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Electrochemical Technologies for the Treatment of Pesticides

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Abstract

Pesticides are worldwide used in large amount to increase yield in agriculture. On the other hand, they are in general toxic/persistent organic pollutants presenting strong adverse effects to the environment and human health, including acute and chronic toxicity. Consequently, water polluted by pesticides should be treated efficiently before its release into receiving water bodies to protect natural aquatic environment. Different methods have been used for treatment of water contaminated by pesticides. Among them, electrochemical technology seems to be very efficient to remove pesticides from water. Therefore this review aims to provide an overview of the recent works on the treatment of pesticide wastewater using electrochemical technology with a special focus on

30 electrochemical advanced oxidation processes which demonstrated high efficiency in
31 removal of various type of pesticides from contaminated water.

32

33 **Keywords:**

34 Electro-Fenton; Pesticide; Electro-oxidation; Organic pollutants; Hydroxyl radicals,
35 Wastewater treatment

36

37 **1. Introduction**

38 The term pesticides cover a large variety of molecules used for improving agricultural
39 productivity. With more than 4 million tons applied worldwide annually, they are among
40 the most widespread xenobiotics released by anthropogenic activities [1]. It has been
41 demonstrated that several pesticides present strong adverse effects on ecosystems
42 (alteration of the biodiversity) and human health, including acute toxicity (accidental
43 deaths by poisoning, particularly in developing countries) and chronic toxicity (even
44 when exposed at low concentrations), as reported, in the case of India for example [2].
45 After being used on agricultural crops, pesticides reach soil, air and water bodies where
46 their accumulation depends on their persistence and can reach significant concentrations
47 in the different environmental compartments [1]. Regulatory authorities are trying to take
48 into consideration this environmental issue by introducing standards for pesticide content
49 in drinking water (e.g., in the European Union, 100 ng L⁻¹ for individual pesticides and
50 500 ng L⁻¹ for the sum of all pesticides detected [3]). Therefore, the removal of pesticides
51 is currently an important challenge for environmental engineers working on soil
52 remediation and water treatment, including drinking water, municipal wastewater and
53 some industrial wastewaters. The development of electrochemical processes might help
54 to address this issue [4**]. While electrocoagulation process is able to separate some of
55 pesticides, electrochemical advanced oxidation processes (EAOPs) are widely recognized
56 for their capacity to remove efficiently and in a non-selective way a very large range of
57 pesticides from water [5]. EAOPs can also be applied for the pesticides removal from
58 groundwater and from soil after a soil washing step [6**]. The objective of this review is
59 to provide a concise overview of the recent reports, including the advantages and
60 drawbacks of electrochemical processes for treating pesticides and to provide new
61 insights on the future of these technologies in this area.

62

63 **2. Which electrochemical technologies are used for treating pesticides?**

64 Different electrochemical technologies were applied to the treatment of pesticides in
65 water and soils. The two EAOPs (electro-Fenton (EF) and electrooxidation (or anodic
66 oxidation (AO)) are the most widely used processes for treatment of pesticides.
67 Electrooxidation is based on generation of hydroxyl radicals ($\cdot\text{OH}$) from electrooxidation
68 of water at the anode surface when using a non-active anode like BDD or PbO_2 . These
69 radicals are physisorbed on anode surface and constitute strongest oxidant species at the
70 vicinity of the electrode [7]. Therefore, oxidation of pollutants requires their transfer to
71 the surface of anode where they are oxidized/mineralized by $\cdot\text{OH}$. Several recent works
72 have demonstrated high efficiency of this process, alone [8–10] or in combination with
73 other technologies [11,12] for the treatment of synthetic or real pesticides wastewater. In
74 contrast, in EF, $\cdot\text{OH}$ are homogeneously generated in the bulk solution from the reaction
75 between electrochemically formed H_2O_2 and a catalyst (generally Fe^{2+} ion) to remove
76 pesticides from water [13,14]. To enhance process efficiency, EF has been coupled to
77 other methods such as photocatalysis [15] and solar photocatalysis [16].
78 Electrocoagulation [17,18] and electrokinetics [19] were also applied to water treatment
79 and soil remediation, respectively.

