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# **Electrochemical technologies coupled with biological treatments**

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## Abstract

When possible, the bioprocesses should be implemented to treat wastewater for their cost-effectiveness. However, many effluents are composed of biorecalcitrant organic pollutants, especially in industrial wastewaters. Advanced physico-chemical treatments are therefore needed to deal with these pollutions. Electrochemical processes could be cost-effective solutions. However, the energy required to reach complete mineralization is often high. One promising combination would be to combine electrochemical processes that can remove xenobiotic compounds from effluent with biotechnologies that are able to mineralize the biodegradable fraction. Therefore, this review presents the most recent articles dealing with this combination, by mainly focusing on electrochemical advanced oxidation processes that demonstrated to have high removal efficiency for organic biorecalcitrant compounds. Additional and imperative information about the treatment strategy and the engineering aspects for the upscaling approach are also given.

## Keywords:

Anodic oxidation; Bioreactor; Biorecalcitrant; Electro-Fenton; Hydroxyl radicals; Wastewater treatment

## 44 **Highlights**

- 45 • A combination strategy between electrochemical and bio- processes is proposed
- 46 • Combinations between anodic oxidation and bioprocesses are reviewed
- 47 • Combinations between Fenton-based treatment and bioprocesses are discussed
- 48 • Combinations between electro-coagulation and bioprocesses are considered
- 49 • The engineering approach, scale up studies and future challenges are exposed

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## 1. Introduction

Electrochemical processes are gaining interest in wastewater treatment area, due to their ability to degrade and mineralize biorecalcitrant organic pollutants using electron as clean reagent [1–4]. In the meanwhile, they can remove the biorecalcitrant part of effluent which makes interesting their coupling with biological technologies [5]. This synergy would also reduce the high energy consumption required in an electrochemical process for complete mineralization.

This review intends to relate the most recent works on this combination in a context of wastewater treatment. The feasibility of combination, needed to address a treatment strategy, is firstly discussed. Then the main electrochemical processes such as electrochemical advanced oxidation processes (EAOPs) (i.e. anodic oxidation (AO), electro-Fenton (EF)) and electrocoagulation (EC) are presented successively. The coupling efficiency with biological technologies (e.g. aerobic, anaerobic, membrane bioreactors, microbial fuel cell) is examined in the meantime. The engineering approach and scale-up studies are finally showcased and the future challenges for industrial applications are highlighted.

## 2. Combination feasibility and treatment strategy

Standardized tests [6,7] can be implemented on the effluent to be treated and on the electrolyzed solutions to estimate the combination feasibility. In these assays, the estimation is based on the dissolved organic carbon (DOC) evolution [6] or the production of carbon dioxide [7] during 28 days of biological culture. Oxygen uptake rate can be also monitored [8]. Biodegradability is often estimated by the biochemical oxygen demand (BOD) after 5 days / chemical oxygen demand (COD) ratio [9,10]. Although this estimation is quicker, it has to be interpreted with some cautions. The ratio value may increase due to some biodegradable compounds in the solution but if the major part of the organic content is still recalcitrant, a significant mineralization cannot be reached [11]. Similarly, a low value does not necessarily mean an absence of biodegradability since an acclimation period can be needed for microorganisms to metabolize the organic content, particularly in the case of industrial effluents with very specific characteristics [12,13]. Ultimate BOD obtained after 21 days of incubation can help with the decision about the biodegradability.

Due to the high response time with microorganisms - at least 5 days - physico-chemical tools were considered as the combination between total organic carbon (TOC) and COD. The average oxidation state (AOS) or COD/TOC ratio can give information on effluent oxidation and then its possible biodegradation [14].

Moreover, toxicity assays can be performed in addition to biodegradability estimation. Microtox is the most widely adopted and concerns acute toxicity [9]. Phytotoxic tests based on germination index can also be considered [15].

Pollutant concentration or molecular structure can influence the biodegradability. For instance, no inhibition of sodium benzoate biodegradation occurred with the addition of tetracycline concentration less than  $5 \text{ mgL}^{-1}$  [7]. Biorecalcitrance of alachlor is due to the chlorine atom and to the amide group in its structure [11]. Furthermore, the formation of biodegradable intermediates depends on the operational conditions of the electrolysis [11,14].

The combination strategy depends on the nature of the effluent and on the estimation of its biodegradability. An electrochemical pre-treatment should be prioritized in the presence of toxic and/or biorecalcitrant and/or inhibitory compounds for microbial activity. A biological pre-treatment can be considered when the biorecalcitrant part of the effluent does not hinder the microbial growth [9,10] (Figure 1).

