 1 L, aeration, 10 mg L ⁻¹ dye, NaCl: 1 g L ⁻¹	0.14 A			91.22 % (a) 93.45% (b)	86.78% in 60 min	0.024 kWh (gCOD) ⁻¹ at 1 h	[115]
System composed of 3 pairs of anode/cathode disc electrodes of 62 mm diameter Solution flows through the different porous electrodes Anodes: Carbon felt activated by ethanol treatment Cathodes: Carbon felt treated first by ethanol then by mixed valence iron FeCl ₂ 4 H ₂ O and FeCl ₃ 6 H ₂ O (0.4 mg Fe m ⁻² of cathode)	Diclofenac	Effective volume 49 mL, flow rate: 10 L h ⁻¹ at 23°C, tap water, ~0.625 mg L ⁻¹ diclofenac, neutral pH, no addition of O ₂	2 V* for each pair of cathode/anode	14.6 s	35%	85%			[110]
Cell with two electrodes of 11 cm ² separated by 6 cm Anode: BBD Cathode: graphite sheet	Imadacloprid	Air bubbling at 1 L min ⁻¹ , working volume 0.15 L, 100 mg L ⁻¹ 4.27g* Fe alginate gel beads (0.05 M Fe ³⁺), pH = 2*	5 V	4 h		90%			[112]

<p>Undivided cell with two square electrodes of 100 cm² separated by 5 mm, flow-by effluent + a reservoir Anode: mesh of platinized titanium (a) or DSA (b) Cathode: thick carbon loaded with carbon black with PTFE</p>	<p>Industrial effluent from a chemical firm 37250 mg L⁻¹ (a) pulp and paper company 328 mg L⁻¹ (b)</p>	<p>Working volume 50 mL, O₂ diffusion through the cathode, 40°C, recirculation (ensure the good mass transfer) flow 900 Lh⁻¹, 0.05 M Na₂SO₄, 1 mM FeSO₄, pH = 3.2 (a), 3 (b), feeding flow calculated to obtain a TOC removal in steady state: 1.2 mL min⁻¹ (a) 1 L h⁻¹ (b)</p>	20 A		80% (a) 60% (b)			Steady state 0.14 kWh (gTOC) ⁻¹ (a) 0.38 kWh (gTOC) ⁻¹ (b)	[113]
<p>Stirred tank reactor of 12 cm * 10 cm * 16.5 cm with 5 electrodes of 15 cm * 10 cm vertical and with an alternating of anode/cathode separated by 2 cm* 2 Anodes: Ti/RuO₂-IrO₂-SnO₂-TiO₂ mesh 3 Cathodes: Ti mesh Fluidized bed reactor composed of a glass column with intern diameter 2 cm height 16 cm Anode: graphite sheet (14*0.7 cm²) Cathode: Ni-Foam half coated with iron-chitosan (14 cm*0.7 cm) separated by 1 cm</p>	<p>Landfill leachate with pH = 8 (COD 2720 mg L⁻¹)</p>	<p>800 mL working volume, magnetic stirring, initial pH = 3*, H₂O₂/Fe²⁺ molar ratio of 6*, H₂O₂ = 0.170 M*</p>	1 A	40 min*			60% in 60 min		[116]
<p>Cylindrical glass reactor with two electrodes of 84.16 cm² separated by 10 cm, flow-by effluent Anode: graphite bar Cathode: graphite bar</p>	<p>Lissamine Green B (a) (30 mg L⁻¹) Reactive Black 5 (b) (100 mg L⁻¹)</p>	<p>Initial pH = 2, mixed by continuous air flow at 0.15 vvm^a, 100 mg L⁻¹ dye, 0.15 L working volume, 0.01 M Na₂SO₄</p>	5 V	45 min and 90 min	75%	> 95%	86%	15.75 kWh kg ⁻¹ dye	[109]
	<p>Lissamine Green B (a) (30 mg L⁻¹) Reactive Black 5 (b) (100 mg L⁻¹)</p>	<p>Catalyst 115 g Fe alginate gel beads made of Sodium alginate, BaCl₂, Fe₂(SO₄)₃ (2.68 mM iron), working volume 1.5 L, air bubbling near the cathode at 1.5 L min⁻¹, pH= 2*, 22°C</p>	3 V*	6 h (a) 12.5 h (b)				81% (a) 87% (b)	[111]

Cylindrical glass reactor with two electrodes of 15 cm ² separated by 4.3 cm, flow-by effluent Anode: graphite sheet Cathode: graphite sheet	Lissamine Green B (a) (8.5 mg L ⁻¹) Azure B (b) (4.83 mg L ⁻¹)	Catalyst: 8.69 g Fe alginate gel beads made of Sodium alginate, BaCl ₂ , FeCl ₃ (0.05 M Fe ³⁺), working volume 0.15 L, air bubbling near the cathode at 1 L min ⁻¹ , pH = 2*	14.19 V	30 min	93% (a) 89% (b)	99%			[118]
Bubble reactor made of a cylindrical glass with two bar electrodes Cathode: Graphite, 100 mm high and 6.35 mm diameter 30 mm of the bottom of the reactor Anode: Graphite 100 mm high and 6.35 mm diameter, 270 mm of the bottom of the reactor	Lissamine Green B (LGB), Methyl Orange (MO), Reactive Black 5 (RB5) Fuchsin Acid (FA)	8.5 mgL ⁻¹ (LGB), 1.5 mg L ⁻¹ (MO), 70 mgL ⁻¹ (RB5), 15 mg L ⁻¹ (FA), 0.04 M Na ₂ SO ₄ , 0.675 L working volume, bubbling compressed air at 1 L min ⁻¹ , pH = 2, 600 mg L ⁻¹ of iron dosage	15 V	21 h*	47%	43% (discoloration)			[79]
An EF cell of 2 L with a hollow cylindrical iron anode (effective surface 289.4 cm ²), cylindrical solid graphite cathode (effective surface 35.8 cm ²) (a) This process follows by two sedimentations and a sand filtration (b) Air supplied at the bottom of the cell	Real wastewater from Mexico	Raw solution COD: 328.2 mg L ⁻¹ , turbidity: 39.3 NTU; pH adjusted to 3.5	1 A*	1 h*	-	92.3% discoloration	7.4% (2h) (a) 74.8% (b)	-	[117]
Bubble glass column reactor of diameter 10.4 cm and height 40 cm with two graphite cathodes of 100 cm ² and one graphite anode in the middle of 80 cm ² . Air purged in the solution.	Rhodamine B (50 mg L ⁻¹)	3 L of electrolyte at 10 mL min ⁻¹ * composed of catalyst: FeCl ₃ at 5* mg L ⁻¹ and at pH: 3*.	3.5 V*	8 h	-	98% dye removal	-	50 Wh (gdye) ⁻¹ at 8 h	[114]

*: Best value for the parameter concerned

a: V_{vm}, volume of air under standard conditions per volume of liquid per minute

3. EF applied to pharmaceuticals

3.1 EF applied to β -blockers

Table 4 gives an overview of EF applied to β -blockers for the last few years. Only three β -blockers have been studied, atenolol, metoprolol and propranolol. They are always degraded in synthetic aqueous solution, with only one study evaluating the synergetic effect of using a solution composed of several β -blockers [119]. The concentration of the pollutants ranges from 26 mg L⁻¹ to 150 mg L⁻¹. Most of these molecules require between 5 and 30 min to be completely oxidized but the mineralization of their solutions takes several hours of electrolysis. This difference of treatment time can be explained by involving several steps in the mineralization procedure while the oxidative degradation occurs in one step. Another reason can be the formation of intermediates products more difficult to oxidize than the initial pollutant.

The MCE reported for these experiments is depending on the treatment time and is always less than 50%; it is partly due to side reactions occurring during the process. A link between the chemical structure and the apparent kinetic rate constant of degradation can be underlined thanks to Isarain-Chávez et al. [120] who performed the degradation of three beta-blockers under the same conditions. Atenolol has the higher degradation rate constant which is about 10 times greater than the value reported for metoprolol and propranolol. This difference can be explained by the chemical formula of atenolol containing an amide group which is more electrophilic than the groups in metoprolol and propranolol. One of the best pseudo first order kinetic constant is obtained for atenolol degradation with a value of $9.5 \cdot 10^{-3} \text{ s}^{-1}$ whereas the other constants are around 10^{-3} s^{-1} (Fig. 8). In spite of this high value the electrical energy consumption is significantly higher ($1.08 \text{ kWh (g TOC)}^{-1}$) than other b-blockers having a value of around $0.30 \text{ kWh (g TOC)}^{-1}$. A compromise should then be reached between an efficient degradation and a cost-effective operating process. More studies taking into account

the cost of the process are required in order to better evaluate the feasibility of this process.

Table 4: EF applied to β -blockers

Products	Electrodes Anode, Cathode, surface and O_2 feeding	Pollutant initial concentration	Solution	Current Voltage	Pollutant removing	Degradation efficiency	Pseudo first order kinetic constant (pollutant degradation)	MCE, Energy consumption	Ref
Atenolol	BDD/GDE (1) Pt/GDE - Pt/Carbon felt (2) BDD/GDE- BDD/Carbon felt (3) 3 cm ² for each electrode <i>GDE fed with air at 20 mL/min</i>	158 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, 35°C, magnetic bar for stirring (800 rpm), 0.5 mM Fe ²⁺	50 mA (1) 50 -12 mA (2) 50 -12 mA (3)	Total removal in: > 60 min (1) 25 min (2) 30 min (3)	in 360 min: 77% (1) 81% (2) 90% (3)	0.39 10 ⁻³ s ⁻¹ (1) 2.03 10 ⁻³ s ⁻¹ (2) 1.56 10 ⁻³ s ⁻¹ (3)	Between: 18 and 50% Δ (1) 22 and 35% Δ (2) 18 and 50% Δ (3)	[121]
Atenolol	Platinized titanium (3*15 cm ²) Graphite* (6 cm ²) <i>With bubbling compressed air at 1L/min</i>	45 mg L ⁻¹	Batch, 0.05* M NA ₂ SO ₄ , pH = 3*, Vsol = 250 mL, 20°C, magnetic bar for stirring (400 rpm), 5* mM Fe ²⁺	0.3* A	-	in 240 min, COD removal: 87%	1.58 10 ⁻⁴ s ⁻¹ (for COD removal)	After 4 h: 22.33% Δ 0.194 kWh (kgCOD) ⁻¹	[122]
Atenolol	Pt mesh (4.5 cm ²) Carbon felt (14*5 cm ²) <i>With bubbling compressed air at 1L min⁻¹</i>	40 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 220 mL, room temperature, magnetic bar for stirring, 0.2 mM Fe ³⁺	300 mA	Total removal in 6 min	in 360 min 97%	9.5 10 ⁻³ s ⁻¹	Between: 3 and 15% Δ 1.08 kWh (gTOC) ⁻¹	[119]
Atenolol Metoprolol Propranolol Metoprolol	BDD onto Si / ADE BDD onto Si /ADE – Pt/Carbon felt each electrode has a surface of 3 cm ² <i>ADE is fed with air at 20 mL/min</i>	40 mg L ⁻¹ 52 mg L ⁻¹ 52 mg L ⁻¹ 0.246 mM 66 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, magnetic bar for stirring (800 rpm), 0.5 mM* Fe ²⁺ 0.1 mM Cu ²⁺ , 35 °C	120 mA 120 - 12 mA	- Total removal in 31 min 17 min	in 480 min 100% in 6h 85% 95%	- 2.0 10 ⁻³ s ⁻¹ 3.7 10 ⁻³ s ⁻¹	0.42 kWh (gTOC) ⁻¹ Between 15 and 25% Δ 15 and 47% Δ	[123]