80

81 **3. Applications for the treatment of pesticides in water**

82 Several kinds of electrochemical processes have been successfully applied to treat a
83 number of pesticides in water including EF and its photo-assisted versions (photoelectro-
84 Fenton (PEF) and solar photoelectro-Fenton (SPEF)), direct or Cl^- mediated anodic
85 oxidation (AO), electrocoagulation (EC) and photoelectrocatalysis (PEC) (Table 1). In
86 general, fast degradation kinetics have been observed, with complete removal of target
87 pesticides ranging from few minutes to few hours depending on the process and
88 experimental conditions used. Besides, high mineralization yields (>50% of TOC
89 removal) are generally achieved within few hours of treatment. It is worthy to note that
90 EF and its photo-assisted variants (PEF and SPEF), along with AO using BDD anodes
91 have shown the fastest degradation kinetics and the highest mineralization yields (almost
92 total TOC removal in few hours) [9*,20–23*], which is attributed to the efficient

93 formation of strong oxidants: homogeneous $\cdot\text{OH}$ (EF) and heterogeneous BDD($\cdot\text{OH}$) (AO
94 and EF with BDD anode) during the process.

95 The use of accessible carbonaceous cathode materials (i.e., carbon felt, carbon cloth,
96 carbon fibers, etc.) constitutes a technical advantage of EF and makes the process
97 economically attractive. In contrast, BDD is still a costly material restraining the
98 application of AO at large-scale [24,25*].

99 Different pesticides have been used as model pollutants to evaluate the performance of
100 new electrode materials. For example, an N-doped graphene cathode for H_2O_2 production
101 and its activation was successfully tested for the degradation of 2,4-
102 dichlorophenoxyacetic acid [26], while a dual anode consisting of one layer of SnO_2 -
103 $\text{Sb}_2\text{O}_3/\text{PbO}_2$, and one of TiO_2 deposited on the opposite sides of a Ti plate was used to
104 treat the herbicide fenuron by photocatalytically assisted AO [27]. The development of
105 high-surface-area and durable electrode materials is an active research field with great
106 improvement opportunities.

107 On the other hand, most of the investigations have been conducted using aqueous
108 solutions of the target compounds (some of them using commercial formulations) to
109 obtain important information about the kinetics, mechanisms, and optimal experimental
110 conditions for the degradation/mineralization of such pollutants. However, the effect of
111 the matrix in real wastewaters is not considered in such works. Hence, more
112 investigations using real water sources contaminated by pesticides are highly
113 recommended in order to evaluate the influence of the matrix (additives, other organics
114 as well as inorganic compounds) on the process performance [25*]. In this sense, the
115 presence of radical scavengers may significantly affect the degradation/mineralization
116 efficiency. Additionally, the concentrations of target pollutants in synthetic solutions are
117 generally orders of magnitude higher than the concentrations in real water sources [28],
118 which may affect the efficiencies under real scenarios, especially considering the mass
119 transport limitations to the electrode surface inherent to electrochemical processes.

120 Another important point to keep in mind is that most studies on electrochemical treatment
121 of pesticides have been carried out in small laboratory-scale devices with capacities rarely
122 exceeding 1 L. With this respect, the design of electrochemical reactors with the capacity
123 to treat greater volumes is fundamental for the application of such treatment methods at
124 industrial scale. Larger-scale systems would give a more reliable assessment of both

125 investment and operating costs of electrochemical processes (operating costs tightly
126 related to electrical energy consumption).

127

128 **4. Applications for the treatment of pesticides in soil**

129 Diffuse pollution of soils is a very complex environmental issue because of the huge
130 amount of soils that might be concerned for remediation and the great complexity of
131 treating contaminated soils. Electrochemical technologies cannot be considered as
132 sustainable solutions in such case. However, manufacturing and handling of pesticides
133 can lead to accidental release and create a localized acute contamination, for which the
134 application of electrochemical technologies might be suitable.