### 3. Anodic oxidation coupled with biological treatments

AO process is an EAOP based on the generation of strong oxidants like hydroxyl radical ( $\cdot\text{OH}$ ) from oxidation of water in the region of water discharge [2,16]. This radical is chemisorbed in the case of active anodes like carbon, Pt or dimensionally stable anode (DSA) (with low oxygen evolution overpotential) whereas it is slightly adsorbed (physisorption) and therefore more available for oxidation of organics in the case of non-active anodes having high oxygen evolution overpotential like boron-doped diamond anode (BDD),  $\text{PbO}_2$ ,  $\text{Ti}_4\text{O}_7$  [17–19]. However, the efficiency of this process depends strongly on the concentration of organic compounds in the solution and mass transport conditions from the solution to the anode surface [20,21]. Other oxidant species can be also generated (persulfate, sulfate radicals, active chlorine, ozone) depending on ions present in the solution and operating conditions [2,22,23].

Several studies have been performed on the combination of AO with a biological treatment in order to improve the cost-effectiveness of the process (Table 1) [6,24–30]. There are three

main advantages from the use of AO as a pre-treatment: (i) AO is well known for its non-selectivity towards organic compounds and can be applied to a large range of effluents (Table 1), (ii) AO is able to avoid the accumulation of toxic organic by-products because of the fast transformation of organics into harmless by-products or even mineral compounds, (iii) higher current efficiency is usually reported for the treatment of concentrated effluents (such as industrial effluents with low biodegradability: landfill leachates, textile industry effluents, etc) with low biodegradability and COD concentration higher than  $100 \text{ mg-O}_2 \text{ L}^{-1}$ .

However, AO presents also some drawbacks for a combination with a biological process. Fast mineralization kinetics but slower degradation kinetics are usually reported compared to other EAOPs such as EF [31]. This phenomenon might affect the combination with a post-biological treatment since initial compounds are more slowly degraded and a large amount of biodegradable compounds is mineralized instead of being accumulated for subsequent cost-effective removal by a biological treatment. The use of active anode would avoid the fast mineralization and therefore may increase the amount of biodegradable intermediates, as recently assessed [25]. It is also important to consider possible formation of toxic by-products that might affect the biomass of the biological treatment, particularly inorganic species such as chlorate, perchlorate or ammonia [32–34]. Finally, it might be not suitable to use AO as a post-treatment following a biological treatment because of strong mass transport limitation and low faradaic efficiency due to the low concentration of organics. However, the use of flow-through electrodes in which the effluent flow through porous conductive materials might be able to address this issue because of the convection-enhanced mass transport of organic compounds [21,35–38].

Another approach recently reported in the literature is the possibility to combine AO with a biological treatment in a hybrid reactor instead of the implementation of a sequential combined process. Particularly, the integration into a membrane bioreactor has been studied in order to address fouling issues and to improve the removal of recalcitrant micropollutants [39–42]. However, further development of such reactor configuration is required for (i) improving electrode activity for removal of organic micropollutants, (ii) reducing mass transport limitations, (iii) studying the influence of the electrical field on bacterial diversity and activity, and (iv) assessing the influence of the large concentration of organic matter in the mixed liquor on the efficiency of AO.

#### **4. Fenton-based electrochemical treatments coupled with biological processes**

The EF process is based on the cathodic production of  $\text{H}_2\text{O}_2$  at a suitable electrode material (generally carbon-based) through the  $2\text{-e}^-$  reduction of  $\text{O}_2$ .  $\text{H}_2\text{O}_2$  entails the generation of  $\cdot\text{OH}$  via the Fenton's reaction in the presence of  $\text{Fe}^{2+}$  ions, which are externally added at a catalytic amount and electrochemically regenerated also at the cathode surface [2]. EF has been applied with success to treat several types of wastewaters contaminated with a variety of pollutants, becoming one of the most widely studied EAOPs [43]. Following the combination trends of AOPs with biological processes, EF has been an excellent option to handle recalcitrant pollutants resisting biological degradation such as most of pesticides, synthetic dyes, industrial chemicals, pharmaceuticals, etc. Therefore, different coupled strategies (either sequenced or integrated processes) have been proposed (Table 2) [15,44–58]. In the case of sequenced processes (pioneered by the groups of Oturan [59] and Fourcade [15]), the most common approach has been the use of EF as pre-treatment step to increase the biodegradability of refractory effluents during a short treatment time (to save electrical energy for cost effectiveness) [59,60], whereas the remaining biodegradable organics are treated by conventional biological means. As a less popular option, EF has also been used as post-treatment following biological degradation to deplete the remaining bio-recalcitrant compounds. In such sequenced methods, conventional EF (catalyzed either by  $\text{Fe}^{2+}$  in solution (homogenous EF) or solid Fe catalysts (heterogeneous EF)) has been generally performed in undivided electrolytic cells with optimization of the main operating parameters affecting the efficiency (current density, electrode materials, catalyst concentration, etc.), while aerobic treatment with different microbial sources has been the preferred option. It is important to note that pH adjustment is generally required after/prior to EF, which is typically conducted at pH 3 in the case of homogeneous EF [2].