Atenolol (1) Metoprolol (2) Propranolol (3)	BDD/ADE	100 mg L ⁻¹ TOC for each compound	Batch recirculation, 0.1 M NA ₂ SO ₄ , pH = 3, Vsol = 10 L, 35°C, 0.5 mM Fe ²⁺ , Flow rate 250 L h ⁻¹	3 A	-	in 360 min: (1) 54% (2) 54% (3) 56%	(1) 2.24 10 ⁻³ s ⁻¹ (2) 0.22 10 ⁻³ s ⁻¹ (3) 0.13 10 ⁻³ s ⁻¹	Between: (1) 10 and 20%, 0.412 kWh (gTOC) ⁻¹ Δ (2) 5 and 15%, 0.421 kWh (gTOC) ⁻¹ Δ (3) 20 and 40%, 0.405 kWh (gTOC) ⁻¹ Δ (1) 20 and 45%, 0.280 kWh (gTOC) ⁻¹ Δ (2) 10 and 40%, 0.291 kWh (gTOC) ⁻¹ Δ (3) 30 and 50%, 0.224 kWh (gTOC) ⁻¹ Δ (1) 20 and 45%, 0.386 kWh (gTOC) ⁻¹ Δ (2) 5 and 30%, 0.359 kWh (gTOC) ⁻¹ Δ (3) 20 and 35%, 0.354 kWh (gTOC) ⁻¹ Δ	[120]
	Pt/ADE-Pt/CF			3-0.4 A	-	(1) 26% (2) 22% (3) 35%	(1) 0.36 10 ⁻³ s ⁻¹ (2) 0.18 10 ⁻³ s ⁻¹ (3) 0.15 10 ⁻³ s ⁻¹		
	BDD/ADE-Pt/CF Each electrode: 10cm*10cm <i>Compressed air flow rate: 150 mL/min</i>			3-0.4 A	-	(1) 61% (2) 66% (3) 65%	(1) 2.43 10 ⁻³ s ⁻¹ (2) 0.74 10 ⁻³ s ⁻¹ (3) 0.91 10 ⁻³ s ⁻¹		
Propranolol	BDD onto Si /Carbon-PTFE 3 cm ² each electrode <i>fed with air at 20mL min⁻¹</i>	154 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, 35°C, magnetic bar for stirring (800 rpm), 0.5 mM Fe ²⁺	10 mA cm ⁻²	-	78 % in 420 min	-	Between 20 and 78% Δ	[124]
				40 mA cm ⁻²	Total removal in 29 min	85% in 420 min		10 and 22% Δ	
				80 mA cm ⁻²	-	91 % in 420 min		2 and 10% Δ	

Propranolol	monopolar connection: Pt/ADE - Pt/CF of 3 cm ² each, ADE fed with 20 mL min ⁻¹ air	154 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, 35 °C, magnetic bar for stirring (800 rpm), 0.5 mM Fe ²⁺	120-12 mA	Total removal in 12 min	70 % in 420 min	4.0 10 ⁻³ s ⁻¹	8 and 32 % Δ	[22]
Propranolol	Ti ₄ O ₇ (4 * 6 cm ²) Carbon-felt (14 * 5 cm ²) Bubbling of compressed air at 1 L min ⁻¹	26 mg L ⁻¹	Batch, Vsol = 230 mL, 0.05 M NA ₂ SO ₄ , pH = 3, 23 °C, magnetic bar for stirring, 0.1 mM Fe ²⁺	120 mA	Total removal in 10 min	96 % in 480 min	12.9 10 ⁻³ s ⁻¹	6 and 18 % Δ	[58]

*: best value for the parameter

(1), (2), (3): letters to identify different conditions of treatment

Δ: MCE between x% and y%: x and y are the two extremum values during the EF treatment

3.2 EF applied to anti-inflammatories and analgesics

Seven anti-inflammatories and analgesics are studied by the EF process. [Table 5](#) gives some details about these experiments and their treatment efficiency. The efficiency of the degradation measured by the TOC removal degree varies significantly as it is of 57% in 8 h for salicylic acid with graphite plates as electrodes whereas it also reached 95% in 1.5 h for ketoprofen using BDD and carbon felt as anode and cathode, respectively. Concerning the pseudo first order kinetics, the apparent rate constant (k_{app}) values range from 10^{-4} to 10^{-3} s^{-1} ([Fig. 8](#)). Finally, as for beta-blockers, the best way to identify the usefulness of the process is the energetic consumption which is available for only five studies, the more cost-effective among them appears to be dipyrone with the DSA-Cl₂/GDE system with 0.049 kWh (g TOC)⁻¹ and with a k_{app} of $1.2 \cdot 10^{-3} \text{ s}^{-1}$ aiming at a TOC removal of 63% in 90 min.

Table 5: EF applied to anti-inflammatories and analgesics

Products	Electrodes Anode, Cathode, surface and O_2 feeding	Pollutant initial concentration	Solution	Current Voltage	Pollutant degradation	TOC removal	Pseudo first order kinetic constant (pollutant degradation)	MCE, Energy consumption	Ref
Diclofenac	BDD onto Nb (64 cm ²) Stainless steel (64 cm ²) with compressed air bubbled separated by 2 cm	50 mg L ⁻¹	Batch recirculation, 0.05 M Na ₂ SO ₄ , pH=3, Vsol = 4L, room temperature, 0.5 mM Fe ²⁺ , flow rate 2 L min ⁻¹	1.56 mA cm ⁻²	-	in 180 min: 62%	-	0.27 kWh (gTOC) ⁻¹	[20]
		100 mg L ⁻¹		6.25 mA cm ⁻²		84%		0.78 kWh (gTOC) ⁻¹	
				1.56 mA cm ⁻²		69%		0.41 kWh (gTOC) ⁻¹	
				² 6.25 mA cm ⁻²		79%		0.68 kWh (gTOC) ⁻¹	
Dipyron	DSA-Cl ₂ 20 cm ² GDE containing CoPc and PTFE (20 cm ²) fed with O ₂ pseudo reference electrode Pt//Ag/AgCl/KCl	50 mg L ⁻¹	Batch recirculation, 0.1 M H ₂ SO ₄ , 0.1 M K ₂ SO ₄ , pH = 3, Vsol = 1.5 L, 20°C, 1 mM Fe ²⁺ , flow rate 50 L h ⁻¹	-2.1 V	90 % removal in 30 min	in 90 min 62.8 %	1.2 10 ⁻³ s ⁻¹	0.049 kWh (gTOC) ⁻¹	[21]
Dipyron	DSA-Cl ₂ 20 cm ² GDE containing CoPc and PTFE (20 cm ²) fed with O ₂ pseudo reference electrode Pt//Ag/AgCl/KCl	50 mg L ⁻¹	Batch, 0.1 M H ₂ SO ₄ , 0.1 M K ₂ SO ₄ , pH = 3, Vsol = 400 mL, 1 mM Fe ²⁺	-0.9* V	96 % removal in 90 min	in 90 min 54.4%	6.7 10 ⁻³ s ⁻¹	0.27 kWh (gTOC) ⁻¹	[125]
Ibuprofen	BDD onto Si (3cm ²) Carbon-PTFE (3cm ²) fed with 20mL min ⁻¹ of O ₂	41 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, 25°C, magnetic bar for stirring, 0.5 mM Fe ²⁺	33.3 mA cm ⁻²	Total removal of Ibuprofen 30 min	81 % (DOC removal) in 6h	4.9 10 ⁻⁴ s ⁻¹	Between 5 and 8% Δ	[126]

Ibuprofen	BDD onto Nb (25cm ²) 3D Carbon felt (14*5 cm ²) with bubbling compressed air at 1L min ⁻¹	41 mg L ⁻¹	Batch, 20% acetonitrile, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 230 mL, 23°C, magnetic bar for stirring, 0.2 mM Fe ³⁺	50 mA	Total removal in 240 min		0.3 10 ⁻³ s ⁻¹		
				500 mA	50 min	-	1.23 10 ⁻³ s ⁻¹	-	[127]
Ketoprofen	BDD onto Nb (24 cm ²) Carbon felt (18*6 cm ²) with air at 1L min ⁻¹	50 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ in tap water pH = 3, Vsol = 250 mL, magnetic bar for stirring (800 rpm), 0.1 mM* Fe ²⁺	100 mA	Total removal in 40min	in 1h30, 60 %	2.3 10 ⁻³ s ⁻¹	Between 15 and 50% Δ	
				750 mA	20 min	95%	3.8 10 ⁻³ s ⁻¹	4 and 15 % Δ	[24]
				2000 mA	15 min	95%	6.4 10 ⁻³ s ⁻¹	4 and 9% Δ	
Naproxen	-DSA-O ₂ (IrO ₂) Carbon-PTFE -BDD Carbon-PTFE Each electrode 20 cm ² fed with atmospheric air at an overpressure of 8.6 kPa separated by 1.2 cm	40 mg L ⁻¹	Batch recirculation, 0.05 M NaClO ₄ , pH = 3, Vsol = 2.5 L, 35 °C, 0.5 mM Fe ²⁺ , flow rate 180 L h ⁻¹			in 6h, 50 %	-	Between 5 and 27 % Δ, 1.2 kWh (gTOC) ⁻¹ (average)	
				50 mA cm ⁻²	Total removal in 12 min	45%	5.2 10 ⁻³ s ⁻¹	5 and 35 % Δ, 2.25 kWh (gTOC) ⁻¹ (average)	[128]
Paracetamol	Pt (3 cm ²) Oxygen diffusion cathode (3 cm ²)	157 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ pH = 3, Vsol = 100 mL, magnetic bar for stirring ,1 mM* Fe ²⁺ + 0.25 mM Cu ²⁺ , 35°C	100 mA	Total removal in 24 min	in 360 min 70%	-	-	[129]

Paracetamol	Pt foils Porous carbon prepared with a N ₂ O ₂ gas flow (2 cm ²) separated by 3 cm O ₂ bubbling	15 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 30 mL, magnetic bar for stirring (800 rpm), 0.2 mM* Fe ²⁺	-20 mA cm ⁻²	-	in 10 h 95%	-	-	[130]
Salicylic acid	BDD onto Si (3 cm ²) Carbon PTFE (3 cm ²) fed with 12 mL min ⁻¹ O ₂	164 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, Vsol = 100 mL, 35°C, 0.5 mM Fe ²⁺ , magnetic bar for stirring	33 mA cm ⁻² 100 mA cm ⁻² (17.1V cell) 150 mA cm ⁻² (21V cell)	Total removal in 30 min -	in 180 min 73% 85% 90%	1.8*10 ⁻³ s ⁻¹ -	at 180 min: 22% 8.4%, 308 kWh m ⁻³ 6.0%, 472 kWh m ⁻³	[131]
Salicylic acid	Graphite plates of 25 cm ² separated by 3 cm, bubbling compressed air near the cathode	100 mg L ⁻¹	Batch, 5 mg L ⁻¹ * NaHCO ₃ , pH = 2.5*, Vsol = 750 mL, 20 mg L ⁻¹ * Fe ²⁺	8V	75% removal in 8h	in 8h 57%	-	-	[132]

*: best value for the parameter(average): the average between the maximum and minimum value for the energy consumption.