135 First, electrokinetic processes based on the application of an electric field in the soil
136 present the great interest to avoid the use of any chemical compounds and to be applied
137 *in situ*. It has been reported at lab-scale that it is possible to recover pollutants in catholyte
138 and anolyte wells by dragging with the electroosmotic flux or by electromigration of ionic
139 compounds [19]. However, it has been highlighted that the influence of these mechanisms
140 is very low when applying this process at pilot scale [19]. As high current intensities have
141 to be applied, the controlling mechanism becomes the electric heating of the soil, which
142 influences pollutant volatilization from soil. Current studies focus mainly on the
143 combination with other processes (e.g., phytoremediation or the use of additives such as
144 oxidants) [33*,34] or by implementing efficiently this technology at pilot-scale
145 (optimization of powering control, inversion of electrode polarity, etc.) [33*,34].

146 Secondly, a treatment strategy involving an electrochemical process as post-treatment
147 step can be applied for treating soil washing solutions [6**]. Soil washing (as first step)
148 aims at transferring pesticides from the soil-sorbed fraction to the aqueous phase.
149 Extracting agents (cyclodextrins or surfactants such as Tween 80, Triton X 100 or sodium
150 dodecyl sulfate) can be used for improving the transfer of hydrophobic pesticides. The
151 soil washing solution is therefore a complex mixture of all compounds that can be
152 mobilized, including target pesticides, soil organic matter, inorganic species, fine
153 particles and extracting agents [6**]. Several studies have reported that EAOPs are able
154 to remove the organic load of these effluents [36,37*]. Recent studies are reported in
155 Table 2. The possibility of combination with a biological treatment has also been assessed

156 for improving the cost-effectiveness [38,39] and few studies focused on selective electro-
157 oxidation of target pollutants in order to be able to reuse extracting agents [39**,40*].
158 However, further studies are required in order to scale up such treatment for field scale
159 applications and for assessing the sustainability of this approach.

160

161 **5. Challenges for full-scale applications**

162 There are several challenges for upscaling the electrochemical technologies regarding the
163 removal of pesticides, especially about the reactor design.

164 When the option consists to treat pesticides from urban wastewater or natural water, their
165 concentrations in solution is very low (from ng L^{-1} to $\mu\text{g L}^{-1}$) [4*]. It means that it is
166 required to strongly favor the contact between the pollutant and the electrodes in AO
167 and/or to enhance the promotion of the homogeneous oxidation with EF process [45].
168 This will enhance the faradaic yield, while keeping high pesticides removal yields.
169 Moreover, these effluents have generally a low electric conductivity [4*], which means
170 that the reactor design need to be also adapted in order to avoid adding a supporting
171 electrolyte. Microfluidic thin film electrochemical reactors have emerged as a possible
172 response towards these issues by intensifying the transport of species and reducing the
173 ohmic resistance [46–48]). Further studies are needed at large scale in order to validate
174 the lab-scale systems.

175 When the pesticides are solubilized in soil washing/flushing effluent, their concentrations
176 in solution can be increased to mg L^{-1} range [28]. Still, the faradaic yield remains low,
177 because the extracting agent represents the main organic source. To make it economically
178 viable at larger scale, the recovery of extracting agent has to be considered while the
179 selective removal of the contaminants should be effective. Combined treatments in hybrid
180 or sequenced reactor(s) required supplementary proofs at high technology readiness
181 levels.

182 In electrokinetics systems, lab-scale experiments could not predict well the pilot and
183 larger scale applications [33*]. The difficulties remain in the ability to have geometrical
184 and operational similarity between the setups [33*], which makes changing the
185 distribution of parameters (pH, conductivity, temperature, pollutants and ions
186 concentrations) and the mechanisms involved [19,49]. Furthermore, the soil

187 characteristics (electric conductivity, granulometry, age of pollution,...) vary a lot from
188 one sample to another, which makes difficult the extrapolation of the results for upscaling
189 studies. Additional large scales studies need to be performed in a comparable way by
190 implementing dimensional analysis.

191

192 **6. Conclusions and future perspectives**

193 Electrochemical processes stand out as promising technologies for the treatment of
194 harmful organic pollutants (pesticides, synthetic dyes, pharmaceutical residues,...) in
195 contaminated water and soils. Particularly, EAOPs present great advantages due to their
196 capacity to remove, in a non-selective way, a large range of pesticides, which can be
197 degraded and even fully mineralized in order to avoid the presence of toxic by-products
198 remaining in the treated solution. Besides application to contaminated water, they can
199 also be employed for the removal of pesticides in soil washing effluents. The next
200 challenge for further development of electrochemical technology and particularly of
201 EAOPs is clearly related to full-scale applications, including the design of suitable
202 reactors and the application to real effluents. This step is required in order to conclude on
203 the sustainability and cost-effectiveness of these processes.