Another kind of Bio-EF system, known as microbial-electro-Fenton (MEF), involves the incorporation of an EF half-cell in a microbial fuel cell (MFC) [61–63]. During MEF, the EF degradation of pollutants takes place in the cathode chamber equipped with a carbonaceous cathode capable of producing  $\text{H}_2\text{O}_2$  and containing a catalyst source ( $\text{Fe}^{2+}$  in the solution or Fe particles impregnated on the cathode). The anodic compartment contains anaerobic electrogenic communities adhered to the anode surface that are able to produce electricity through the oxidation of an organic substrate (i.e. acetate or wastewater). Wastewater treatment can occur at both the biological and the EF chambers, generally with electricity output, though low potentials have also been applied to enhance the performance. The main advantage of MEF is the sustainable generation of electricity by the microorganisms.



However, long stabilization and treatment times (several weeks) are required unlike sequenced systems, with short EF treatment times (few hours), but prolonged biological incubations. Despite the great potential of bio-EF systems, further research is needed mainly in the treatment of real wastewaters and the development of larger-scale (bio)electrochemical reactors.

## **5. Electrocoagulation combined with biological treatments**

The EC process consists on the use of iron or aluminum based-sacrificial anode material that will generate the coagulants responsible for the coagulation of colloidal matter [64–67]. It can remove the color, suspended solids and partial COD from wastewater [64,65]. EC processes have been proposed as pre-treatment [64] or polishing treatment [65] when combined with biological processes. The main most recent studies on this coupling have been described in Table 3. This combination has been implemented to treat industrial wastewaters such as landfill leachate [68], oil shale wastewater [69], dairy wastewater [70] and tannery wastewater [71]. EC was mainly responsible in COD removal in the combined process, which allowed reaching the COD guidelines for effluent discharge [64,65]. However, the management of hydroxides' precipitates produced during EC need to be considered in the reactor design since the potentially toxic sludge can limit the efficiency of the bioprocess in an hybrid combination [64,65]. Moreover, most of the studies have been performed at lab-scale, which is not sufficient to assess the efficiency of combination. Still, one recent study presents a systematic comparison at lab-scale, pilot-scale and full-scale [69], demonstrating the ability to apply this combination at industrial scale. Further studies are required to optimize the scale up.

## **6. Engineering approach and scale up**

If scale-up of conventional biological processes (activated sludge, biofilm reactors) is relatively mature, scale-up of electrochemical reactors is still under development in this area [72]. In the aim at optimizing the efficiency of the combined process, several engineering aspects need to be considered. An important factor concerns the design and sizing of the electrochemical and biological reactors. The choice of the electrochemical reactor configuration must depend on the effluent characteristics [73,74]. For low to moderate concentrated effluents with a low amount of particles, the mass transfer should be intensified by implementing flow-through mode with porous electrode materials and/or thin-film reactors

(e.g. micro-reactor [75–78], reactive electrochemical membrane (REM) [21], reactive electro-mixing reactor [36]). For concentrated effluents, other configurations can be proposed such as flow-by cells, reactive electro-mixing reactors [36] and flow electrochemical reactors [79]. For the pre or post biological treatment, most of the works have been focused on biodegradability test and/or on batch activated sludge treatments [15]. Therefore, there is a real need to better characterize and control the biological processes involved (transformation, inhibition, etc.) in order to optimize the synergism between the two processes, especially by defining the optimal operating conditions with real matrices. Only few studies are available regarding the combined electrochemical/biological treatment at pilot-scale [57,80] and full scale [69]. However, these studies lack of dimensional analysis and scale-up approach for a better optimization of the design and sizing. Moreover, further experiments need to be performed under controlled operating conditions combined to kinetic models, residence time distribution approach and computational fluid dynamics simulations. The use of statistical analysis is lacking and need to be also done in order to address the reproducibility of the results to ensure their robustness, especially when they are used for technico-economic study and sizing estimation.

## 7. Conclusions and future perspectives

The efficiency of combination between electrochemical processes and biological treatment has been demonstrated in literature, especially recently. The optimal electrochemical conditions such as current density, electrode materials and retention time have been widely investigated. This is important to note that the optimal conditions required in electrochemical process alone are not typically the same than when the combination with a biological process is considered. The biodegradability and therefore the kind of generated by-products need to be also taken into account. There is a compromise to find between the high degradation and mineralization yield to reach and the high biodegradability of effluent required for the combination. Preliminary full-scale applications show promising opportunities of the coupling, but chemical and electrochemical engineering approaches are the next crucial steps for its viable application.