Δ: MCE between x% and y%: x and y are the two extremum values during the EF treatment

3.3 EF applied to antibiotics and diuretics

More studies were done on antibiotics as they are a large group of pharmaceuticals widely used all over the world. The k_{app} values are in the same range for beta-blockers and anti-inflammatories which demonstrates the ability of this process to treat pharmaceuticals (Fig. 8). The better value ($26 \cdot 10^{-3} \text{ s}^{-1}$) is obtained for flumequine degradation using a BDD/carbon felt cell. 17 different pharmaceuticals were degraded through an EF system (Table 6). The treatment time for complete oxidative degradation of pollutant is quite different from one system to another; it can be of 4.5 h for cefalexin or of 3 min for flumequine; it is around 30 min for most cases. The TOC total or the DOC total (dissolved organic carbon) removal is around 6 h for most of the experiments. Concerning the MCE, for almost all the experiments the values are around 15%, only in one study, its value reached up to 55% for chloramphenicol, due probably to the very high pollutant (245 mg L^{-1}). The energy consumption is also in the same range as for the other pharmaceuticals being around $1 \text{ kWh (g TOC)}^{-1}$ or kWh (g DOC)^{-1} .

To sum up, the EF is a clearly efficient process able to degrade lots of different groups of pharmaceuticals. Some points have yet to be studied more deeply. First in order to apply this process at the industrial scale, pilot studies are required to treat issues that have been explained previously like, for instance mass transfer. Our group is actually working on a pilot in order to evaluate the scaling-up of the EF. To prepare the transition to industrial scale, the EF needs to be studied in continuous mode; this has only been done a few times (Table 3). The concentration of the pollutant ranges from around 50 mg L^{-1} to 150 mg L^{-1} which is higher than the concentration in wastewater as seen in the introduction section. In order to simulate the efficiency of the process better and in a more similar context of real treatment, smaller concentrations should be involved or real effluent should be used which has only been done a few times [113,117]. Indeed, in a real effluent, due to the presence of several

pharmaceuticals, some interactions between them can slow down the process. As the cost remains high, combining this process with a biological treatment could decrease significantly the operating costs. Therefore the cost of the process is to be considered more deeply. The bio-treatment being more cost-effective than the EF, a comparison of their efficiency was done by analyzing their apparent kinetic constant for the same pharmaceuticals (Fig. 8). For all the data given in Fig. 8 the EF is significantly more efficient. However, the scale of the process is not the same as for the bio-treatment an industrial scale is used whereas for the electro-Fenton the volume is around 300 mL. But, for the biological degradation, the limiting parameter is the kinetic of degradation, this implies that the scale-up of the process is not impacting too much on the process; this enables the comparison between both processes. Because of this difference of efficiency, the solution to degrade efficiently and at a lower cost can be to combine both processes.

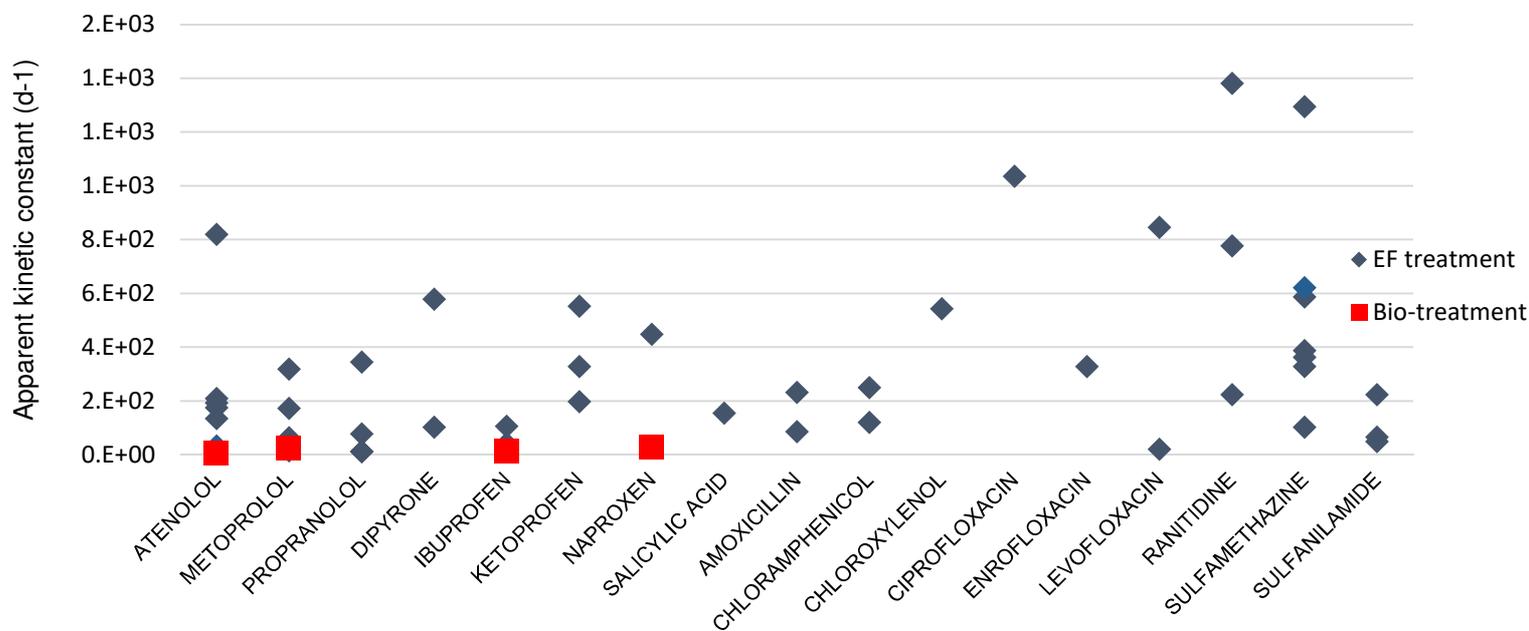


Fig. 8: Apparent kinetic constants for different pharmaceuticals treated by EF process or by a bio-treatment

Table 6: EF applied to antibiotics and diuretics

Products	Electrodes Anode, Cathode, surface and O_2 feeding	Pollutant initial concentration	Solution	Current Voltage	Pollutant degradation	TOC removal	Pseudo first order kinetic constant (pollutant degradation)	MCE, Energy consumption	Ref
Amoxicillin	BDD (4.5cm ²) Carbon felt (77 cm ²) With compressed air	48 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 250 mL, magnetic bar for stirring, 0.2 mM Fe ²⁺	60 mA	Total removal in 20 min	In 10 h: 80 %	2.7 10 ⁻³ s ⁻¹	Between 10 and 30 % Δ	[19]
				300 mA	10 min	> 90 %	1.0 10 ⁻³ s ⁻¹	3 and 11 % Δ	
Amoxicillin	Ti ₄ O ₇ (4 * 6 cm ²) Carbon-felt (14 * 5 cm ²) Bubbling of compressed air at 1 L min ⁻¹	20 mg L ⁻¹	Batch, V _{sol} = 230 mL, 0.05 M NA ₂ SO ₄ , pH = 3, 23 °C, magnetic bar for stirring, 0.1 mM Fe ²⁺	120 mA	Total removal in 5 min	In 6h 90 %	10.3 10 ⁻³ s ⁻¹	Between 10 and 25 % Δ 0.2 and 0.7 kWh gTOC ⁻¹	[59]
Cefalexin	RuO ₂ /Ti mesh 54 cm ² Activated carbon felt (54 cm ²) with pure oxygen at 0.1L min ⁻¹	200 mg L ^{-1*}	Batch, 0.05 M NA ₂ SO ₄ , pH = 3*, V _{sol} = 500 mL, room temperature, magnetic bar for stirring, 1 mM* Fe ²⁺	6.66* mA cm ⁻²	Total removal in 4.5 h	In 8 h 60%	-	Between 7.5 and 22% Δ	[133]
Chlorophene	BDD onto Si (3 cm ²) Carbon-PTFE (3 cm ²) fed with 20mL min ⁻¹ of O ₂ (1) BDD onto Si (3 cm ²) Carbon felt (70 cm ²) bubbling compressed air 1 L min ⁻¹ (2)	84 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 200 mL, 20°C, magnetic bar for stirring, 4 mM Fe ³⁺ (1) or 0.2 mM Fe ³⁺ (2)	60 mA		In 6 h 67 % (1)		Between 7 and 27% (1) Δ	[134]
				300 mA	Total removal in 90 min (1)	(1) 25% (2) 100%	-	4 and 12% (1) 4 and 22% (2) Δ	