204

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Table 1. Compilation of recent works on the electrochemical treatment of pesticides in water.

Pesticide	Process	Cell configuration	Operating conditions	Removal efficiency	Energy consumption	Ref.
1,2-dichlorobenzene (0.1 mM = 14.7 mg L ⁻¹)	EF	Undivided cylindrical cell (230 mL), Nb/BDD anode (4 cm x 6 cm), carbon felt cathode (16 cm x 4 cm x 0.5 cm), with constant air supply	$I = 500$ mA, pH = 3, in Na ₂ SO ₄ 0.05 M, Fe ²⁺ = 0.1 mM	Complete degradation in 10 min. $k^a = 294.6$ min ⁻¹ $k_{abs}^b = 1.61 \times 10^9$ M ⁻¹ s ⁻¹ >90% TOC removal (3 h)	2.5 kWh (g-TOC) ⁻¹	[20]
Chloramben (herbicide) (1.19 mM = 245.1 mg L ⁻¹) spiked in urban wastewater (TOC ₀ = 15 mg L ⁻¹)	PEF ^c	Undivided cell (100 mL) Carbon-PTFE GDE ^d cathode (3 cm ²), BDD anode UVA lamp ($\lambda = 365$ nm)	$j = 33.3$ mA cm ⁻² , pH = 3.4, in Na ₂ SO ₄ 0.05 M, Fe ²⁺ = 0.05 mM, TOC ₀ = 115 mg L ⁻¹ , T = 35 °C	96% degradation in 40 min $k^a = 0.13$ min ⁻¹ 82% TOC removal (3 h)	N/A	[21]
Tebuthiuron (0.18 mM = 41.1 mg L ⁻¹) and ametryn (0.09 mM = 20.5 mg L ⁻¹) from commercial formulations	SPEF ^e	Flow plant with a filter-press cell and a planar solar photoreactor, BDD anode (20 cm ²) and carbon-PTFE GDE cathode (20 cm ²), V = 2.5 L	$j = 50$ mA cm ⁻² , pH = 3, in 0.05 Na ₂ SO ₄ , Fe ²⁺ = 0.5 mM, TOC ₀ = 30 mg L ⁻¹ , liquid flow rate = 200 L h ⁻¹	Time for complete degradation: 240 min for tebuthiuron and 120 min for ametryn. $k^a_{tebuthiuron} = 0.098$ min ⁻¹ , $k^a_{ametryn} = 0.26$ min ⁻¹ 53% TOC removal (6 h)	2.1 kWh (g-TOC) ⁻¹	[16]
Imidacloprid (insecticide) (23.7 mg L ⁻¹) in softened natural groundwater	AO-BDD	Undivided cylindrical cell (150 mL), Si/BDD anode, Fe cathode (both 10 cm ²)	$j = 5$ mA cm ⁻² , pH = 6.8, TOC ₀ = 10 mg L ⁻¹ , T = 25 °C, NO ₃ ⁻ = 129.4 mg L ⁻¹	Complete degradation at 210 min. $k^a = 0.014$ min ⁻¹ 61.5% TOC removal (4 h)	N/A	[29]

