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Emmanuel Mousset, Kyle Doudrick

► **To cite this version:**

Emmanuel Mousset, Kyle Doudrick. A review of electrochemical reduction processes to treat oxidized contaminants in water. *Current Opinion in Electrochemistry*, 2020, 22, pp.221-227. 10.1016/j.coelec.2020.07.008 . hal-02993274

**HAL Id: hal-02993274**

**<https://hal.science/hal-02993274>**

Submitted on 5 Dec 2020

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1 **A Review of Electrochemical Reduction Processes to Treat Oxidized**  
2 **Contaminants in Water**

3  
4 Emmanuel Mousset<sup>a\*</sup> and Kyle Doudrick<sup>b</sup>  
5

6 <sup>a</sup>Laboratoire Réactions et Génie des Procédés, UMR CNRS 7274, Université de Lorraine, 1 rue  
7 Grandville BP 20451, 54001 Nancy cedex, France

8 <sup>b</sup>University of Notre Dame, Department of Civil and Environmental Engineering and Earth  
9 Sciences, Notre Dame, Indiana 46556  
10

11 **Accepted version**

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13 **Current Opinion in Electrochemistry**  
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16 **\*Corresponding Author Address:**

17 Emmanuel Mousset, Laboratoire Réactions et Génie des Procédés, UMR CNRS 7274, Université de  
18 Lorraine, 1 rue Grandville BP 20451, 54001 Nancy cedex, France

19 Phone: 0033 3 72 74 37 44

20 e-mail: [emmanuel.mousset@univ-lorraine.fr](mailto:emmanuel.mousset@univ-lorraine.fr)

21 **Abstract**

22

23 This purpose of this review is to provide a short overview of electrochemical reduction processes for  
24 oxidized contaminants in water. The major parameters affecting the electro-reduction mechanisms and the  
25 impact of electrode choice are discussed with reference to both inorganic and organic pollutants that are  
26 either regulated or emerging (e.g., non-metal oxyanions, per- and polyfluoroalkyl substances (PFAS)). To  
27 conclude, a discussion is presented on the future directions and challenges that must be addressed to develop  
28 these electrochemical reduction processes at a larger, commercialized scale.

29

30

## 31 **Introduction**

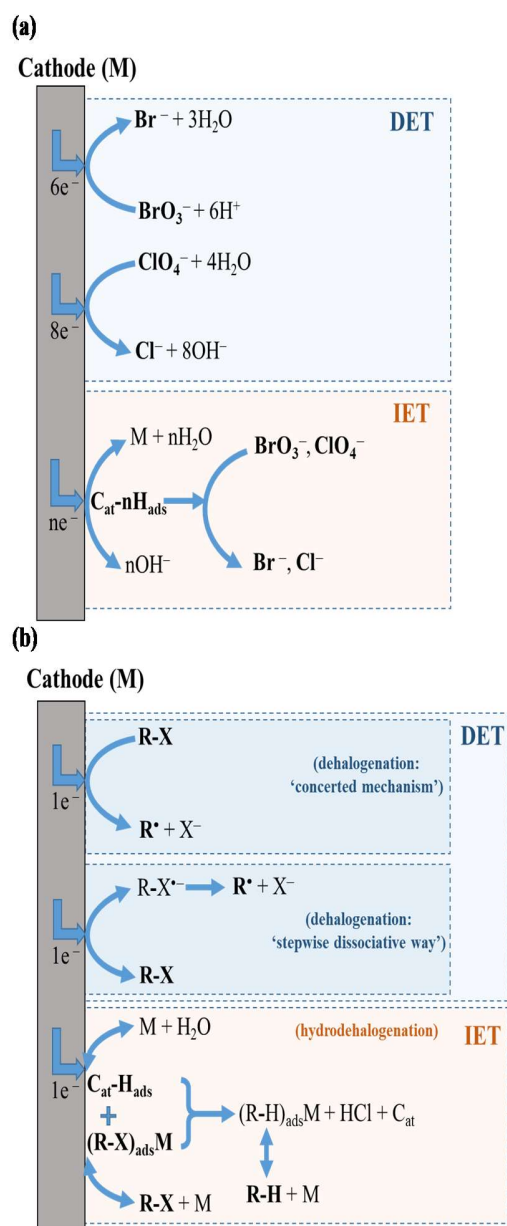
32 There are several emerging organic and inorganic contaminants in drinking water and wastewater that fall  
33 under a broad classification termed oxidized contaminants. These include, but are not limited to, oxyanions  
34 (e.g., nitrate), halogenated compounds (e.g., trichloroethylene), and nitrogenous compounds (e.g.,  
35 nitrosamines). While physical treatment processes such as reverse osmosis or ion exchange can separate  
36 the contaminant from the source water, they generate a highly concentrated brine waste that must still be  
37 treated. This leads to unnecessary costs and hazards. Chemical or biological treatment methods are more  
38 promising because they convert the contaminant, but due to the recalcitrant nature of many oxidized  
39 contaminants, even these may be insufficient. Biological processes (e.g., activated sludge) are typically  
40 used for wastewater treatment, but they are not efficient at treating bio-recalcitrant contaminants such as  
41 per- and polyfluoroalkyl substances (PFAS). Instead, the treatment of oxidized contaminants requires more  
42 sophisticated reduction processes that generate high energy electrons or reactive species.