Chloramphenicol	BDD (3 cm ²) Carbon-PTFE (3 cm ²) <i>fed with 300 mL/min of air (1)</i>	245 mg L ⁻¹	0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 100 mL (1), 35°C, magnetic bar for stirring (800 rpm), 0.5 mM Fe ²⁺	33.3 mA cm ⁻² (1)	Total removal in 27 min (1)	DOC removal 81 % after 6 h (1)	2.9 10 ⁻³ s ⁻¹ (1)	Between 18 and 55% (1) Δ	[135]
	Pt (3 cm ²) air diffusion filter press (2)		(2) 10 L at a flow rate of 200L h ⁻¹	100 mA cm ⁻² (2)	60 min (2)	DOC removal 40% after 6h (2)	1.4 10 ⁻³ s ⁻¹ (2)	2 and 18 % Δ 1.1 kWh (gDOC) ⁻¹ (2) (average)	
Chloroxylenol	BDD onto Si (3 cm ²) Carbon-PTFE (3 cm ²) <i>fed with 20mL min⁻¹ of O₂</i>	100 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH= 3, V _{sol} = 100 mL, 25°C, magnetic bar for stirring, 1 mM Fe ²⁺	33 mA cm ⁻²	Total removal in 20 min	82 % in 6 h	6.3 10 ⁻³ s ⁻¹	Between 10 and 25% Δ	[136]
Ciprofloxacin	Pt mesh height 5 cm i.d. 3 cm Carbon felt 14 cm *5 cm	50 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 230 mL, 23°C, magnetic bar for stirring, 0.1* mM Fe ²⁺	400* mA	Total removal in 8 min	in 6 h 94.62%	12 10 ⁻³ s ⁻¹	Between 2.5 and 7% Δ	[23]
Enrofloxacin	BDD onto Si (3 cm ²) Carbon-PTFE (3 cm ²) <i>fed with 12 mL min⁻¹ of O₂</i>	158 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 100 mL, 35°C, magnetic bar for stirring (700 rpm), 0.5 mM Fe ²⁺	33 mA cm ⁻²	Total removal in 20 min	78 % in 6 h	3.8 10 ⁻³ s ⁻¹	Between 15 and 28% Δ 0.47 kWh (gTOC) ⁻¹ (0.2 mM Fe ²⁺)	[137]
Flumequine	BDD (3 cm ²) Carbon PTFE air diffusion electrode (3 cm ²) <i>fed with pumped air at 300 mL min⁻¹ separated by 1 cm</i>	62 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 100 mL, 35°C, magnetic bar for stirring (800 rpm), 2 mM* Fe ²⁺	50 mA	Total removal in 25 min	in 6 h 70 %	3.2 10 ⁻³ s ⁻¹	Between 10 and 22% Δ	[138]
				300 mA	3 min	87%	26 10 ⁻³ s ⁻¹	2.5 and 10% Δ	
Furosemide	BDD (25 cm ²) Carbon felt piece <i>with bubbling compressed air</i>	33 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 230 mL, room temperature, magnetic bar for stirring, 0.1 mM* Fe ²⁺	100 mA	-	in 4 h 80%	-	Between 6 and 18% Δ	[139]
				300 mA	Total removal in 7 min	90%	17 10 ⁻³ s ⁻¹	2 and 9% Δ	
				500 mA	5 min	95%	20 10 ⁻³ s ⁻¹	-	

Levofloxacin	BDD (6 cm ²) Carbon felt (60 cm ²) <i>with compressed air bubbled at 1L min⁻¹</i>	83 mg L ⁻¹	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, V _{sol} = 200 mL, magnetic bar for stirring, pyrite 1g L ⁻¹ * (0.2 mM Fe ²⁺), 25°C	100 mA (a)	Total removal in 210 min	-	0.25 10 ⁻³ s ⁻¹	-	[140]
				300 mA (b)	-	in 8 h 98 %	-	Between 3 and 6.5% Δ 2.5 kWh (gTOC) ⁻¹ (average) Instantaneous current efficiency: between 5 and 17 %	
Levofloxacin	Pt (5 cm ²) three-dimensional carbon felt (10 cm * 8 cm) <i>with air bubbling</i>	54 mg L ⁻¹	Batch, 0,05 M Na ₂ SO ₄ pH = 3, V _{sol} = 200 mL, room temperature, 0.1* mM* Fe ²⁺	400* mA	Total removal in 10 min	COD removal in 6 h 91.2%	9.8 10 ⁻³ s ⁻¹	Between 6 and 18% Δ	[141]
Ranitidine	BDD onto Nb (25 cm ²) Carbon felt (15*4 cm ²) <i>with bubbling compressed air at 1L min⁻¹</i>	31 mg L ⁻¹	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, V _{sol} = 230 mL, room temperature, magnetic bar for stirring, 0.1 mM Fe ²⁺	100 mA	90 % removal 30 min	in 6 h 70 %	9.0 10 ⁻³ s ⁻¹	Between 6 and 18% Δ	[142]
				500 mA	Total removal in 10 min	95%	16 10 ⁻³ s ⁻¹	2 and 5% Δ	
Ranitidine	Filter-press Pt (20 cm ²) Carbon PTFE (20 cm ²) <i>fed with air at an overpressure of 8.6 kPa</i>	33.8 mg L ⁻¹ (1) 112.6 mg L ⁻¹ (2)	Batch recirculation, 0.05 M Na ₂ SO ₄ , pH = 3, V _{sol} = 2.5 L, 35 °C, 0.5 mM Fe ²⁺ flow rate 200 L h ⁻¹	25 mA cm ⁻²	-	in 6 h: 24% (2)	1.1 10 ⁻³ s ⁻¹ (2)	between 10 and 25% Δ, 0.8 kWh (gTOC) ⁻¹ (2) (average)	[143]
				100 mA cm ⁻²	Total removal in 30 min (2)	60% (1) 44% (2)	2.6 10 ⁻³ s ⁻¹ (2)	5 and 22% Δ, 2.1 kWh (gTOC) ⁻¹ (2) (average) 3 and 11% Δ, 4.8 kWh (gTOC) ⁻¹ (average) (1)	
Sulfachloropyridazine	BDD onto Nb (25 cm ²) Carbon felt (14,2*4,3 cm ²) <i>with bubbling compressed air</i>	59 mg L ⁻¹	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, V _{sol} = 220 mL, room temperature, 0.2 mM Fe ²⁺ , magnetic bar for stirring	60 mA (a)	Total removal in 40 min	in 10 h 72% in 4h 34%	1.9 10 ⁻³ s ⁻¹	-	[144]
				300 mA (b)	20 min	in 10 h > 95% in 4 h 79%	10 10 ⁻³ s ⁻¹	-	

Sulfamethazine	BDD onto Si (3 cm ²) Carbon-PTFE (3 cm ²) <i>fed with 300mL min⁻¹ of air</i>	193 mg L ⁻¹	0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 100 mL, 35°C, magnetic bar for stirring (800 rpm), 0.5 mM Fe ²⁺	33.3 mA cm ⁻²	Total removal in 20 min	DOC removal in 7 h: 81%	3.8 10 ⁻³ s ⁻¹	Between 10 and 20 % Δ	[145]
				66.7 mA cm ⁻²	15 min	90%	6.8 10 ⁻³ s ⁻¹		
				100 mA cm ⁻²	10 min Total removal in 20 min (1) (2)	94% in 8 h:	15 10 ⁻³ s ⁻¹ in s ⁻¹		
Sulfamethazine	BDD/GF (1) DSA/GF (2) GF/GF (3) GF (graphite felt) cathode: 17.5 cm * 5 cm anode 24 cm ²	56 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 300 mL, room temperature, magnetic bar for stirring (800 rpm), 0.2 mM Fe ²⁺	20.83 mA cm ⁻²	15 min (3)	(2) 75% (1) 95%	4.2*10 ⁻³ (1) 4.5 10 ⁻³ (2) 7.2 10 ⁻³ (3)	-	[146]
				2.08 mA cm ⁻²	60 min (1) (2)	(3) 73%	1.2 10 ⁻³ (1) 1.0 10 ⁻³ (2) 3.7 10 ⁻³ (3)	-	
					30 min (3)				
Sulfamethazine	BDD (25 cm ²) Carbon felt (15 cm * 4 cm) <i>with compressed air bubbling 1L min⁻¹</i>	56 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , V _{sol} = 200 mL, room temperature, magnetic bar for stirring, (1) 0.2 mM Fe ²⁺ pH= 3 (2) 2 g L ⁻¹ Pyrite and pH= 6.1	300 mA	Total removal in 40 min (2)	in 8 h: 92% (1) 94% (2)	1.710 ⁻³ s ⁻¹ (2)	Between: 3 and 11% (1) 3 and 12% (2) Δ	[147]
Sulfamethoxazole	BDD onto Nb (25cm ²) Carbon felt (14 cm * 5 cm), <i>air flow rate = 1 L min⁻¹</i>	53 mg L ⁻¹	Batch, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 220 mL, 23 °C, magnetic bar for stirring, 0.2 mM Fe ²⁺	30 mA cm ⁻²	Total removal in -	in 10 h: 86%	-	-	[148]
				100 mA cm ⁻²	20 min	94%	-		
				300 mA cm ⁻²	15 min	98%	4.3 10 ⁻³ s ⁻¹		
Sulfanilamide	Filter-press with Pt/Carbon PTFE Electrodes surface: 20 cm ² <i>fed with air at an overpressure of 8.6 kPa</i>	239 mg L ⁻¹	Batch recirculation, 0.05 M NA ₂ SO ₄ , pH = 3, V _{sol} = 2.5 L, 35°C, 0.5 mM Fe ²⁺ , flow rate 200 L h ⁻¹	50 mA cm ⁻²	Total removal in 100 min	DOC removal in 4 h: 25%	5.7*10 ⁻⁴ s ⁻¹	Between: 18 and 20% Δ, 0.75 kWh (gDOC) ⁻¹ (average)	[149]
				150 mA cm ⁻²	50 min	50%	7.7 10 ⁻⁴ s ⁻¹	5 and 10% Δ, 1.8 kWh (gDOC) ⁻¹ (average)	

Sulfanilamide	BDD (25 cm ²) Carbon felt (15 cm * 4 cm) <i>with</i> <i>compressed air</i> <i>bubbling 1L min⁻¹</i> BDD onto NB (24 cm ²) Carbon felt (14 cm*5 cm) (1)	103 mg L ⁻¹	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, Vsol = 230 mL, room temperature, magnetic bar for stirring, 0.2 mM Fe ²⁺	100 mA	Total removal	80% in 6 h	-	Between: 17 and 23% 6 and 14% Δ 4 and 11% Δ	[150]
				300 mA	in: - 30 min	98% in 6 h	2.6 10 ⁻³ s ⁻¹		
				1000 mA 500 mA	- Total removal, -	100% in 6 h after 6 h, 99% (1) 22% (2) 81% (3)	- -		
Tetracycline	DSA (24 cm ²) Carbon felt (2) Pt (24 cm ²)/ Carbon felt (3) <i>with compressed air</i> <i>bubbling 1L min⁻¹</i> BDD onto Si (3 cm ²) Carbon-PTFE (17 cm * 4.1 cm) <i>fed with 12</i> <i>mL min⁻¹ of O₂</i>	100 mg L ⁻¹	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, Vsol = 220 mL, 23°C, magnetic bar for stirring, 0.1 mM Fe ³⁺	200 mA	30 min (1) 50 min (2) 40 min (3)	-	3.0 10 ⁻³ s ⁻¹ (1) 2.0 10 ⁻³ s ⁻¹ (2) 2.3 10 ⁻³ s ⁻¹ (3)	-	[27]
Triclosan		Triclosan: 50 mg L ⁻¹ (1)	Batch, 0.05 M Na ₂ SO ₄ , pH = 3, Vsol = 200 mL, 20°C, magnetic bar for stirring, 0.2 mM Fe ³⁺	60 mA	Total removal 120 min (1) (2)	-	-	-	[151]
Triclocarban		Triclocarban: 5 mg L ⁻¹ (2)		300 mA	90 min (2)	-	-	-	

(average): the average between the maximum and minimum value for the energy consumption.