Lindane (10 mg L ⁻¹)	AO-BDD	Undivided cylindrical cell (230 mL), Nb/BDD anode (24 cm ²), carbon felt cathode (18 cm x 5 cm x 0.5 cm)	$j = 8.33 \text{ mA cm}^{-2}$, pH = 6.5, in Na ₂ SO ₄ 0.05 M, TOC ₀ = 2.45 mg L ⁻¹	Total removal (10 min) $k^a = 0.25 \text{ min}^{-1}$ 80% TOC removal (4 h)	15 kWh (g-TOC) ⁻¹	[9*]
2,4-dichlorophenoxyacetic acid (20 mg L ⁻¹) (herbicide)	PS ^f activation by AO-Blue TiO ₂	Undivided cell (100 mL), Blue TiO ₂ anode, SS cathode	$j = 2.5 \text{ mA cm}^{-2}$, pH = 3.5, PS = 30 mM	Complete degradation in 60 min $k^a = 0.07 \text{ min}^{-1}$ 83% TOC removal (2 h)	0.14 kWh m ⁻³	[10]
Oxyfluorfen (100 mg L ⁻¹) from commercial formulations (Fluoxil 24 EC)	EC ^g	Single-compartment flow cell (5 L-capacity), Fe anode, SS ⁱ cathode (both 100 cm ²)	$j = 5 \text{ mA cm}^{-2}$, pH = 7, in Na ₂ SO ₄ 0.02 M, TOC ₀ = 72 mg L ⁻¹ , $q = 0.6 \text{ L h}^{-1}$, $Q = 0.836 \text{ A h dm}^{-3}$	99% depletion in 100 min 45% TOC removal (1.7 h)	N/A	[18]
2,4-dichlorophenoxyacetic acid (10 mg L ⁻¹)	Solar PEC	3-electrode undivided cell (quartz), Ti/Blue TiO ₂ photoanode (2.5 x 2.5 cm), SS cathode	E = 2.4 V vs SCE, pH = 5, in Na ₂ SO ₄ 0.05 M, sunlight (200 W Xenon lamp, 80 mW cm ⁻²)	Total depletion in 120 min. $k^a = 0.03 \text{ min}^{-1}$	N/A	[30]
2,4-dichlorophenoxyacetic acid (20 mg L ⁻¹)	H ₂ O ₂ -based electrochemical oxidation	3-electrode undivided cell (150 mL), Ti/RuO ₂ -IrO ₂ anode, N-doped graphene cathode (both 3 cm x 4 cm).	E = 4 V vs SCE, pH = 7, in 0.05 M Na ₂ SO ₄	Total depletion in 60 min. $k^a = 0.04 \text{ min}^{-1}$ 88% TOC removal (8 h)		[26]
Monolinuron (herbicide) (0.1 mM = 21.5 mg L ⁻¹)	EF	Undivided cylindrical cell (230 mL), BDD anode (24 cm ²), carbon felt cathode, continuous air supply	$I = 500 \text{ mA}$, pH = 3, in Na ₂ SO ₄ 0.05 M	Complete degradation in 10 min. $k^b_{abs} = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ 98% TOC removal (8 h)	10 kWh (g-TOC) ⁻¹	[22]

Fenuron (0.1 mM = 16.42 mg L ⁻¹)	Photocatalytically-assisted electrochemical oxidation	Undivided cell (250 mL), dual anode: Ti/SnO ₂ -Sb ₂ O ₃ /PbO ₂ (electrocatalytic side), Ti/TiO ₂ (photocatalytic side), SS cathode	$j = 30 \text{ mA cm}^{-2}$, natural pH, in Na ₂ SO ₄ 0.05 M, $\lambda = 254 \text{ nm}$.	97.5% degradation in 60 min 97.4% COD removal (4 h)	N/A	[27]
1-chloro-2,4-dinitrobenzene (0.25 mM = 50.6 mg L ⁻¹)	AO-BDD	3-electrode undivided cell (150 mL), Si/BDD anode, graphite rod cathode, Hg/Hg ₂ SO ₄ reference electrode	$j = 30 \text{ mA cm}^{-2}$, pH = 3, in Na ₂ SO ₄ 0.05 M, T = 30 °C	90% removal (230 min) $k^a = 0.01 \text{ min}^{-1}$ 62% TOC removal (3.8 h)	N/A	[31]
Glyphosate from commercial formulations (TOC = 100 mg L ⁻¹)	Cl ⁻ mediated AO	Undivided cell (100 mL), Ti/Ru _{0.36} Ti _{0.64} O ₂ anode (14.76 cm ²), SS cathode (22.62 cm ²)	$j = 40 \text{ mA cm}^{-2}$, pH = 3, NaCl = 0.15 M	60% TOC removal (3 h) (Complete degradation in 120 min for solutions prepared with the pure chemical, with $k^a = 0.02 \text{ min}^{-1}$ and >90% TOC removal)	1 kWh -g-TOC ⁻¹ (for solutions with the pure chemical)	[32]

^a apparent rate constant of oxidation reaction, ^b absolute (second order) rate constant of oxidation of 1,2-dichlorobenzene by ^cOH, ^c photoelectro-Fenton, ^d gas diffusion electrode,

^e solar photoelectro-Fenton, ^f persulfate, ^g electrocoagulation, ⁱ stainless steel

Table 2. Examples of application of electrochemical technology to treatment of pesticides in soils and groundwater.