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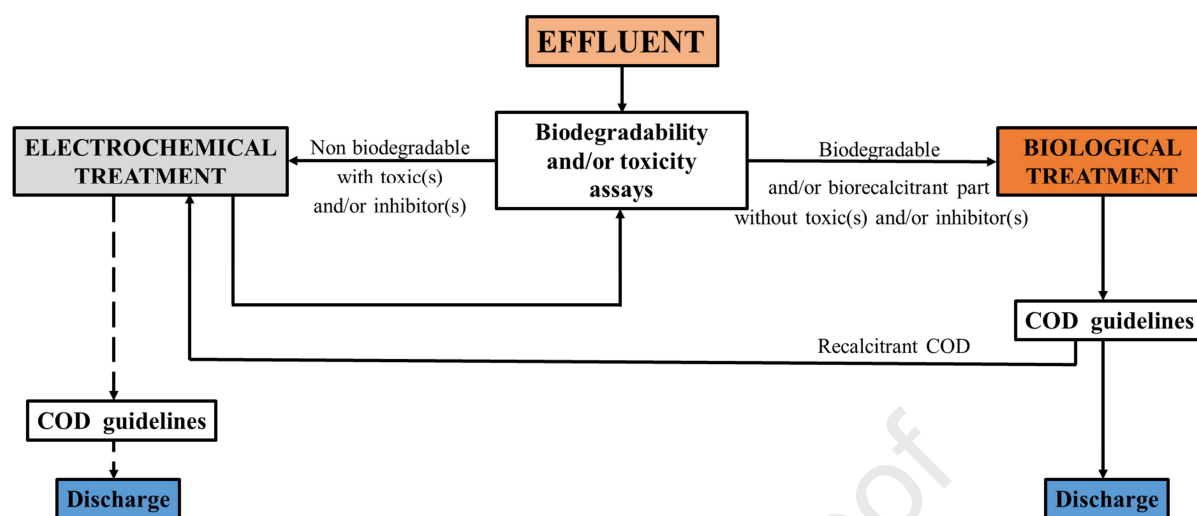
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**Figure 1.** Combination strategy between electrochemical treatments and biological processes.

**Table 1.** Summary of recent reports on the coupling between AO and a biological post-treatment.

Treatment system / Wastewater	Experimental setup of AO / biological treatment	Operating conditions for AO	Removal efficiency	Biodegradability increase	Energy consumption	Ref.
AO with a biological post-treatment  Synthetic soil washing solution (25 mg L <sup>-1</sup> of phenanthrene and 1.31 g L <sup>-1</sup> of Tween 80 ; 2.7 g L <sup>-1</sup> of COD)	- Undivided, cylindrical, open batch reactor (330 mL). Anode: Nb-BDD anode. Cathode: SS cathode.  - BOD tests and operation of an aerobic batch biological reactor	[Na <sub>2</sub> SO <sub>4</sub> ] = 50 mM  j = 7 – 36 mA cm <sup>-2</sup>	AO alone: 27% COD removal  Biological treatment alone: 44% COD removal  Combined process: 80% COD removal	The ratio between the ultimate BOD and the COD increased from 50% (untreated solution) to 60 – 95% depending on treatment time / current intensity.	39 kWh (kg COD) <sup>-1</sup>	[24]
AO with a biological post-treatment.  Clopyralid-containing soil washing effluent (no	- Electrochemical flow cell with a feed tank of 5 L. Anodes: Ir-MMO, Ru-MMO, pSi-BDD or carbon felt.	Ions mobilized from the SW step	Ir-MMO and Ru-MMO: <10% degradation and mineralization anodes: <10%	Biodegradability was assessed with CF at 5 mA cm <sup>-2</sup> (optimal conditions for degradation of clopyralid and	-	[25]

extracting agent ; 180 mg L <sup>-1</sup> of clopyralid)	Cathode: stainless steel  - BOD and respirometric tests	$j = 5 - 60 \text{ mA cm}^{-2}$	degradation and mineralization  pSi-BDD: 75% degradation and 85% mineralization at 4 Ah L <sup>-1</sup>  Carbon felt: 60% degradation and 30% mineralization at 4 Ah L <sup>-1</sup>	accumulation of by-products). The ratio BOD <sub>5</sub> / COD increased from 0.02 to 0.23 and the oxygen uptake rate from -10 to 40 mg (h gVSS) <sup>-1</sup> at 3.8 Ah L <sup>-1</sup>		
Electrocoagulation + AO with a biological post-treatment  Landfill leachates (21.7 g L <sup>-1</sup> of COD)	- Batch electrocoagulation reactor with iron electrodes  - Electrochemical flow cell for AO. Anode: BDD. Cathode: stainless steel	Natural conductivity of the electrolyte (36 mS cm <sup>-1</sup> )  $j = 30 - 70 \text{ mA cm}^{-2}$ for AO	60 – 70% COD removal after 2 or 3 h of electrocoagulation and 8 h of AO (30 mA cm <sup>-2</sup> )	The ratio BOD <sub>5</sub> / COD increased from 0.3 to 0.45 – 0.9 depending on operating conditions	11.2 – 17.5 kWh (kg COD) <sup>-1</sup>	<a href="#">[26]</a>