Δ: MCE between x% and y%: x and y are the two extremum values during the EF treatment

*: best value for the parameter

(1), (2), (3): letters to identify different conditions of treatment

4. Combined process and its application to treat pharmaceuticals

4.1 AOPs as a pretreatment for biodegradability improvement

Conventional biological processes in WWTP do not always provide satisfactory results in terms of pharmaceuticals removal [7–9], since many of these organic substances are toxic or resistant to microorganisms. Therefore, one feasible option to remove the persistent organic compounds is to combine biological treatment with EAOPs such as EF. This attractive potential alternative is a solution to reduce the global cost which increases with treatment time in EF.

Two properties of the solution are considered in the literature to assess the feasibility of a biological treatment: biodegradability and toxicity.

Biodegradability of the solution is a parameter of great importance when combined treatments are considered. It is often defined thanks to the ratio of BOD_5/COD , with BOD_5 the biochemical oxygen demand at 5 d. Usually, when this ratio is greater than 0.4, the solution is considered as biodegradable [152]. Less commonly one can also find the ratio of BOD_{14}/COD with BOD_{14} being the biochemical oxygen demand at 14 d. The limitation of the BOD test is mainly due to the fact that micro-organisms used as inoculum in the BOD tests may not be initially adapted to transform the organic compounds present. Thus, a lag phase is often observed during the first days in the BOD curve that can lead to very low values of the BOD after 5 d. However, after this lag phase, degradation of the organic compounds can occur leading to a strong increase in the BOD curve. So, to overcome this potential underestimation of the biodegradability of the solution, the ultimate BOD (BOD_u) can be used [153]. Another bias of the use of BOD test is that in many papers, the concentration used in the BOD test is not the same as in the EF process. Thus, as the rate of biodegradation appears to vary with concentration, the inhibiting effect of the organic compounds can be underestimated. For

these two main reasons, results of BOD tests should be interpreted with caution.

Another way to indirectly measure the biodegradability of organic effluents which was used in the most recent studies is the ratio between COD and TOC. Indeed, a decrease in COD (including oxidation of the pollutant) can promote the decrease of the solution toxicity. A decrease of the ratio COD/TOC is a favorable trend for biological treatment as there are fewer oxidative products (pollutant) and the amount of organic carbon is sufficient to feed bacteria [154,155]. From these two parameters, the AOS (average oxidation state) can be estimated which is given in Eq. 18. This parameter enables to approximate the degree of oxidation of a solution. The lowest value is -4 for CH₄ and 4 for CO₂ [28].

$$\text{AOS} = 4 (\text{TOC} - \text{COD}) / \text{TOC} \quad (18)$$

with TOC in mg L⁻¹ and COD in mg O₂ L⁻¹.

Measuring the toxicity can also be interesting. However, there are usually errors in the interpretation of results. Several methods are used to measure the toxicity of solutions electrochemically pre-treated. In general, ecotoxicological bioassays standards are used. The most commonly used is the bacterial assay Microtox® which is based on natural or provided ability of bioluminescence of a bacterial strain. However, as it is a marine strain, doubts are arising due to its application as a reference when a combined treatment is considered. It should be highlighted that the toxicity measured is not representative of the toxicity of adapted consortia that are usually employed when biological treatments are considered. Thus with this method, a high toxicity value does not mean that all the micro-organisms from a consortia will be inhibited or killed by the solution.

The choice of the relevance of the combined process and the order in which to apply it, whether the biological treatment first and the AOP after or the contrary, are in general based on the biodegradability and toxicity of the solution. A first methodology was proposed by

Scott and Ollis who divided the wastewaters into four types. The first group gathers large-size molecules that are not biodegradable (polymers, pesticides, herbicides, emulsifying agents,...). In this case, a chemical treatment is advised first to hydrolyze the big molecules into smaller biodegradable molecules to allow their degradation. Mantzavinos and Psillakis [155] explained this phenomenon: bigger molecules are less likely to be degraded by a biological treatment as their size prevents them from permeating cell walls. The second group is formed of molecules with a high biodegradability rate but that contains a small amount of non-biodegradable molecules which will require a post-chemical treatment to eliminate the resistant pollutants. Here it is cost-effective to start with a biological treatment and then use an AOP. The third group is composed of molecules with a toxic activity. In this case, an AOP pre-treatment could be preferred, but it is not always the case. Finally, the fourth group is made of solutions that contain molecules that are biologically transformed into dead-end intermediates compounds that cannot be further biologically degraded and can lead to strong inhibition of the biological activity. Thus, an additional AOP treatment should be performed in order to degrade these intermediate molecules [28].

This classification was completed by Comninellis et al. [156] who added the notion of TOC to classify the pollutants. They defined 4 groups, one with biodegradable compounds which correspond to the second group of Scott and Ollis and three groups with non-biodegradable compounds: (i) wastewaters with a high TOC ($> 0.1 \text{ g L}^{-1}$) requiring a pre-treatment with an AOP before a biological treatment; (ii) wastewaters with a low TOC ($< 0.1 \text{ g L}^{-1}$) but with a high toxicity, in this case a suitable AOP is necessary to degrade the toxic compounds but a biological treatment is not recommended as wastewaters have little metabolic value for the bacteria; (iii) wastewaters containing non-biodegradable molecules at low TOC and toxicity but with a characteristic which prevents their release are, for example colored wastewaters. Here only an AOP is advised.

As it was seen with both classifications, most of the time an AOP is performed first followed or not by a biological treatment as illustrated by Mantzavinos and Psillakis as 2/3 of the work showed a rise in biodegradability and/or a decrease in toxicity with an AOP pre-treatment. But sometimes it is not the case [157,158] for several reasons: (i) stable intermediates formed may be less degradable than the parent compound; (ii) AOPs are not specific, so the biodegradable molecules can be degraded before persistent ones; (iii) finding the good conditions for the pre-treatment is needed: if too short, the solution will not change enough to be treated by activated sludge and if too long the process will not be cost-effective; (iv) the compounds used during the AOP can be toxic for the biological treatment for example O₃ or H₂O₂: if not eliminated the second treatment will not be efficient and (v) if a high concentration of halides is used, the AOP process could form toxic organic halogens which increase the toxicity of the solution [159].

As a conclusion, even if some guidelines have been found to classify wastewaters, performing each treatment separately and studying the synergetic effect as well as measuring the toxicity and the biodegradability during each treatment is necessary in order to find the best combination with the highest efficiency and the lowest cost.

4.2 Effects of EF on effluents characteristics

4.2.1 Enhancement of biodegradability

Table 7 gives an overview of the recent studies in which biodegradability of pharmaceutical solutions is investigated, except for the combination of EF with a biological treatment, which will be more detailed in sub-section 4.3. According to this Table, among the twelve studies, only three studies were performed with both treatments: in two works, an EF treatment is followed by a biological degradation step and in the third one, the treatment is performed in the opposite order. In four cases, an EF followed by a biological treatment was found quite

inappropriate as only in one case the solution obtained was very toxic (L) [160], in two studies the final solution have a BOD₅/COD lower than 0.3 after EF treatment (G-H) [161,162] and only in one study was the biodegradability level over the limit but the time of treatment was 24 h which made the process too expensive (B) [133]. Meanwhile for those four experiments (B-G-H-L) the biodegradability was improved. It is only by performing the biological treatment that it will be possible to confirm if this treatment is actually useless. For the others experiments the efficiency of combining both processes should work and for some of them it can be really interesting in order to reduce the operating costs as the EF treatment allows to have a biodegradable solution in a short treatment time (C-D-E-F) [155,163–165].

Table 7: Biodegradability studies with EF and biological treatments

Raw Solution	Biological treatment	Treatment EF	Order of treatment	Efficiency of EF	Efficiency of biological treatment	Effect of both treatment	Evolution of toxicity	Evolution of biodegradability	Ref
Lurgi coal gasification wastewater collected after a treatment plant with COD: 140-190 mg L ⁻¹ , BOD ₅ /COD: 0.05-0.09, TOC: 90-125 mg L ⁻¹	Sludge desolved activated carbon from sewage	Undivided 1 L cell with Ti/SnO ₂ as anode and Active carbon fiber as cathode (20 cm ²) for 1h at 10 mA cm ⁻² , raw pH	B-EF-B	TOC removal (1h) 42%, COD removal (1h): 50 %	COD removal: 45.82%, Color removal: 46.28% in 8 hours	COD removal: 82.72%, Color removal: 95.26%, TOC removal: 84%	-	0.45 after 1h	[166] (A)
Synthetic solution of cefelaxin at 200 mg L ⁻¹ (COD= 325 mg L ⁻¹), solution non-biodegradable	-	Undivided cell with as anode: RuO ₂ /Ti (54 cm ²) as cathode: activated carbon felt (54 cm ²), 500 mL of Na ₂ SO ₄ at 0.05 M, pH: 3*, 1 mM* Fe ²⁺ , 6.66* mA cm ⁻² , O ₂ at 0,1 L min ⁻¹ , 8h*	EF	COD removal (8h): 72%, Total removal of Cefelaxin (4 h)	-	-	-	At 2h BOD ₅ /COD: 0.05 and BOD ₁₄ /COD: 0.08 at 4.5 h: BOD ₅ /COD: 0.1 and BOD ₁₄ /COD: 0.2 at 8 h: BOD ₅ /COD: 0.26 and BOD ₁₄ /COD: 0.43 at 24 h: BOD ₅ /COD: 0.71 and BOD ₁₄ /COD: 1.0	[133] (B)