1- Target pollutant 2- Washing solution	Process	Cell configuration Operating conditions	Removal efficiency	Ref.
1- Atrazine (spiked clay) 2- Sodium dodecyl sulphate (100 – 5000 mg L ⁻¹) and NaHCO ₃ (500 mg L ⁻¹)	AO	Continuous circulation (200 L h ⁻¹) of the effluent (1 L) in a flow-by cell using BDD anode and steel (diameter = 10 cm). $I = 30 \text{ mA cm}^{-2}$	Complete degradation of atrazine and sodium dodecyl sulphate and >90% TOC removal at 30 Ah L ⁻¹ .	[36]
1- Oxyfluorfen (spiked clay) 2- Sodium dodecyl sulphate (100 – 5000 mg L ⁻¹) and NaHCO ₃ (500 mg L ⁻¹)	AO and sono-AO	Continuous circulation (200 L h ⁻¹) of the effluent (1 L) in a flow-by cell using BDD anode and steel cathode (diameter = 10 cm). $I = 30 \text{ mA cm}^{-2}$ Auxiliary tank for irradiated experiments (24 kHz, 250 W L ⁻¹)	Complete degradation of oxyfluorfen at 25 Ah L ⁻¹ for AO and 40 Ah L ⁻¹ for sono-AO. >90% TOC removal at 30 Ah L ⁻¹ .	[42]
1- Lindane (spiked clay soil) 2- Sodium dodecyl sulphate (100 – 5000 mg L ⁻¹) and NaHCO ₃ (500 mg L ⁻¹)	AO	Continuous circulation (60 L h ⁻¹) of the effluent (1 L) in a flow-by cell using BDD anode and steel cathode (diameter = 10 cm). $I = 50 \text{ mA cm}^{-2}$	Complete degradation of lindane at 15 Ah L ⁻¹ or 80 Ah L ⁻¹ depending on extracting agent concentration.	[43]
1- Clopyralid 2- Synthetic groundwater	EF	Batch undivided cylindrical glass reactor (800 mL) with Pt anode (32 cm ²) and carbon felt cathode (112 cm ²). Continuous air bubbling. $[\text{Fe}^{2+}]_0 = 0.1 - 5 \text{ mM}$. pH = 3 $I = 50 - 300 \text{ mA}$	80% degradation of clopyralid, 30% mineralization and biodegradability increase after 480 min of treatment at 200 mA.	[44]
1- Phenanthrene (not a pesticide) 2- Cyclodextrin (9000 mg L ⁻¹)	EF and AO	Batch undivided cylindrical glass reactor (400 mL) with Pt, DSA or BDD anode and carbon felt cathode (150	Complete removal of degradation after 240 min at 500 mA for EF-BDD ($k_{\text{app}} = 0.012 \text{ min}^{-1}$) and 9% TOC removal.	[38]

		cm ²). [Na ₂ SO ₄] = 0.15 M. [Fe ²⁺] = 0.2 mM and air bubbling for EF. <i>I</i> = 500 - 2000 mA		
1- Phenanthrene or several PAHs (not pesticides) 2- Tween [®] 80 (6550 mg L ⁻¹)	AO	Batch undivided cylindrical glass reactor (400 mL) with BDD anode and stainless steel cathode (150 cm ²). [Na ₂ SO ₄] = 0.05 M. <i>I</i> = 2.1 - 42 mA cm ⁻²	Selective degradation of target pollutants. 75 – 90% removal of PAHs after 23 h at 2.1 mA cm ⁻² , while the extraction capacity was only 5% lower than the fresh one.	[40**]