	- BOD tests					
<p>AO with a biological post-treatment</p> <p>500 mg L<sup>-1</sup> of 2,4-dichlorophenoxyacetic acid</p>	<p>- Flow-through electrochemical cell.</p> <p>Anode: carbon felt.</p> <p>Cathode: carbon paper. Separation with a cationic exchange membrane</p> <p>- BOD tests</p>	<p>100 mM Na<sub>2</sub>SO<sub>4</sub></p> <p>V<sub>a</sub> = +1.6 V vs SHE</p>	<p>After a single passage: 96% degradation; 41% COD removal</p>	<p>The ratio BOD<sub>5</sub> / COD increased from 0.04 to 0.25</p>	<p>5 kWh m<sup>-3</sup></p>	<p>[27]</p>
<p>AO with a biological post-treatment</p> <p>Human urines spiked with chloramphenicol (100 mg L<sup>-1</sup>)</p>	<p>- Undivided, batch reactor. Anode: BDD or RuO<sub>2</sub>. Cathode: stainless steel.</p> <p>- Rapid biodegradability assay and Zahn-Wellens standard biodegradability test</p>	<p>Natural conductivity of urines</p> <p>j = 1.25 – 5 mA cm<sup>-2</sup></p>	<p>&gt;95% removal of chloramphenicol and 35% TOC removal at 4 Ah L<sup>-1</sup> with BDD anode</p> <p>Very low degradation and mineralization with RuO<sub>2</sub>.</p>	<p>The standard biodegradability was 60% after 28 days of incubation and treatment at 1.25 mA cm<sup>-2</sup> and 8 Ah L<sup>-1</sup></p>	<p>-</p>	<p>[6]</p>

COD, chemical oxygen demand; BOD, biochemical oxygen demand; BDD, boron-doped diamond; MMO, mixed metal oxide; HPCD, hydroxypropyl-beta-cyclodextrin; VSS, volatile suspended solids

**Table 2.** Summary of recent reports on the coupling between EF and biological processes.

Treatment system / wastewater	Experimental setup of EF / biological treatment	Operating conditions	Removal efficiency	Biodegradability increase <sup>1</sup>	Energy consumption / Power generation <sup>2</sup>	Ref.
Homogeneous EF + Bio  Ionic liquid 1-butyl-1-methylpyrrolidinium chloride (1 mM = 177.7 mg L <sup>-1</sup> ), TOC <sub>0</sub> = 108 mg L <sup>-1</sup>	EF: cylindrical undivided cell (230 mL), carbon felt cathode (19 cm × 7 cm × 0.5 cm) and BDD anode (25 cm <sup>2</sup> )  Bio: bacteria consortium ( <i>Pseudomonas</i> , <i>Bacillus</i> , <i>Rhodococcus</i> ), lab scale aerobic reactor (flasks)	EF: $I = 1000$ mA, pH = 3, in 0.05 M Na <sub>2</sub> SO <sub>4</sub> , Fe <sup>2+</sup> = 0.1 mM, continuous air supply  Bio: mineral nutrients, pH = 7, T = 30 °C	EF: 57% TOC removal (30 min)  Bio: 49% TOC removal (7 days)  Combined process: 78% TOC removal	Increase of the average oxidation state (AOS) from 0.48 to 1.43 after EF	N/A	[44]
Bio + homogeneous EF	Bio: plant A.	Bio: 200 mL nutrient	Bio: 85.9% removal	N/A	28 kWh (kg	[51]

Phenazopyridine (analgesic drug) (20 mg L <sup>-1</sup> )	<i>filiculoides</i> lab-scale aerobic reactor  EF: undivided cell (250 mL), graphite cathode and anode (1.2 cm × 3.6 cm × 0.3 cm)	solution with air supply, 20 g of plant, pH = 7, continuous air supply  EF: $I = 200$ mA, pH = 3, in 0.05 M Na <sub>2</sub> SO <sub>4</sub> , 0.3 g of Fe <sub>2</sub> SO <sub>4</sub>	of the drug and 57.6% TOC removal (at 48 h)  EF: 22.25% TOC removal (12 h)  Combined process: 79.9% TOC removal (60 h)		TOC) <sup>-1</sup>	
Heterogeneous EF + Bio  Stabilized landfill leachate  (COD = 7184 mg L <sup>-1</sup> , BOD <sub>5</sub> /COD = 0.03)	EF: undivided cell (750 mL), Ti/TiO <sub>2</sub> anode (8 cm × 7 cm × 0.4 cm), graphite cathode (8 cm × 7 cm × 0.5 cm)  Bio: soil bacteria, 100 mL aerobic reactor	EF: $E_{cell} = 5$ V, pH = 3, 50 mg L <sup>-1</sup> FeMoPO nanoparticles, constant air supply  Bio: 100 mL nutrient solution with 1 mL of isolated colonies, pH = 8, T = 37 °C	EF: 82% COD removal (1.5 h)  Bio: 15% COD removal (5 days)  Combined process: 97% COD removal	BOD <sub>5</sub> /COD increase from 0.03 to 0.4 by EF (1.5 h)	N/A	[52]

