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1 **Electrochemical technologies coupled with biological treatments**

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23

24 **Abstract**

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

37

38

39 **Keywords:**

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

42

43

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

50

51

Journal Pre-proof

52 **1. Introduction**

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

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

67

68 **2. Combination feasibility and treatment strategy**

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

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

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

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

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

99

100 **3. Anodic oxidation coupled with biological treatments**

101 AO process is an EAOP based on the generation of strong oxidants like hydroxyl radical
102 ($\cdot\text{OH}$) from oxidation of water in the region of water discharge [2,16]. This radical is
103 chemisorbed in the case of active anodes like carbon, Pt or dimensionally stable anode (DSA)
104 (with low oxygen evolution overpotential) whereas it is slightly adsorbed (physisorption) and
105 therefore more available for oxidation of organics in the case of non-active anodes having
106 high oxygen evolution overpotential like boron-doped diamond anode (BDD), PbO_2 , Ti_4O_7
107 [17–19]. However, the efficiency of this process depends strongly on the concentration of
108 organic compounds in the solution and mass transport conditions from the solution to the
109 anode surface [20,21]. Other oxidant species can be also generated (persulfate, sulfate radicals,
110 active chlorine, ozone) depending on ions present in the solution and operating conditions
111 [2,22,23].

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

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

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

136 Another approach recently reported in the literature is the possibility to combine AO with a
137 biological treatment in a hybrid reactor instead of the implementation of a sequential
138 combined process. Particularly, the integration into a membrane bioreactor has been studied
139 in order to address fouling issues and to improve the removal of recalcitrant micropollutants
140 [39–42]. However, further development of such reactor configuration is required for (i)
141 improving electrode activity for removal of organic micropollutants, (ii) reducing mass
142 transport limitations, (iii) studying the influence of the electrical field on bacterial diversity
143 and activity, and (iv) assessing the influence of the large concentration of organic matter in
144 the mixed liquor on the efficiency of AO.

145

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

147 The EF process is based on the cathodic production of H_2O_2 at a suitable electrode material
148 (generally carbon-based) through the 2-e^- reduction of O_2 . H_2O_2 entails the generation of $\cdot\text{OH}$
149 via the Fenton's reaction in the presence of Fe^{2+} ions, which are externally added at a catalytic
150 amount and electrochemically regenerated also at the cathode surface [2]. EF has been applied
151 with success to treat several types of wastewaters contaminated with a variety of pollutants,
152 becoming one of the most widely studied EAOPs [43]. Following the combination trends of
153 AOPs with biological processes, EF has been an excellent option to handle recalcitrant
154 pollutants resisting biological degradation such as most of pesticides, synthetic dyes,
155 industrial chemicals, pharmaceuticals, etc. Therefore, different coupled strategies (either
156 sequenced or integrated processes) have been proposed (Table 2) [15,44–58]. In the case of
157 sequenced processes (pioneered by the groups of Oturan [59] and Fourcade [15]), the most
158 common approach has been the use of EF as pre-treatment step to increase the
159 biodegradability of refractory effluents during a short treatment time (to save electrical energy
160 for cost effectiveness) [59,60], whereas the remaining biodegradable organics are treated by
161 conventional biological means. As a less popular option, EF has also been used as post-
162 treatment following biological degradation to deplete the remaining bio-recalcitrant
163 compounds. In such sequenced methods, conventional EF (catalyzed either by Fe^{2+} in solution
164 (homogenous EF) or solid Fe catalysts (heterogeneous EF)) has been generally performed in
165 undivided electrolytic cells with optimization of the main operating parameters affecting the
166 efficiency (current density, electrode materials, catalyst concentration, etc.), while aerobic
167 treatment with different microbial sources has been the preferred option. It is important to
168 note that pH adjustment is generally required after/prior to EF, which is typically conducted at
169 pH 3 in the case of homogeneous EF [2].

170 Another kind of Bio-EF system, known as microbial-electro-Fenton (MEF), involves the
171 incorporation of an EF half-cell in a microbial fuel cell (MFC) [61–63]. During MEF, the EF
172 degradation of pollutants takes place in the cathode chamber equipped with a carbonaceous
173 cathode capable of producing H_2O_2 and containing a catalyst source (Fe^{2+} in the solution or
174 Fe particles impregnated on the cathode). The anodic compartment contains anaerobic
175 electrogenic communities adhered to the anode surface that are able to produce electricity
176 through the oxidation of an organic substrate (i.e. acetate or wastewater). Wastewater
177 treatment can occur at both the biological and the EF chambers, generally with electricity
178 output, though low potentials have also been applied to enhance the performance. The main
179 advantage of MEF is the sustainable generation of electricity by the microorganisms.