Synthetic solution of Sulfamethazine at 0,2 mM (COD= 88 mgO ₂ L ⁻¹), solution non-biodegradable	-	Undivided recirculation cell with as anode: Pt (10 cm ²) as cathode: carbon felt (208 cm ²), 1 L of Na ₂ SO ₄ at 0.05 M, pH: 3*, 0,1 mM* Fe ²⁺ , compressed air at 450 mL min ⁻¹ , solution flow rate: 2 L min ⁻¹ , 18°C	EF	COD removal at 60 min (500mA) : 38%, at 120 min (500 mA): 60%, at 120 min (300 mA): 56% COD/COD ₀ (3 h): 42% TOC/TOC ₀ (3 h): 30%, total removal of Sulfamethazine : 50 min	-	-	-	BOD ₅ /COD: at 60 min (500 mA): 0.5, at 120 min (500 mA): 0.8, at 120 min (300 mA): 0.97 BOD ₅ /COD at 60 min: 0.25, at 180 min: 0.51 at 360 min: 0.30 and TOC/COD: at 60 min 1,62 at 360 min: 1,51	[163] (C)
Synthetic solution of Enoxacin at 50 mg L ⁻¹ (COD/TOC= 2.4, BOD ₅ /COD=0) solution non-biodegradable	-	Undivided cell with as anode: Pt (34.6 cm ²) as cathode: carbon felt (45 cm ²), 250 mL of Na ₂ SO ₄ at 0.05 M, pH: 3, 0.2 mM* Fe ²⁺ , 300* mA compressed air, 18°C, 3h	EF	Total removal of Rhodamine B in 20 min, TOC removal (1 h 30): 87%	-	-	-	BOD ₅ /COD at 1h30: 0.331	[155] (D)
Synthetic solution of Rhodamine B at 50 mg L ⁻¹ (0,1 M, BOD ₅ /COD=0.04 9) solution non-biodegradable	-	Undivided cell with as anode: Pt (6 mm ²) as cathode: GDE modified with polytetrafluoroethylene-carbon black (25 cm ²), 500 mL of Na ₂ SO ₄ at 0.05 M, pH: 3, 0.5 mM* Fe ²⁺ , 5* mA cm ⁻² , compressed air at 1L min ⁻¹ , 25°C, 1 h 30*	EF	TOC removal in 240 min: 7.5% (250 mg L ⁻¹ m-cresol)	-	-	-	TOC removal in 240 min: (140 mg L ⁻¹ TOC) 43%	[164] (E)
Synthetic solution of m-cresol at 200 mg L ⁻¹ (EF) 250 mg L ⁻¹ (Biological treatment)	Aerobic treatment with activated sludge	Undivided cell with as anode: Ti/SnO ₂ -Sb ₂ O ₅ -IrO ₂ (38 cm ²) as cathode: CNT (32 cm ²) fed with air at 25 mL s ⁻¹ , 200 mL of Na ₂ SO ₄ at 0.1 M, pH: 3, 0.4 mM Fe ²⁺ , -1V (cathodic potential), 25°C	EF-B or B	TOC removal in 240 min: 7.5% (250 mg L ⁻¹ m-cresol)	-	-	-	Evaluated by the experiments using an aerobic treatment	[165] (F)

<p>Synthetic solution of whether Orange II (OR) (COD: 142 mgO₂ L⁻¹) or Methyl Red (MR) (COD: 144 mgO₂ L⁻¹), Biebrich Scarlet (BS) (COD: 106 mgO₂ L⁻¹); for all the solution BOD₅/COD: 0</p>	<p>Undivided cell with as anode: Pt (31.4 cm²) as cathode: graphite felt (74.5 cm²), saturated calomel electrode as reference electrode with compressed air, 400 mL, pH: 1*, 0.1* mM Fe³⁺, -0.5V*, 30°C*</p>	<p>EF</p>	<p>COD 45 min: OR: 144 mgO₂ L⁻¹, MR: 140 mgO₂ L⁻¹, BS: 104 mgO₂ L⁻¹, 28h: OR: 29 mgO₂ L⁻¹, MR: 90 mgO₂ L⁻¹ 22h: BS: 26 mgO₂ L⁻¹</p>	<p>-</p>	<p>-</p>	<p>-</p>	<p>BOD₅/COD 45 min: OR: 0, MR: 0.23, BS: 0, 28 h: OR: 0.81, MR: 0.14, 22 h: BS: 0.1</p>	<p>[161] (G)</p>
<p>Synthetic solution of Methyl Red (MR) (DOC: 61.3 mg L⁻¹, COD: 192 mgO₂ L⁻¹), the solution BOD₅/COD: 0, high toxicity: EC₅₀: 3%, AOS: -0.7</p>	<p>Two-compartment cell: first one contains the azo dye, graphite felt as cathode (378 cm²) and Saturated calomel electrode as reference electrode -0.5V applied with compressed air 0.1* mM Fe³⁺, pH: 3, the second one contains Pt as anode (31.4 cm²) pH: 1*, 30°C</p>	<p>EF</p>	<p>COD (24 h): 116 mgO₂ L⁻¹ (48h) 82 mgO₂ L⁻¹, DOC (24 h): 54. mgO₂ L⁻¹ (48h) 47.7 mg L⁻¹</p>	<p>-</p>	<p>-</p>	<p>Low toxicity EC₅₀: 165% on <i>vibrio fischeri</i></p>	<p>AOS (24h): 0.8 (48 h) 1.42 BOD₅/COD (48 h): 0.24</p>	<p>[162] (H)</p>
<p>Synthetic solution of Levofloxacin at 200 mg L⁻¹, BOD₅/COD: 0</p>	<p>Undivided cell with as anode: RuO₂/Ti mesh (57 cm²) as cathode: activated carbon fiber felt (54 cm²), with O₂ at 100* mL min⁻¹, 500 mL solution, Na₂SO₄ at 0,05 M pH: 3*, 1.0* mM Fe³⁺, room temperature, 6.67* mA cm⁻²</p>	<p>EF</p>	<p>TOC removal (6h) 61%, COD removal (6h): 54%, total removal of Levofloxacin in 120 min</p>	<p>-</p>	<p>-</p>	<p>-</p>	<p>BOD₅/COD: (6 h) 0.24, (10 h): 0.41</p>	<p>[167] (I)</p>

Winery wastewater from a Port wine company in the northeast of Portugal, DOC: 4298 mg L ⁻¹ , COD: 12,000 mgO ₂ L ⁻¹ , BOD ₅ /COD = 0.7	Aerobic treatment with activated sludge	Flow plant recirculation containing a filter press with as anode: BDD (10 cm ²) and as cathode carbon-PTFE air diffusion (10 cm ²), 25 °C, pH: 2.8, 1.3 L treated, 35 mg L ⁻¹ , Fe ²⁺ , 25 mA cm ⁻²	B-EF	DOC removal in 240 min: 54%	COD removal: 97% (residual content: 380 mgO ₂ L ⁻¹ , DOC removal: 97% (residual content: 130 mg L ⁻¹) in 10 d	DOC: 59 mg L ⁻¹ , DOC removal: 98,6%	-	BOD ₅ /COD: 0.4 (after biological treatment)	[168] (J)
Synthetic solution of Acid Red 14 at 200 mg L ⁻¹ , BOD ₅ /COD: 0, AOS: -0.24	-	Undivided cell with as anode: RuO ₂ /Ti mesh (57 cm ²) as cathode: activated carbon fiber felt (20 cm ²), with O ₂ at 100* mL min ⁻¹ , 500 mL solution, Na ₂ SO ₄ at 0,05 M pH: 3, 1.0* mM Fe ²⁺ , 0.36 A	EF	TOC removal: 70% (6h)	-	-	-	BOD ₅ /COD (1 h 30): 0.05, (3h): 0.075, (6h): 0.4, AOS (1 h 30): -0.05, (6 h): 0.12	[169] (K)
Synthetic solution of Phenanthrene 0,09 mM	-	Undivided cell with as anode: BDD (20 cm ²) as cathode: carbon felt (150 cm ²), with compressed air at 0.25 L min ⁻¹ , 400 mL, pH: 3, 0.2 mM Fe ²⁺ , 22 °C, 0.150 M Na ₂ SO ₄	EF	Mineralization: 25% (7 h)	-	-	Toxicity (% inhibition) 96% (7 h)	BOD ₅ /COD (7 h): 0.33	[160] (L)

B: biological treatment

*best value for the parameter

(A)...(L): identification of the article in the text

4.2.2 Toxicity assessment

With biodegradability, toxicity is the second very important parameter for a biological treatment. A dozen studies reported the toxicity assessment of solutions during EF treatments. Most of them used the Microtox[®] test. This was applied to herbicides such as mesotrione and diuron, to azo dyes such as acid orange 7 or to pharmaceuticals such as sulfamethoxazole, sulfamethazine and sulfanilamide. For all those studies an increase of the toxicity was observed after the beginning of the EF treatment, this was due to the formation of more toxic intermediate compounds than the parent compound. This increase in solution toxicity was usually attributed to cyclic/aromatic by-products which are formed after a few minutes of electrolysis. As an example, one of these intermediates can be hydroquinone, obtained both in the degradation of phenol [170] and chlorophenol [171]. Then after reaching a plateau in the percentage of inhibition, solution toxicity decreases due to the destruction of aromatic/cyclic intermediates and formation of carboxylic acids (which are much less toxic) and to the progress in the mineralization of the solution. Depending on the starting pollutant, the 0% of inhibition (complete removal of toxicity) can be achieved in 2 h as for the sulfamethazine or after 8.33 h for the mesotrione. Indeed, as for the efficiency of the EF process, the decrease of toxicity is also different when using, for example, different anode materials (mainly BDD or Pt) or different operating parameters such as current intensity or initial concentration of pollutant [147,150,172–175]. In the study concerning the degradation of the herbicide diuron, the authors performed the toxicity assessment both on *Vibrio Fischeri* (Microtox[®]) and *green algae* and found a really different behavior for these two different tests. For the algae, toxicity decreases rapidly whereas for the bacteria the toxicity rises because of the intermediates formed and then decreases. These results highlight that the toxicity observed depends on the organism used in the test. To give an overall information on the toxicity and thus to be more reliable, tests need to be done on several different species or methods [175]. Other toxicity

assessments were done by using other species. Coledam et al. [176] studied the degradation of the antibiotic norfloxacin and measured the evolution of toxicity using the bacteria *E. Coli* showing that the toxicity remained very high during the first two hours of EF treatment before starting to decrease. By identifying reaction intermediates, they attributed the toxicity of the solution to fluoroquinolone, a cyclic compound that remained in the medium during two h before being degraded [176]. This test was also performed on *Daphnia magna*, a freshwater crustacean, for the degradation of the azo dye orange II. The same scheme appeared, a rise in toxicity after 5 min of treatment and then a decrease of this toxicity until no inhibition after one hour of treatment [177]. Among all those studies, one assessed the cytotoxicity during the degradation of the herbicide sulfentrazone on sheep corneal epithelial cells and no toxicity was found for both the parent compound and the by-products [178].

Toxicity was also measured by the oxidative stress which is a pathophysiological mechanism coming from the imbalance of the production of reactive species and organism defenses that can lead from molecular damage to the cell death. In a study on the degradation of Yellow 9 performed by EF, the activity of catalase was measured in order to evaluate the oxidative stress. Indeed, the enzyme catalase is involved in protecting the cell from oxidative stress. Thus a high concentration of catalase means that the cell is fighting against this process. It was found that only Yellow 9 induced toxicity as the catalase activity decreased with the time of electrolysis [179]. Another study looked at toxicogenomics and evaluated in addition the type of stress. Three well-known molecules were studied: bisphenol A, triclosan and ibuprofen; they were chosen because their degradation pathway is quite reliable. For bisphenol A, a large range of stress response was found whereas for its by-products the stress was concentrated on DNA and membrane. For triclosan, an oxidative stress was evaluated for the parent compound and for the intermediates; an anomalous production of proteins and an alteration of the cell membrane was assessed. Finally, for ibuprofen, the parent compound

alters the cell transport function and induces a high membrane stress. The by-products as far as they are concerned, promote membrane, protein and DNA stress [180]. This type of study is really interesting to understand better how the toxicity operates and then it is easier to work with and to know when a bio-treatment could be useful.