<p>SPEF + Bio</p> <p>Valsartan (antihypertensive drug) (20 mg L<sup>-1</sup>)</p>	<p>SPEF: undivided cell (200 mL), Ti/IrO<sub>2</sub>-SnO<sub>2</sub> anode (2.89 cm<sup>2</sup>), carbon felt air diffusion cathode (2 cm<sup>2</sup>), UV lamp with <math>\lambda = 368</math> nm</p> <p>Bio: aerobic reactor (900 mL) with aerobic sludge from a food processing plant</p>	<p>SPEF: <math>j = 3.46</math> mA cm<sup>-2</sup>, in 0.05 M NaCl, Fe<sup>2+</sup> = 0.036 mM, pH = 3</p> <p>Bio: 4000 mg L<sup>-1</sup> of biomass, pH = 7, T = 37 °C</p>	<p>SPEF: total degradation (45 min) and &gt;20% TOC removal (90 min)</p> <p>Bio: 80% TOC removal (8 days)</p>	<p>N/A</p>	<p>N/A</p>	<p>[53]</p>
<p>EF + Bio</p> <p>Metrodinazole (antibiotic) (100 mg L<sup>-1</sup>)</p>	<p>EF: undivided cell (250 mL), graphite felt cathode (42 cm<sup>2</sup>), Pt anode (32 cm<sup>2</sup>)</p> <p>Bio: aerobic reactor (500 mL) with activated sludge</p>	<p>EF: <math>j = 0.07</math> mA cm<sup>-2</sup>, in 0.05 M Na<sub>2</sub>SO<sub>4</sub>, pH = 3, Fe<sup>2+</sup> = 0.1 mM, constant air supply</p> <p>Bio: mineral nutrient solution with 5 g L<sup>-1</sup> of activated sludge, pH = 7, T = 25 °C</p>	<p>EF: total degradation (20 min) and 4.4% TOC removal (1 h)</p> <p>Bio: 84.6% TOC removal (21 days)</p> <p>Combined process: 98% TOC removal</p>	<p>BOD<sub>5</sub>/COD increase from 0 to 0.46 by EF (1 h)</p>	<p>N/A</p>	<p>[15]</p>

	from a municipal wastewater plant					
<p>Bio + Coagulation + PEF + Bio</p> <p>Leather tannery landfill leachate</p> <p>(COD = 13966 mg L<sup>-1</sup>, alkalinity = 28,800 mg L<sup>-1</sup>, BOD<sub>5</sub>/COD = 0.31, NH<sub>4</sub><sup>+</sup> = 8403 mg L<sup>-1</sup>, TN = 10390 mg L<sup>-1</sup>, TSS = 1187 mg L<sup>-1</sup>, pH = 8.6)</p>	<p>Bio: Continuous flow anoxic/aerobic reactor (9 L-anoxic tank, 7 L-aerobic tank, 3.2 L-clarifier)</p> <p>Coagulation: 10 L coagulation tank</p> <p>PEF: filter-press recirculation reactor (2.5 L), carbon-PTFE cathode (10 cm<sup>2</sup>), BDD anode (10 cm<sup>2</sup>), tubular photoreactor with UVA lamp</p> <p>Bio: Zhan-Wellens</p>	<p>Bio: Nitrification-denitrification, flow rate = 0.3 L day<sup>-1</sup>, 1.2 L day<sup>-1</sup> returning activated sludge, 1h sedimentation, sludge removal</p> <p>Coagulation: pH = 3, Fe = 400 mg L<sup>-1</sup> (FeCl<sub>3</sub>), 3 h sedimentation</p> <p>SPEF: <math>j = 300 \text{ mA cm}^{-2}</math> Fe = 150 mg L<sup>-1</sup>, pH = 2.8, flow rate = 55 L h<sup>-1</sup>, neutralization, 3h sedimentation</p> <p>Bio: 28 days Zhan-Wellens test, 1 h sedimentation,</p>	<p>Bio: 97% alkalinity removal, 40% COD removal, &gt;99% NH<sub>4</sub><sup>+</sup> removal, 95% TN removal</p> <p>Coagulation: 49% TSS removal, 66.3% COD removal, 50% TN removal (30 min)</p> <p>SPEF: 96.4% COD removal, 95% TSS removal, 38.5 TN removal (9.3 h)</p> <p>Bio: 45% COD removal, 18.8% TN removal</p>	<p>BOD<sub>5</sub>/COD increase from 0.003 to 0.2 by PEF</p>	<p>469 kWh m<sup>-3</sup> (PEF)</p> <p>20 MJ m<sup>-3</sup> (UVA lamp operation)</p>	[54]