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

185

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

187 The EC process consists on the use of iron or aluminum based-sacrificial anode material that
188 will generate the coagulants responsible for the coagulation of colloidal matter [64–67]. It can
189 remove the color, suspended solids and partial COD from wastewater [64,65]. EC processes
190 have been proposed as pre-treatment [64] or polishing treatment [65] when combined with
191 biological processes. The main most recent studies on this coupling have been described in
192 Table 3. This combination has been implemented to treat industrial wastewaters such as
193 landfill leachate [68], oil shale wastewater [69], dairy wastewater [70] and tannery wastewater
194 [71]. EC was mainly responsible in COD removal in the combined process, which allowed
195 reaching the COD guidelines for effluent discharge [64,65]. However, the management of
196 hydroxides' precipitates produced during EC need to be considered in the reactor design since
197 the potentially toxic sludge can limit the efficiency of the bioprocess in an hybrid combination
198 [64,65]. Moreover, most of the studies have been performed at lab-scale, which is not
199 sufficient to assess the efficiency of combination. Still, one recent study presents a systematic
200 comparison at lab-scale, pilot-scale and full-scale [69], demonstrating the ability to apply this
201 combination at industrial scale. Further studies are required to optimize the scale up.

202

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

204 If scale-up of conventional biological processes (activated sludge, biofilm reactors) is
205 relatively mature, scale-up of electrochemical reactors is still under development in this area
206 [72]. In the aim at optimizing the efficiency of the combined process, several engineering
207 aspects need to be considered. An important factor concerns the design and sizing of the
208 electrochemical and biological reactors. The choice of the electrochemical reactor
209 configuration must depend on the effluent characteristics [73,74]. For low to moderate
210 concentrated effluents with a low amount of particles, the mass transfer should be intensified
211 by implementing flow-through mode with porous electrode materials and/or thin-film reactors

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

228

229 **7. Conclusions and future perspectives**

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

241

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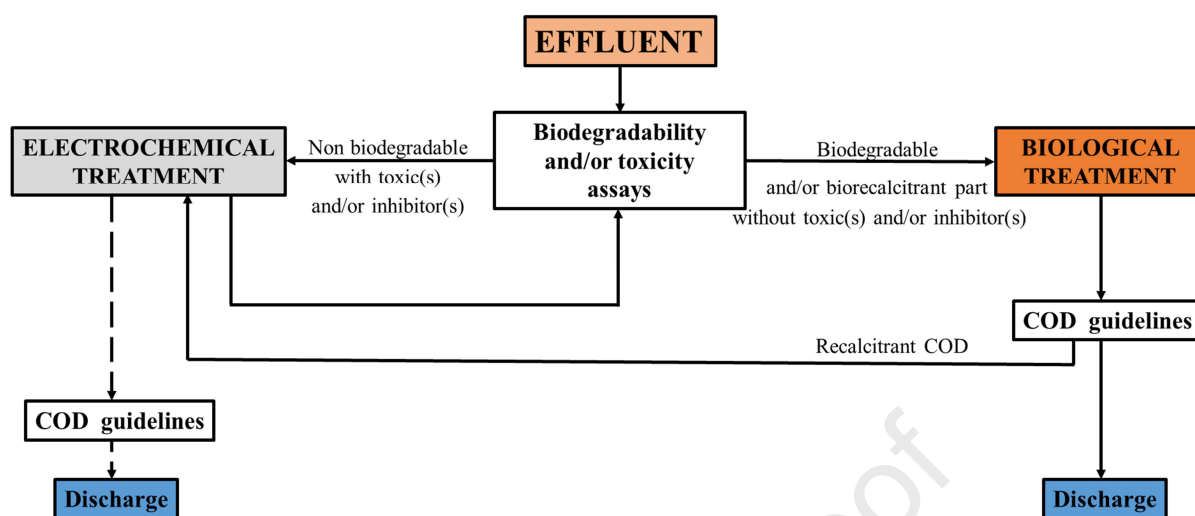
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568 **Figure 1.** Combination strategy between electrochemical treatments and biological processes.

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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 ⁻¹ of phenanthrene and 1.31 g L ⁻¹ of Tween 80 ; 2.7 g L ⁻¹ 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 ₂ SO ₄] = 50 mM j = 7 – 36 mA cm ⁻² | 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) ⁻¹ | [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 ⁻² (optimal conditions for degradation of clopyralid and | - | [25] |

| | | | | | | |
|--|---|--|--|--|--|------|
| extracting agent ; 180 mg L ⁻¹ 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 ⁻¹ Carbon felt: 60% degradation and 30% mineralization at 4 Ah L ⁻¹ | accumulation of by-products). The ratio BOD ₅ / COD increased from 0.02 to 0.23 and the oxygen uptake rate from -10 to 40 mg (h gVSS) ⁻¹ at 3.8 Ah L ⁻¹ | | |
| Electrocoagulation + AO with a biological post-treatment Landfill leachates (21.7 g L ⁻¹ 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 ⁻¹) $j = 30 - 70 \text{ mA cm}^{-2}$ for AO | 60 – 70% COD removal after 2 or 3 h of electrocoagulation and 8 h of AO (30 mA cm ⁻²) | The ratio BOD ₅ / COD increased from 0.3 to 0.45 – 0.9 depending on operating conditions | 11.2 – 17.5 kWh (kg COD) ⁻¹ | [26] |