In the five last years, only two studies were found dealing with both biodegradability and toxicity (H-L) [160,162]. In order to perform the combination of both EF and biological treatment more studies are in fact needed.

4.3 Combined process applied to pharmaceuticals removal

4.3.1 Anodic oxidation as pre-treatment for a post-biodegradation process

A few studies reported the experiment of a combined process using an AOP and a biological treatment applied to pharmaceutical wastewater. To the best of our knowledge, the first attempt of an hybrid process combining bio-treatment and an electrochemical process was done by Carvalho et al. in 2007 [181,182]. Biotic degradation products formed during biological treatment of a synthetic solution of dye Acid Orange 7 was carried out by anodic oxidation using BDD anode obtaining a COD removal of 90% and a TOC removal of 30% after 8 h treatment. Then a system combining biodegradation and EF process was carried out [182–185]. During the combined process, EF was used as a pre-treatment step followed by an anaerobic digestion and an ultrafiltration to reach 88% of COD removal, 72.5% of color removal and 90% of total suspended solids removal with a residence time of 4 h in the EF reactor. The use of an aerobic treatment was also investigated.

Yahioui et al. [186] used an anodic oxidation process as AOP as a pre-treatment step for a biological treatment to degrade the antibiotic tetracycline. The optimal operating conditions were evaluated on a synthetic solution using a central composite design with an electrolytic cell equipped with Pb/PbO₂ anode and Pt cathode. In order to keep enough organic carbon to

perform a biological treatment, the solution was electrolyzed through the following conditions: 40 °C, 275 mA, and 100 mg L⁻¹ initial concentration until the complete disappearance of tetracycline. Biodegradability was also assessed along the electrolysis and reached a value of 0.41 after 5 h of treatment. At this point, 36.7% of the DOC remained in the medium. The aerobic treatment using activated sludge confirmed the beneficial effect of the biological treatment as the combined process reached 76% DOC removal.

4.3.2 Coupling between EF and bio-treatment

The combination between EF and biological treatment called bio-electro-Fenton (Bio-EF) has been performed by Oturan's group [29,187,188] performing EF step as pre-treatment or post-treatment for coupling with a biological treatment applied to the removal of pharmaceuticals such as metoprolol (beta-blocker), furosemide (diuretic), ranitidine (antihistaminic H₂) and real pharmaceutical wastewater (Table 8). In particular, the study reported by OlveraVargas et al. [29] constitutes a complete and systematic research including toxicity assessment by Microtox method as well as MCE and EC data in addition to the evaluation of the biodegradability (BOD₅/COD) during EF treatment (Fig. 9). The biodegradability ratio of 0.4 was reached only after 1 h EF treatment (at 500 mA) with 47% TOC removal during treatment of a solution of the beta-blocker metoprolol. A mineralization rate of 90% is attained after 4 d of biological treatment (Fig. 10). The shortness of the EF step allowed the reduction of a significant energy consumption (6 times) compared to EF alone. The evolution of solution toxicity was also monitored by using Microtox® assay (Fig. 11).

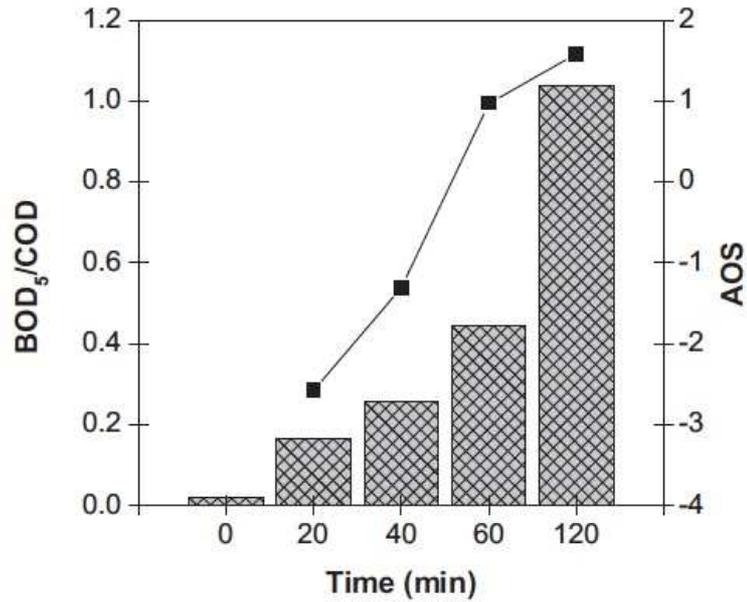


Fig. 9: BOD₅/COD ratio (▨) and AOS (■) evolution as a function of time for the EF of 0.22 L of 0.1 mM of metoprolol solution in 0.05 M Na₂SO₄ and 0.1 mM Fe²⁺ at pH 3 using BDD anode at 300 mA and room temperature. Reprinted with permission from ref. [29]. Copyright Elsevier, 2016.

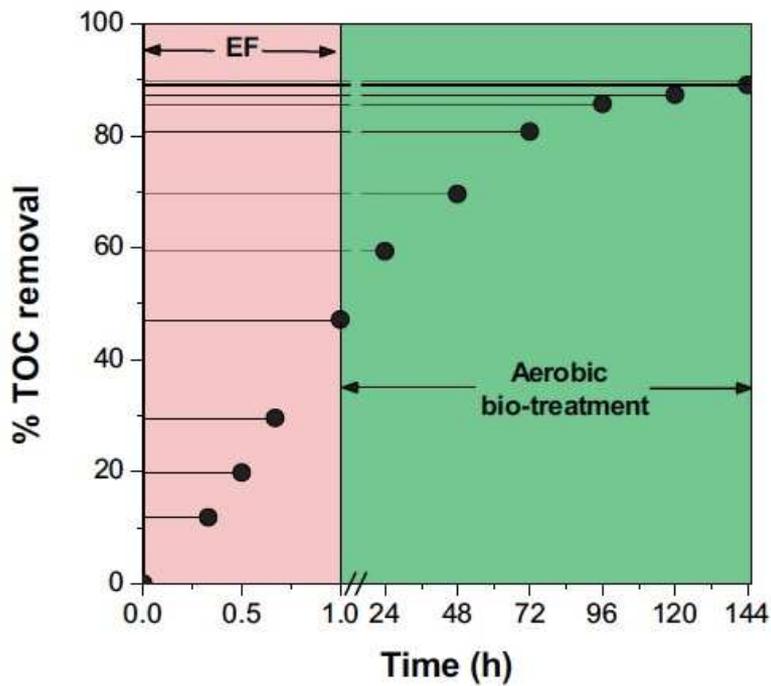


Fig. 10: TOC removal during the combine treatment of a 26.74 mg L⁻¹ of metoprolol solution. The EF treatment was conducted in the condition of Fig. 9 and the biological treatment used 12 pure cultures of microorganisms under aerobic conditions. Reprinted with permission from ref. [29]. Copyright Elsevier, 2016.

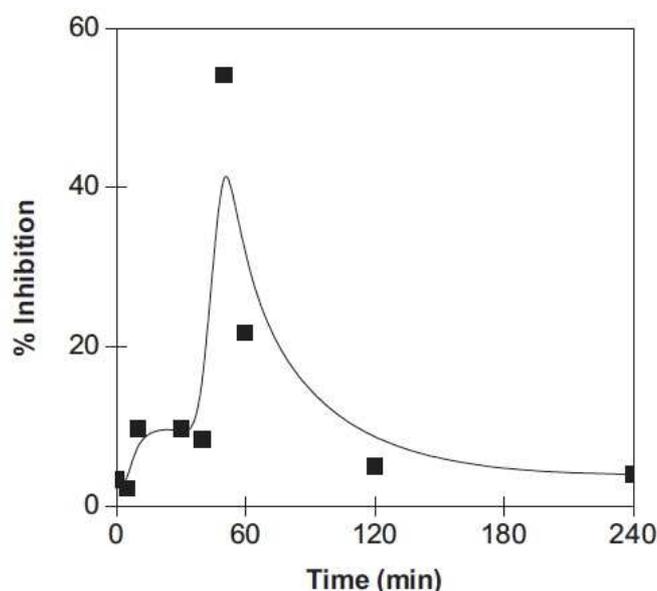


Fig. 11: % of inhibition of bioluminescence of *V. fischeri* bacteria after 15 min for the EF treatment of 0.22 L of 0.1 mM of metoprolol solution in 0.05 M Na₂SO₄ and 0.1 mM Fe²⁺ at pH 3 using BDD anode at 300 mA and room temperature. Reprinted with permission from ref. [29]. Copyright Elsevier, 2016.

For furosemide and ranitidine, some economic considerations were done using the French industrial price for electricity: 0.08 kWh. For 1 h electrolysis the energy cost was of 7.66 and 9.33 € (kg TOC)⁻¹ for furosemide and ranitidine, respectively, whereas for 8 h electrolysis to achieve nearly total mineralization the price was of 43.03 and 46.77€ (kg TOC)⁻¹ for furosemide and ranitidine respectively with EF alone [185]. This clearly justifies the use of the combined process. For all the combined processes applied to pharmaceutical, the EF was used as a pre-treatment (except the report of Ganzenko et al. [187] in which pre- and -post EF scenarios have been performed) usually due to the toxicity of the compounds and the low biodegradability of the solution. In his work Ganzenko compared the degradation and mineralization of a pharmaceutical effluent spiked with caffeine and 5-fluorouracil with two different orders of treatment (EF-B or B-EF) (Table 8). The results demonstrated a quite similar mineralization (more than 90% of COD removal) for both orders but using the EF as pre-treatment appeared to be cost saving. Indeed, the best condition for EF-B was 2h at 200

mA whereas for B-EF it required 4h at 500 mA [187].

The combination of EF treatment with a biological treatment on pharmaceutical pollutants was also carried out by Ferrag-Siagh et al. [189]. They showed the efficiency of combining electro-Fenton process with a biological treatment for the degradation of the antibiotic tetracycline. They evaluated different parameters to find the best conditions for the EF which were described in Table 8. The treatment of tetracycline by biological treatment attained a TOC removal of 10% which clearly showed the inadequacy of this process due to the low biodegradability rate ($BOD_5/COD = 0.02$) of the initial drug solution. To obtain a biodegradable solution, EF pre-treatment was applied to reach 46% and 72% TOC removal and, 0.33 and 0.44 BOD_5/COD ratio at 4 and 4 h treatment, respectively. Then the activated sludge treatment was performed during 25 d for the two electrolyzed solutions, obtaining an improvement of 23% and 14% in TOC removal for 2 h and 4 h EF pre-treated solutions, respectively [189]. The same group also investigated the degradation of tylosin, sulfamethazine and trimethoprim using the combined process obtaining a biodegradable solution (BOD_5/COD ratio ≥ 0.4) after EF pre-treatment step before biological treatment. The coupled process was then successfully applied to the treatment of a real effluent coming from a pharmaceutical industry [190–193].