	tests	sludge removal				
EF/Persulfate + Bio  Mixed industrial wastewater  (COD = 1152 mg L <sup>-1</sup> , pH = 7.32)	EF/Persulfate: undivided cell (1 L), Ti/Pt mesh anode (2 pieces), graphite felt cathode (2 pieces) (25 cm <sup>2</sup> )  Bio: aerobic treatment with soil bacteria (100 mL)	EF/Persulfate: $E_{cell} = 10$ V, pH = 3, persulfate = 200 mg L <sup>-1</sup> , Fe <sup>2+</sup> = 10 mg L <sup>-1</sup> , continuous air supply  Bio: 1 mL consortium of bacteria extracted from soil	EF: 60% COD removal (1 h)  Bio: 34% COD removal (4 days)  Combined process: 94% COD removal	BOD <sub>5</sub> /COD increase from 0.34 to 0.52 by EF/Persulfate (1 h)	N/A	<a href="#">[55]</a>
MEF  Carbamazepine (drug) (10 mg L <sup>-1</sup> )	Undivided MFC (28 mL), Fe-Mn-impregnated carbon brush anode and carbon-PTFE gas diffusion cathode (7 cm <sup>2</sup> )	Substrate = acetate (1 g L <sup>-1</sup> ), nutrient-rich buffer at neutral pH, 10 $\Omega$ external resistance	90% removal (24 h)  6.3% TOC removal (24 h)	N/A	112 mW m <sup>-2</sup>	<a href="#">[56]</a>

MEF  Pharmaceutical mixture in municipal wastewater matrix (clofibric acid, diclofenac, carbamazepine, naproxen, ibuprofen, ketoprofen)  (0.5 mg L <sup>-1</sup> each)	20-L MFC with CEM, 20 carbon brush anodes (5.9 cm diameter × 6.9 cm), 20 graphite plate cathodes (4.5 cm × 4.5 cm)	Cathode chamber (9 L): $E = 0.2$ V vs SCE, in 0.05 M Na <sub>2</sub> SO <sub>4</sub> , pH = 2.8, Fe <sup>2+</sup> catalyst, 0.1 $\Omega$ external resistance, constant air supply.  Anode chamber: domestic wastewater with 1 g L <sup>-1</sup> acetate in nutrient medium	58%, 87%, 76%, 96%, 92%, and 86% degradation of clofibric acid, diclofenac, carbamazepine, naproxen, ibuprofen, ketoprofen, respectively (26 h)	5.84 € m <sup>3</sup>	N/A	[57]
MEF  Erythromycin (antibiotic)  (0.05 mg L <sup>-1</sup> )	Divided MFC with CEM (150 mL), CNT/ $\gamma$ -FeOOH/SS cathode, carbon cloth anode (28.3 cm <sup>2</sup> )	Cathode chamber (76.3 mL): pH = 7 (phosphate buffer), constant air supply 1000 $\Omega$ external resistance, T = 30 °C, effluent was first introduced in the anode chamber  Anode chamber: MFC effluent with nutrients and 1	Overall, 88.7% removal (48 h)  86.8% COD removal (48 h)	N/A	0.193 W m <sup>-3</sup> (0.583 A m <sup>-2</sup> )	[58]



		g L <sup>-1</sup> acetate				
MEF  Medicinal herb wastewater (COD = 6183 mg L <sup>-1</sup> , pH = 12.15)	Divided MFC, Fe@Fe <sub>2</sub> O <sub>3</sub> /graphite cathode and graphite anode (22 cm <sup>2</sup> )	Cathode chamber (350 mL): pH = 3, constant air supply, 100 Ω external resistance, T = 30 °C, organic loading rate = 0.58 g L <sup>-1</sup> day <sup>-1</sup> , the effluent was first treated in the anode chamber  Anode chamber: sludge from wastewater treatment plant, pH = 7	Overall, 93% COD removal (83.3 h)	N/A	183.1 mW m <sup>-2</sup> (603.9 mA cm <sup>-2</sup> ) (0.286 kW m <sup>-3</sup> of normalized energy recovery)	[45]
MEF  Non-steroidal anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen, naproxen) (0.04 mg L <sup>-1</sup> each)	Divided MFC with bipolar membrane, carbon brush cathode and graphite anode	Cathode chamber (175 mL): $E_{cell} = 0.3$ V, pH 2 in 0.05 M Na <sub>2</sub> SO <sub>4</sub> , Fe <sup>2+</sup> = 7.5 mM, 1 Ω external resistance  Anode chamber: wastewater from primary clarifier with acetate (20 mM)	Degradation of 61%, 97%, 86%, 81% of ketoprofen, diclofenac, ibuprofen and naproxen, respectively (5 h)	N/A	3.8 € m <sup>3</sup>	[46]

<sup>1</sup> Does not apply for MEF systems.

<sup>2</sup> Power generation only in the case of MEF.

CEM, cation exchange membrane; CNT, carbon nanotubes; FeMoP, iron molybdenum phosphate; PTFE, polytetrafluoroethylene; PEF, photoelectro-Fenton; SPEF, solar photoelectro-Fenton; SS, stainless steel; TN, total nitrogen; TSS, total suspended solids.