43 Electrochemical reduction processes (ERPs) are an emerging treatment approach for oxidized  
44 contaminants. ERPs have many advantages over conventional reduction processes (e.g., chemical reduction  
45 using iron). ERPs can be operated at ambient temperature and pressure and there is no chemical addition  
46 required or waste production [1]. The reactors are easily customizable and a small footprint area can be  
47 maintained, which makes them the ideal for point-of-use treatment or to retrofit treatment plants constrained  
48 by size. Additionally, because the applied potential (i.e., thermodynamics and reactivity) can be controlled,  
49 high potential electrons can be generated, and the desired byproduct can often be selected.

50 In ERPs, electrons are transferred to the oxidized contaminant through a direct or indirect pathway. In a  
51 direct electron transfer (DET), electrons are transferred from the cathode to the oxidized contaminant that  
52 is adsorbed at the electrode-electrolyte interface. In an indirect electron transfer (IET), the electrons are  
53 transferred to the oxidized contaminant through an electron-shuttling mediator such as a catalyst or other  
54 adsorbed species. Wherein, the electrons are first transferred to the mediator, which then reacts with the  
55 contaminant and thus reduces the contaminant and oxidizes the mediator back to its original state. The  
56 processes can occur indefinitely, and the contaminant does not have to be bound to the electrode for  
57 reduction to occur.

58 In this review, we discuss the recent literature for the use of ERPs to treat oxidized contaminants present in  
59 drinking water and wastewater. As an advanced oxidation processes, electrochemical treatment processes  
60 have been one of the most studied [2,3]. By comparison, there has been a significantly smaller body of  
61 knowledge for ERPs. Reviews exist on the electrochemical reduction of specific oxidized contaminants  
62 such as organic halogenated compounds [4], nitrate [5], or perchlorate [6]. Instead, this review intends to  
63 provide a critical recent overview on prevalent compounds, either organic or inorganic, that align with  
64 current and emerging drinking water regulations (e.g., non-metal oxyanions, halogenated organics). There  
65 is a large body of work on the treatment of nitrate (and nitrite) oxyanions using ERPs [5], unlike the electro-  
66 reduction of bromate and perchlorate and its reduction byproducts (e.g. chlorate and chlorite). In parallel,  
67 the removal of organic halides (R-X) contaminants has been often considered by electro-reduction (e.g. 2,4-  
68 dichlorophenoxyacetic acid (2,4-D) [7,8], 2,4-dichlorobenzoic acid (2,4-DCBA) [9],  
69 hexachlorocyclohexane [10], chloropicolinic acids [11], chloroacetic acid [12], trichloroethylene [13],  
70 1,1,2,2-tetrachloroethane [14], PFAS [15], fluoroaromatic compounds [16]), due to their molecular  
71 structure that contains reducible groups (C-Cl, C-F). Therefore, this short review is focused on bromate,  
72 perchlorate, R-Cl, and R-F electro-reduction. Their main mechanisms of electro-reduction by either DET  
73 or IET are depicted in Fig. 1, based on literature (oxyanions: [17–21], organic halides: [7,8,11,13,16,22]).