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

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

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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 ¹ | Energy consumption / Power generation ² | Ref. |
|---|--|--|--|--|--|------|
| Homogeneous EF + Bio Ionic liquid 1-butyl-1-methylpyrrolidinium chloride (1 mM = 177.7 mg L ⁻¹), TOC ₀ = 108 mg L ⁻¹ | EF: cylindrical undivided cell (230 mL), carbon felt cathode (19 cm × 7 cm × 0.5 cm) and BDD anode (25 cm ²) 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 ₂ SO ₄ , Fe ²⁺ = 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 ⁻¹) | <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 ₂ SO ₄ , 0.3 g of Fe ₂ SO ₄ | 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) ⁻¹ | |
| Heterogeneous EF + Bio Stabilized landfill leachate (COD = 7184 mg L ⁻¹ , BOD ₅ /COD = 0.03) | EF: undivided cell (750 mL), Ti/TiO ₂ 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 ⁻¹ 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 ₅ /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⁻¹)</p> | <p>SPEF: undivided cell (200 mL), Ti/IrO₂-SnO₂ anode (2.89 cm²), carbon felt air diffusion cathode (2 cm²), UV lamp with $\lambda = 368$ nm</p> <p>Bio: aerobic reactor (900 mL) with aerobic sludge from a food processing plant</p> | <p>SPEF: $j = 3.46$ mA cm⁻², in 0.05 M NaCl, Fe²⁺ = 0.036 mM, pH = 3</p> <p>Bio: 4000 mg L⁻¹ of biomass, pH = 7, T = 37 °C</p> | <p>SPEF: total degradation (45 min) and >20% TOC removal (90 min)</p> <p>Bio: 80% TOC removal (8 days)</p> | N/A | N/A | [53] |
| <p>EF + Bio</p> <p>Metrodinazole (antibiotic) (100 mg L⁻¹)</p> | <p>EF: undivided cell (250 mL), graphite felt cathode (42 cm²), Pt anode (32 cm²)</p> <p>Bio: aerobic reactor (500 mL) with activated sludge</p> | <p>EF: $j = 0.07$ mA cm⁻², in 0.05 M Na₂SO₄, pH = 3, Fe²⁺ = 0.1 mM, constant air supply</p> <p>Bio: mineral nutrient solution with 5 g L⁻¹ 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> | BOD ₅ /COD increase from 0 to 0.46 by EF (1 h) | N/A | [15] |

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

| | tests | sludge removal | | | | |
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| EF/Persulfate + Bio Mixed industrial wastewater (COD = 1152 mg L ⁻¹ , pH = 7.32) | EF/Persulfate: undivided cell (1 L), Ti/Pt mesh anode (2 pieces), graphite felt cathode (2 pieces) (25 cm ²) Bio: aerobic treatment with soil bacteria (100 mL) | EF/Persulfate: $E_{cell} = 10$ V, pH = 3, persulfate = 200 mg L ⁻¹ , Fe ²⁺ = 10 mg L ⁻¹ , 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 ₅ /COD increase from 0.34 to 0.52 by EF/Persulfate (1 h) | N/A | [55] |
| MEF Carbamazepine (drug) (10 mg L ⁻¹) | Undivided MFC (28 mL), Fe-Mn-impregnated carbon brush anode and carbon-PTFE gas diffusion cathode (7 cm ²) | Substrate = acetate (1 g L ⁻¹), nutrient-rich buffer at neutral pH, 10 Ω external resistance | 90% removal (24 h) 6.3% TOC removal (24 h) | N/A | 112 mW m ⁻² | [56] |