**Table 3.** Summary of recent reports on the coupling between EC and biological processes.

Treatment system / wastewater	Experimental setup of EC / biological treatment	Operating conditions	Removal efficiency	Biodegradability increase	Energy consumption	Ref.
EC + biofiltration as post-treatment  Landfill leachate: COD <sub>0</sub> = 6325 mg L <sup>-1</sup> , NH <sub>3</sub> = 1256 mg L <sup>-1</sup> , NO <sub>3</sub> <sup>-</sup> = 1.76 mg L <sup>-1</sup>	EC: parallelepiped undivided reactor (2 L), iron or aluminum anode (110 mm × 100 mm), stainless steel cathode (110 mm × 100 mm)  Bio: anoxic tank = 20 L, oxic tank = 20 L, settling tank = 3.8 L	EC: $j = 3 \text{ A m}^{-2}$ , electrode gap = 7 cm, pH = 8  Bio: aeration/pause mode = 60:60 min, loading rate = 5 L day <sup>-1</sup>	EC: 77% COD, 25% ammonia, and 90% nitrate (60 min)  Combined process: 95% COD, 98% ammonia and 90% nitrate	-	-	[68]
EC-biological in hybrid system  Lab-scale: synthetic wastewater (COD = 600 mg L <sup>-1</sup> , NH <sub>4</sub> <sup>+</sup> = 200 mg	Lab-scale: four sequencing batch reactor (SBRs) (8 L each) including 2 SBRS with Fe anode and carbon cathode (150 x 60 x 5 mm each)	Lab-scale: (EC: 0.01 A, electrodes gap = 6-8 cm; bio: HRT = 16 h at different temperature)	Lab-scale: combined process = 92% COD and 55% nitrate	-	-	[69]

<p><math>\text{L}^{-1}</math>, <math>\text{NO}_3^- = 200 \text{ mg L}^{-1}</math>)</p> <p>Pilot-scale: synthetic wastewater (<math>\text{COD}_0 = 2000 \text{ mg L}^{-1}</math>, <math>\text{NH}_4^+ = 944 \text{ mg L}^{-1}</math>, <math>\text{NO}_3^- = 1214 \text{ mg L}^{-1}</math>)</p> <p>Full-scale: oil shale wastewater (petroleum = <math>157\text{-}781 \text{ mg L}^{-1}</math>, <math>\text{COD}_0 = 6143\text{-}7251 \text{ mg L}^{-1}</math>, <math>\text{NH}_4^+ = 4571\text{-}5575 \text{ mg L}^{-1}</math>)</p>	<p>Pilot-scale: bioreactor (120 L) with 2 aerobic zones, 1 anoxic zone, 3 anaerobic zones and one MBR zone and two pairs of Fe anodes and Carbon cathodes (350 x 120 x 2 mm)</p> <p>Full-scale: 2 biochemical pools (<math>52,872 \text{ m}^3</math> each), one MBR pool, and two EC devices with 50 Fe electrodes (2000 x 1800 x 5 mm)</p> <p>Bio: activated sludge with nitrogen removal bacteria (Nitrosomonas, Nitrobacter, Paracoccus, Thauera and Enterobacter)</p>	<p>Pilot-scale: (EC: 0.2 A, electrodes gap = 8 cm; bio: HRT = 5 days at different temperature)</p> <p>Full-scale: (EC: 430 A (2-4 V), electrodes gap = 20 cm; bio: HRT = 15 days at different temperature)</p>	<p>Pilot-scale: combined process = 85% COD and 81% ammonium</p> <p>Full-scale: combined process = 50% COD and 99% ammonium</p>			
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EC + phytoremediation as post-treatment  Dairy industry wastewater: $COD_0 = 5600 \text{ mg L}^{-1}$ , $NO_3^- = 616 \text{ mg L}^{-1}$	EC: parallelepiped undivided reactor (1 L), iron (50 mm $\times$ 100 mm $\times$ 3 mm) or aluminum anode (50 mm $\times$ 100 mm $\times$ 2 mm), electrodes gap = 10 mm  Bio: <i>Canna indica</i> plant	EC: 2.5-5 V, continuous air supply  Bio: plant growth during six weeks with nutrients coming from the wastewater itself (not the soil)	EC: 86% COD and 76% nitrate (120 min)  Combined process: 98% COD and 84% nitrate	No increase of biodegradability after EC and after phytoremediation	-	[70]
EC + biological fungal post-treatment  Tannery wastewater: $COD_0 = 18800 \text{ mg L}^{-1}$ , $Cr^{6+} = 22.3 \text{ mg L}^{-1}$	EC: parallelepiped undivided reactor (0.8 L), iron cathode and aluminum anode (60 mm $\times$ 85 mm $\times$ 1 mm), electrodes gap = 20 mm  Bio: <i>Aspergillus niger</i> fungi	EC: pH 8, 0.18 A  Bio: pH 5, 2% inoculum rate, 36 h	EC: 64% COD and 90% $Cr^{6+}$ (60 min)  Combined process: 96% COD and 97% $Cr^{6+}$	-	1.73 \$ m <sup>-3</sup>	[71]

HRT, hydraulic retention time