74



75

76 **Fig. 1.** Schematic detailing the main electro-reduction mechanisms by either DET or IET of (a) oxyanions  
 77 ( $\text{BrO}_3^-$  and  $\text{ClO}_4^-$ ) and (b) organic halides ( $\text{R-X}$ ) compounds. M refers to the cathode material (i.e., the  
 78 catalyst ( $\text{C}_{\text{at}}$ ) or the support of catalyst), while  $\text{C}_{\text{at}}\text{-H}_{\text{ads}}$ ,  $(\text{R-X})_{\text{ads}}\text{M}$ , and  $(\text{R-H})_{\text{ads}}\text{M}$  are the hydrogen atom,  
 79  $\text{R-X}$ , and  $\text{R-H}$  compounds, respectively, adsorbed on the cathode material.

80

### 81 Major Parameters Influencing the Electrochemical Reduction Efficiency

82 The catalyst loading is crucial for the electrocatalytic efficiency. Generally, an increase in the catalyst  
 83 loading results in increased activity until a limiting amount is reached, at which point the activity either  
 84 steadies or decreases (i.e., volcano plot). When the catalyst loading is too high the substrate will contain  
 85 multiple catalyst layers and the effective number of active sites does not increase and electron transfer

86 distance to/from the electrode is increased [8]. In the case of nano-sized catalysts such as Pd, the particles  
87 will aggregate at higher loading, which results in excessive local H<sub>2</sub> evolution [20]. The accumulation of  
88 H<sub>2</sub> bubbles then restricts the diffusion and the access of the contaminant (e.g., bromate) towards the catalyst  
89 and substrate [20].

90 The thermodynamics and kinetics of an electroreduction reaction are controlled by the cathodic potential  
91 value. This potential is directly related to the current (i.e., Butler-Volmer). Generally, a reaction will have  
92 an optimal cathodic potential or current density. If the current density is too high, then an abundance of  
93 hydrogen bubbles from the hydrogen evolution reaction (HER) could retard the ability for oxidized  
94 contaminants to adsorb on the electrode due to mass transport limitation in the vicinity of the cathode [23–  
95 25]. In this scenario, mass transport becomes the rate-limiting step.

96 The water quality characteristics of the source are critical to the reduction efficiency and lifetime of the  
97 electrode. Generally, lower pH results leads to increased adsorb hydrogen atom (H<sub>ads</sub>) formation from the  
98 electro(catalytic) reduction of H<sub>2</sub>O at the cathode surface [26]. This increases the efficiency of electro-  
99 reduction reactions following an H<sub>ads</sub>-based mechanism [17,25]. Moreover, the pH also influences the  
100 molecular structure of R-X (e.g., pK<sub>a</sub> of functional groups, length of C-X bonds) and therefore their  
101 adsorption behavior due to modification of surface adsorption geometry and electrostatic  
102 attraction/repulsion [11]. The presence of certain ions and the ionic strength can also impact performance.  
103 An increased ionic strength will decrease the electric double layer at the cathode, making adsorption to the  
104 electrode easier. Further, ion adsorption to the cathode can modify the potential and the current at the  
105 electrode surface, which depends on the cathode properties [27]. For example, nitrate has been shown to  
106 drastically decrease the reduction rate of R-X, while the role of carbonate and chloride ions were negligible  
107 [28]. Additionally, reduced sulfur compounds can poison the Pd electrocatalyst through the formation of  
108 Pd sulfide, which impedes H<sub>ads</sub> adsorption [28]. The presence of dissolved organic matter can also inhibit  
109 electro-reduction, as observed for bromate [20].

110

### 111 **Importance of Electrode Selection on the Electro-Reduction Mechanism**

112 The electrode material (i.e., the substrate with or without a catalyst) plays a major role in the  
113 electro(catalytic) reduction mechanism. When using a catalyst, its support material may influence the  
114 electrochemical efficiency since it may change the electronic structure of the catalyst or influence the  
115 adsorption behavior of reducible compounds [11]. Table 1 shows the major electrode materials tested for  
116 electro-reduction of bromate, perchlorate, and organic halides. It is interesting to note that (bi)metallic-  
117 based, carbon-based, and metal/carbon-based materials have been tested for the electro-reduction of all  
118 these contaminants.