The efficiency of the combination of both treatment is demonstrated in terms of TOC or COD removal but hardly ever the biodegradability or the toxicity of the solution resulting is taken into consideration. This point is of major interest as this treatment aims at delivering a clean water in the environment. One study performed toxicity tests on the treated solution [194]. Phytotoxicity tests on *Vigna radiata* seeds and microbial toxicity tests on *Pseudomonas aeruginosa* and *Bacillus sp.* were performed in order to demonstrate the efficiency of their combined process for the degradation of textile wastewater. Both tests showed a decrease in toxicity. No such test could be found concerning the pharmaceutical effluent which is

upsetting.

In all the experiments performed on synthetic effluents as well as on real wastewater effluents; the cost-effectiveness and the efficiency of the coupling between EF and bio-treatment was proved. However, it should be noticed that as mentioned in section 2.3.5, the electrical consumption may be significantly different at pilot and full scale. It is also very important to underline one of the major drawbacks; the solution pH which is adjusted around 3 in EF step should be raised around 7 for the bio-treatment.

5. Conclusions and perspectives

Wastewaters from hospitals and pharmaceutical industries contain relatively high concentrations of pollutants as this wastewater has not already been mixed with other effluents. As highlighted in different publications, the EF process is faster, more efficient and more cost-effective on concentrated solutions of pharmaceuticals. Thus the best approach to treat this wastewater with EF seems to treat the pharmaceuticals directly at the exit of hospitals or pharmaceutical production plants.

A major advantage of EF compared to other non-AOP treatments is that the EF is able to destroy quite every type of pollutants thanks to the non-selectivity of the hydroxyl radicals and to reach almost complete mineralization of treated solutions.

One major problem concerning the EF is its relatively high treatment cost when using longer treatment time required to reach high mineralization degree to destroy resistant intermediates formed during the process. Research was done to reduce this treatment cost or enhance the efficiency of the EF treatment. These studies were based on improvements of geometrical parameters or flowing characteristics in order to improve mass transfer and to limit electrical resistance that are in general the limiting steps, on avoiding the addition of external O₂ or on using micro-fluidic. Several reactor configurations were proposed and their advantages and

drawbacks as well as the best configurations depend on the objectives, on the nature of the wastewater (organic pollutants, presence of solid particles, etc.). In order to reach the industrial scale with the EF process, more research is needed to assess the feasibility: (i) to operate in continuous mode, (ii) to treat real wastewaters, (iii) to decrease the cost associated to catalyst by testing at pilot scale solid catalyst. In terms of engineering, a better characterization of the hydrodynamic of the reactors at pilot scale is required to develop models coupling mass transfer phenomena, hydrodynamic behavior, electrochemical reactions, etc in order to predict the efficiency of the reactors and helping to resolve a number of design aspects required for a midterm pre-industrialization. In addition, more studies at pilot scale are required to get more information about the energetical consumption of each configuration. Only few studies gathered one of those parameters this is why it is an important research focus.

EF process has demonstrated its efficiency but the treatment cost is still very high (at least $0.39 \text{ Wh (g TOC)}^{-1}$) and a good way for saving energy in order to industrialize it, is to combine one of this EF apparatus with a biological treatment. In the case of pharmaceuticals, EF process as a pre-treatment followed by a biological treatment proved its accuracy. All these experiments were performed at laboratory scale and under batch conditions. However, for a pre-industrialization of the combined treatment, experiments must be conducted at pilot scale and the feasibility of conducting continuous or semi-continuous reactors must be assessed. The extent of conditioning of the active biomass used for the biological treatment to the parent compound, to the reaction intermediates, or to the compound mixtures also needs to be addressed. In addition, more work is needed to determine the monitoring parameters to control the reactor's operation.

Table 8: Combined process applied to pharmaceuticals

Raw Solution	Biological treatment	Treatment EF	Order of treatment	Efficiency of EF alone	Efficiency of biological treatment alone	Effect of both treatment	Evolution of biodegradability	Refs
100 mg/L tetracycline BOD ₅ /COD: 0.02, COD: 128 mgO ₂ /L	Activated sludge at 25°C, during 21 to 25 days in 500 mL with a cellulose cap to ensure the oxygenation by batch	Undivided Cell 1 L with a carbon felt cathode (194 cm ²) and a cylindrical platinum anode (5 cm * 1 cm) under agitation and O ₂ flow, 800 mL of solution containing 0.1* mmol Fe ²⁺ pH: 3*, 0.05* mol/L Na ₂ SO ₄ , at 300* mA current	EF-B	COD removal at 2 h: 66% 4 h: 86% 6 h: 93% TOC removal at 2 h: 46% 4 h: 72%	TOC removal after 25 days: 10%	TOC removal after 2 h of EF: 69%, after 4 h of EF: 86%	BOD ₅ /COD at 2h: 0.33, at 4h 0.44, at 6h 0.56	[189]
100 mg/L Tylosin BOD ₅ /COD: 0, COD: 136 mgO ₂ /L AOS: 0.52	Activated sludge under aerobic conditions at 25°C, during 25 days in 500 mL by batch	Divided Cell of 1 L with a carbon felt cathode (194 cm ²) and a cylindrical platinum anode (5 cm * 1 cm) under agitation and O ₂ flow, 800 mL of solution containing 0.1* mM Fe ²⁺ pH: 3*, 0.05* mol/L Na ₂ SO ₄ , at 300* mA current	EF-B	TOC removal after 2h: 45%, 4h: 62%, 6h: 88%	TOC removal 0%	TOC removal after 2 h of EF: 77%, after 4 h of EF: 88%	BOD ₅ /COD at 2h: 0.3, at 4h 0.5 AOS at 2h: 1.87 4h: 1.95	[192]
0.2 mM of Sulfamethazine	Fresh activated sludge at 25°C under continuous stirring by batch	Undivided Cell 1 L with a carbon felt cathode (208 cm ²) and a cylindrical platinum anode (5 cm * 2 cm) under agitation and O ₂ flow rate of 450 mL/min, the electrolyte containing: 0.5 mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 500 mA and 18°C	EF-B	TOC removal after 6h: 6.5% (with 0.1 mM pollutant 0.1 mM Fe ²⁺ and at 200 mA)	TOC removal 0%	TOC removal after 0.5 h of EF: 61.4%, after 1 h of EF: 78.8% after 4 h: 93.9%	BOD ₅ /COD at 0.5h: <0.4, at 1h 0.5	[190]
Wastewater from a pharmaceutical industry from Tunisia, 0.2 g/L Sulfamethazine, TOC: 188.7 mg/L, BOD ₅ /COD: 0.17	Fresh activated sludge at 25°C under continuous stirring by batch	Undivided Cell 1 L with a carbon felt cathode (208 cm ²) and a cylindrical platinum anode (5 cm * 2 cm) under agitation and O ₂ flow rate of 450 mL/min, the electrolyte containing: 0.5* mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 500* mA and 18°C*	EF-B	TOC removal after 100 min: 7.5%	-	TOC removal after 100 min EF: 81.4%	BOD ₅ /COD after 100 min: 0.35	[193]
Industrial pharmaceutical effluent containing 0.2 mM of Trimethoprim BOD ₅ /COD: 0.14	Activated sludge treatment during 15 days at 25°C by batch	Undivided Cell 1 L with a carbon felt cathode (208 cm ²) and a cylindrical platinum anode (5 cm * 2 cm) under agitation and O ₂ flow rate of 450 mL/min, the electrolyte containing: 0.69* mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 466* mA and 18°C*	EF-B	TOC removal at 3h: 14% at 5h: 16%	TOC removal 50%	TOC removal after 3h EF: 80% after 5h EF: 89%	BOD ₅ /COD at 3h: 0.45, at 5h: 0.47	[191]

Synthetic solution of 0.1 mM of Metoprolol BOD ₅ /COD: 0.02	Aerobic biological treatment at 30°C during 7 days by batch	Undivided Cell 300 mL with a carbon felt cathode and a BDD anode (25 cm ²) under agitation and compressed air bubbling, the 220 mL electrolyte containing: 0.1 mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 300 mA	EF-B	TOC removal (1h): 47%	Very low TOC removal	TOC removal after 1h EF: 90%	BOD ₅ /COD at 1h: 0.44, AOS at 1h: 1.0	[29]
Synthetic solution of 0.1 mM of Furosemide	Aerobic biological treatment at 30°C during 7 days by batch	Undivided Cell 300 mL with a carbon felt cathode and a BDD anode (24 cm ²) under agitation and compressed air bubbling, the 230 mL electrolyte containing: 0.1 mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 500 mA	EF-B	TOC removal (1h): 64%	-	TOC removal after 1h EF: 93%	BOD ₅ /COD at 1h: 0.41	[185]
Synthetic solution of 0.1 mM Ranitidine	Aerobic biological treatment at 30°C during 7 days by batch	Undivided Cell 300 mL with a carbon felt cathode and a BDD anode (24 cm ²) under agitation and compressed air bubbling, the 230 mL electrolyte containing: 0.1 mM Fe ²⁺ , pH: 3, 0.05 M Na ₂ SO ₄ , at 500 mA	EF-B	TOC removal (1h): 59%	-	TOC removal after 1h EF: 94%	BOD ₅ /COD at 1h: 0.37	[185]
Industrial pharmaceutical effluent spiked with 0.1 mM of Caffeine and 0.1 mM of 5-fluorouracil BOD ₅ /COD: 0.03	Pre-treatment: Activated sludge treatment during 24 h in batch Post-treatment:	Undivided Cell 1.4 L with a carbon felt cathode (475 cm ²) and a BDD anode (193 cm ²) under agitation and aeration, the 230 mL electrolyte containing: 0.2 mM Fe ²⁺ , pH: 2.9, 0.05 M Na ₂ SO ₄ , at 200 or 500 mA	EF-B and B-EF	EF-B: 90% of removal of caffeine and 5-fluorouracil and COD removal of 60% in 2h at 200 mA	B-EF: 3% of caffeine, 38% of 5-fluorouracil and 43% of COD were removed in 24h	EF-B: more than 90% of COD removal in 3 d of bio-treatment B-EF: 99% of COD removal after 4h of EF at 500 mA	BOD ₅ /COD at 2h: 0.61	[187]

B: biological treatment

*best value for the parameter

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