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| <p>MEF</p> <p>Pharmaceutical mixture in municipal wastewater matrix (clofibric acid, diclofenac, carbamazepine, naproxen, ibuprofen, ketoprofen)</p> <p>(0.5 mg L⁻¹ each)</p> | <p>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)</p> | <p>Cathode chamber (9 L): $E = 0.2$ V vs SCE, in 0.05 M Na₂SO₄, pH = 2.8, Fe²⁺ catalyst, 0.1 Ω external resistance, constant air supply.</p> <p>Anode chamber: domestic wastewater with 1 g L⁻¹ acetate in nutrient medium</p> | <p>58%, 87%, 76%, 96%, 92%, and 86% degradation of clofibric acid, diclofenac, carbamazepine, naproxen, ibuprofen, ketoprofen, respectively (26 h)</p> | <p>5.84 € m³</p> | <p>N/A</p> | <p>[57]</p> |
| <p>MEF</p> <p>Erythromycin (antibiotic)</p> <p>(0.05 mg L⁻¹)</p> | <p>Divided MFC with CEM (150 mL), CNT/ γ-FeOOH/SS cathode, carbon cloth anode (28.3 cm²)</p> | <p>Cathode chamber (76.3 mL): pH = 7 (phosphate buffer), constant air supply 1000 Ω external resistance, T = 30 °C, effluent was first introduced in the anode chamber</p> <p>Anode chamber: MFC effluent with nutrients and 1</p> | <p>Overall, 88.7% removal (48 h)</p> <p>86.8% COD removal (48 h)</p> | <p>N/A</p> | <p>0.193 W m⁻³ (0.583 A m⁻²)</p> | <p>[58]</p> |

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|---|---|--|---|-----|--|------|
| | | g L ⁻¹ acetate | | | | |
| MEF Medicinal herb wastewater (COD = 6183 mg L ⁻¹ , pH = 12.15) | Divided MFC, Fe@Fe ₂ O ₃ /graphite cathode and graphite anode (22 cm ²) | Cathode chamber (350 mL): pH = 3, constant air supply, 100 Ω external resistance, T = 30 °C, organic loading rate = 0.58 g L ⁻¹ day ⁻¹ , 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 ⁻² (603.9 mA cm ⁻²) (0.286 kW m ⁻³ of normalized energy recovery) | [45] |
| MEF Non-steroidal anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen, naproxen) (0.04 mg L ⁻¹ 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 ₂ SO ₄ , Fe ²⁺ = 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 ³ | [46] |

¹ Does not apply for MEF systems.

² 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.

Journal Pre-proof

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 ₀ = 6325 mg L ⁻¹ , NH ₃ = 1256 mg L ⁻¹ , NO ₃ ⁻ = 1.76 mg L ⁻¹ | 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 ⁻¹ | 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 ⁻¹ , NH ₄ ⁺ = 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] |

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| <p>L^{-1}, $\text{NO}_3^- = 200 \text{ mg L}^{-1}$)</p> <p>Pilot-scale: synthetic wastewater ($\text{COD}_0 = 2000 \text{ mg L}^{-1}$, $\text{NH}_4^+ = 944 \text{ mg L}^{-1}$, $\text{NO}_3^- = 1214 \text{ mg L}^{-1}$)</p> <p>Full-scale: oil shale wastewater (petroleum = $157\text{-}781 \text{ mg L}^{-1}$, $\text{COD}_0 = 6143\text{-}7251 \text{ mg L}^{-1}$, $\text{NH}_4^+ = 4571\text{-}5575 \text{ mg L}^{-1}$)</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 ($52,872 \text{ m}^3$ 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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| <p>EC + phytoremediation as post-treatment</p> <p>Dairy industry wastewater: $COD_0 = 5600 \text{ mg L}^{-1}$, $NO_3^- = 616 \text{ mg L}^{-1}$</p> | <p>EC: parallelepiped undivided reactor (1 L), iron (50 mm × 100 mm × 3 mm) or aluminum anode (50 mm × 100 mm × 2 mm), electrodes gap = 10 mm</p> <p>Bio: <i>Canna indica</i> plant</p> | <p>EC: 2.5-5 V, continuous air supply</p> <p>Bio: plant growth during six weeks with nutrients coming from the wastewater itself (not the soil)</p> | <p>EC: 86% COD and 76% nitrate (120 min)</p> <p>Combined process: 98% COD and 84% nitrate</p> | <p>No increase of biodegradability after EC and after phytoremediation</p> | <p>-</p> | <p>[70]</p> |
| <p>EC + biological fungal post-treatment</p> <p>Tannery wastewater: $COD_0 = 18800 \text{ mg L}^{-1}$, $Cr^{6+} = 22.3 \text{ mg L}^{-1}$</p> | <p>EC: parallelepiped undivided reactor (0.8 L), iron cathode and aluminum anode (60 mm × 85 mm × 1 mm), electrodes gap = 20 mm</p> <p>Bio: <i>Aspergillus niger</i> fungi</p> | <p>EC: pH 8, 0.18 A</p> <p>Bio: pH 5, 2% inoculum rate, 36 h</p> | <p>EC: 64% COD and 90% Cr^{6+} (60 min)</p> <p>Combined process: 96% COD and 97% Cr^{6+}</p> | <p>-</p> | <p>1.73 \$ m⁻³</p> | <p>[71]</p> |

HRT, hydraulic retention time