119 Metallic catalysts have been widely tested in ERPs. A good catalyst allows high bonding strength on the  
120 surface, which is related to the number of d-electrons of the metal [29]. Numerous monometallic metal  
121 catalysts have been tested for perchlorate reduction and the following order of perchlorate reduction rate  
122 has been observed: Cd>Pt>Cr>Mo>Sc>>Rh>Ru~Sn>Pd>V~Ti >Zn >Mn >Ni >Zr >Co >Cu >Pb) [29].  
123 The best catalytic activity for perchlorate reduction was given with Group VIII of transition metals over  
124 Groups I, IIB, and IV to VII from periodic table [29]. Numerous noble metals have been also tested for  
125 electrocatalytic hydrodechlorination such as Pd, Pt, Ru, and Rh, while Pd gave the best performance for its  
126 superior ability to adsorb atomic H<sub>ads</sub> for subsequent reduction [8]. Considering the dechlorination  
127 mechanism, it has been shown that among Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag cathode materials, Ag had  
128 the highest electrocatalytic activity for the electro-reduction of organic halides [30].

129 Bimetallic catalysts have shown synergistic effects compared to monometallic materials (e.g., increased  
 130 efficiency, reduced poisoning [31,32]. Adding In to a Pd catalyst improved the reduction of bromate,  
 131 depending on their respective proportion [33]. This enhancement was presumably due to the increase in  
 132 zeta potential of the Pd-In catalyst, which facilitated the adsorption of bromate before its reduction. Between  
 133 Rh, Pt, Ir, Ru, and Pd catalysts loaded onto different cathode metallic supports (Ni foam, Cu foam, Ag  
 134 mesh), Rh/Ni foam gave the best performance for hydrodefluorination, which could be due to the small  
 135  $Rh^{n+}/Rh^0$  ratio value of 0.66 [16]. The modification of bimetallic materials may also enhance the  
 136 electrocatalytic efficiency. Adding nano-sized titanium nitride (nTiN) on Pd/Ni foam increased the HER  
 137 and therefore increased the amount of electrogenerated  $H_{ads}$ , while the nanostructure provided an increase  
 138 in the number of active sites [8]. The introduction of anchored  $Ni(OH)_2$  catalyst on a Pd/Ni structure  
 139 increased the  $H_{ads}$  production and thus enhanced the dechlorination rate at low Pd loadings [7]. The low  
 140 cost and abundance of  $Ni(OH)_2$  and its superior ability to produce  $H_{ads}$  makes it an attractive alternative  
 141 over noble metals such as Pd [7]. The same trend could be observed with the intercalation of  $MnO_2$  between  
 142 an Ni foam substrate and Pd nanoparticles [9].  $MnO_2$  enhanced  $H_{ads}$  production, while Pd enhanced  $H_{ads}$   
 143 adsorption [9]. The synergetic effect increased the electrocatalytic activity while minimizing the required  
 144 Pd loading [9].

145 An alternative to expensive metallic materials is the development of carbon-based materials to enhance the  
 146 electrocatalytic activity. Bromate was reduced using polyaniline (PANI) coated on a glassy carbon material  
 147 through a reaction that involved the loss of electrons from nitrogen atoms of the PANI chains [34].  
 148 Alternatively, nanostructured copolymer poly(aniline-co-o-aminophenol) (PANOA) coated on glassy  
 149 carbon selectively adsorbed perchlorate when PANOA was polarized, which enhanced the subsequent  
 150 perchlorate reduction through an anion-exchange mechanism [35]. The glassy carbon material itself can  
 151 potentially electro-reduce organic halides, especially alkyl halides, which was partly due to its surface  
 152 properties [22]. However, modified carbon materials such as boron-doped diamond (BDD) have a  
 153 negligible activity for reducing organic halides compared to metallic materials [30]. Another way to  
 154 improve the catalytic activity of carbon materials is to combine a carbon nanostructure with metallic and  
 155 carbon/metallic electrodes. Reduced graphene oxide (rGO) sheets enhanced the electron transfer for a Pd  
 156 catalyst, which accelerated the  $H_{ads}$  formation and led to a faster indirect bromate reduction by  $H_{ads}$  [20].  
 157 The same trend was observed for Pd/rGO coated on carbon fiber paper [25].  
 158

159 Thus, numerous efforts have been made to develop advanced electrode materials to enhance the  
 160 electrocatalytic reduction. In this context, the stability and long-term use of the materials are important to  
 161 be assessed for practical applications. For example, after five successive cycles using a nTiN/Pd/Ni foam  
 162 electrode, the metallic catalyst was enriched by hydrogen, resulting in swelling and pulverization of the  
 163 metal-hydrogen system [28]. The interaction between materials in advanced composite materials must be  
 164 maximized to increase the life span of electrode materials. For a Pd/rGO/CFP composite electrode, the  
 165 stability was enhanced through strong interaction between surface oxides of rGO and Pd, resulting in a  
 166 constant reduction efficiency over ten cycles; however, the efficiency decreased after 20 cycles [25].

167 **Table 1.** Main electrode materials tested for electro-reduction of bromate, perchlorate and organic  
 168 halides.

Electrode materials tested	Bromate	Perchlorate	Organic halides
<b>Monometallic</b>			
Pt		X ([36])	X ([30])
Zn		X ([18])	X ([30])
Sn		X ([37])	X ([30])
Bi			X ([30])

Pb		X ([29])	X ([30])
Au			X ([30])
Cu		X ([29])	X ([30])
Ag			X ([10], [12], [14], [30])
Cd		X ([29])	
Cr		X ([29])	
Co		X ([29])	
Mo		X ([29])	
Mn		X ([29])	
Sc		X ([29])	
Pd		X ([29])	
V		X ([29])	
Zr		X ([29])	
Ni		X ([38])	
Ti		X ([39], [40])	
Ir		X ([41])	
Rh		X ([42], [43])	
Ru		X ([44])	
Re		X ([45])	
<b>Bimetallic</b>			
Pd/In	X ([33])		
Rh/Cu		X ([46])	
Rh/Ru		X ([46])	
Ag/Cu			X ([13])
Rh/Ni foam			X ([16])
Pt/Ni (foam)		X ([38])	X ([16])
Pd/Ni foam			X ([8], [9], [11], [16])
<b>Modified bimetallic</b>			
Pd-anchored Ni(OH) <sub>2</sub> /Ni			X ([7])
Pd/MnO <sub>2</sub> /Ni foam			X ([9])
nTiN-Pd/Ni foam			X ([8])
<b>Metal/metal oxide-carbon composites</b>			
WC		X ([47])	
Pd/rGO/CFP	X ([25])		
graphene-modified Pd/C	X ([20])		
Pd/GAC particles	X ([20])		
Nanoscale zero valent Fe (nZVI)/activated carbon fiber	X ([17])		
<b>Carbon</b>			
Glassy carbon			X ([30], [22])
Compact graphite			X ([12])
<b>Modified carbon</b>			
Surfactant/carbon nanotubes (CNT) nanostructured PANOA/glassy carbon		X ([35])	X ([15])
PANI/glassy carbon	X ([34])		
<b>Metalloid/carbon</b>			
BDD			X ([30])



## 170 **Emerging process combinations for enhancement of removal efficiency**

171 Some promising combinations between ERPs and other treatment processes have been suggested to further  
172 improve the removal efficiency.

173 The recent synergistic combination of ultraviolet (UV) light with electro-reduction by DET showed  
174 promising removal efficiency of PFAS, while minimizing the energy requirement [15]. The hypothesis was  
175 that the DET increased the PFAS adsorption efficiency on the surfactant modified-carbon nanotubes (CNT)  
176 cathode and lowered the activation energy of the C-F bond under low potential conditions, while the UV  
177 produced hydrated electrons that cleaved the C-F bond [15].

178 The combination of ERPs with advanced electro-oxidation involving high overvoltage O<sub>2</sub> evolution using  
179 a BDD anode has been proposed in undivided cells. BDD permits the electro-generation of hydroxyl  
180 radicals (<sup>•</sup>OH) that have a high oxidation power [48]. The removal of 1,1,2,2-tetrachloroethane [14] and  
181 chloroacetic acid [12] in this hybrid reactor showed considerable enhancement. The ability of oxidized  
182 contaminant elimination by electro-oxidation has been highlighted in a recent paper that evidence the  
183 oxidation mechanism involving <sup>•</sup>OH with perhalogenocarbon compounds (e.g., CCl<sub>4</sub>) having very high  
184 oxidation state [49]. This oxidation pathway was supplemental to the indirect reduction of such compounds  
185 by superoxide ion (O<sub>2</sub><sup>•-</sup>). It further emphasized the possible degradation of PFAS by <sup>•</sup>OH. However, such a  
186 combination needs to avoid the re-oxidation of reduced oxyanions or reduced organohalogenated  
187 byproducts, otherwise the oxidation state will remain the same and there will be no elimination.

188 Another interesting feature is the combination of electro-reduction with biological processes. A late study  
189 proposed the removal of adsorbable organic halogens (AOX) by combining dehalogenating bacteria using  
190 AOX as terminal electron acceptors in their metabolism with electrolysis in a hybrid bioelectrochemical  
191 process [50]. The electrochemically-assisted bioprocess improved the organohalogenated compounds  
192 removal while the decrease of cathodic potential was favorable for methane production. Still, improvements  
193 are needed to increase the coulombic efficiency and the scalability.

## 194 **Conclusions and Future Outlook**

195 This brief review depicts the potential of ERPs to treat primary and emerging oxidized contaminants in  
196 water. There are still some challenges to overcome to commercialize these technologies and bring them to  
197 full scale, including reducing the cost of electrodes, increasing the stability of modified electrodes, reducing  
198 the formation of unwanted byproducts, increasing the process efficiency in real waters, reducing the energy  
199 requirements, and increasing the treatment capacity.

200 The price of electrodes is usually high in the overall cost of ERPs since noble metals are often used to  
201 increase the selectivity and activity; however, some studies have shown that cheaper materials such as  
202 carbon or nickel could also be efficient. Further progress is needed to improve the cathode surface properties  
203 of cheap supports and catalyst materials. Moreover, the electro-reduction efficiency and the possible  
204 formation of intermediates must be assessed in real matrices, since many existing studies focus only on  
205 ultrapure systems. Other constituents in the water are likely to reduce efficiencies and induce fouling and  
206 poisoning of the electrodes. The energy consumption could be minimized by implementing thin film  
207 electrochemical reactors with micro-distances between electrodes as previously suggested [12]. However,  
208 the treatment capacity in such a configuration is lower than in macro-reactors. Thus, improvements in  
209 overall electrochemical reactor design and modeling is needed for scale-up.

210 Another treatment strategy is the possible valorization of the so-called “pollutants” by making them a source  
211 of formation of highly added-value compounds (i.e., waste-to-value). The combination of electro-reduction  
212 with electro-synthesis would be promising for treating the wastewater while upgrading the effluent content  
213 for subsequent promotion. The electrochemical dehalogenation of cyclopropane derivative for drug

214 synthesis has primary shown interesting opportunities [51,52] and could be adapted for the valorization of  
215 water content.

216 **Acknowledgments**

217 Kyle Doudrick acknowledges the U.S. Fulbright Scholar Program, in collaboration with the Reactions and  
218 Chemical Engineering Laboratory (LRGP), a joint unit of French National Center for Scientific Research  
219 (CNRS) and University of Lorraine in Nancy, Grand-Est, France.

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223 **References**

224

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389 **Annotations regarding references with special interest (\*) or outstanding interest (\*\*):**

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391 \*[5] →A complete review covering the electrochemical reduction of nitrate, including reaction  
392 mechanisms and pathways, nano-enabled electrodes, combined technologies, and future directions  
393 and scale-up.

394 \*[7] →This research paper proposes the use of a bifunctional cathode using nickel hydroxide that  
395 reduces the need for expensive noble metal catalysts like Pd.

396 \*\*[15] →This research paper describes one of the first successful electro-reduction (i.e.  
397 defluorination) strategies for perfluorooctanesulfonic acid. Electrochemistry is combined with  
398 direct photolysis and adsorption (to carbon nanotubes) for energy efficient reduction to shorter-  
399 chain perfluoroalkyl acids.

400 \*[17] →This research paper proposes a new electrode for bromate electro-reduction using earth  
401 abundant elements, iron and carbon.

402 \*[49] →This research article propose a new mechanism of action for perhalogenocarbon oxidation  
403 by OH radicals in parallel to their reduction by superoxide ion. This novel feature enlarges the  
404 possible treatment of PFAS by both ERPs and electro-oxidation processes.