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1 **Recent advancements in peroxicoagulation process: An updated review**

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13

14 **Abstract**

15 The present article describes the recent advancements (since 2018) in peroxicoagulation (PC)
16 process, which was introduced by Professor Enric Brillas and his group in 1997. Instead of
17 checking the efficiency of PC process to degrade a targeted pollutant in synthetic wastewater,
18 researchers started testing its efficacy for the treatment of complex real wastewater.
19 Applications like disinfection and removal of heavy metals as well as oxidative removal of
20 arsenite from water were tested recently. To improve the efficiency of PC process,
21 modifications were made for electrode materials (both anode and cathode) and electrolytic
22 cells. Performance of PC process in combination with other treatment technologies is also
23 discussed.

24 **Keywords:** Peroxicoagulation; Electro-Fenton; Electrocoagulation; Hydroxyl radical;
25 Electrochemical Advanced Oxidation Processes

26 1. Introduction

27 Peroxicoagulation (PC) process is a combination of a well-known electrochemical
28 advanced oxidation process, namely electro-Fenton (EF) process, with an electrochemical
29 separation process, known as electrocoagulation process (EC). With this coupling, PC process
30 inherited most of the advantages of EC and EF technologies as shown in **Fig. 1** (Nidheesh et
31 al., 2021, 2018). PC system allows generating hydrogen peroxide (H_2O_2) (**Eq. 1**) and
32 subsequently hydroxyl radicals ($\cdot OH$) via Fenton reaction (**Eq. 2**), which is a property of EF
33 process.



36 By generating radicals with higher oxidation potential, PC process is able to mineralize
37 recalcitrant organic pollutants, enhance biodegradability and reduce toxicity. PC and EC
38 technologies also behave similarly. They are able to neutralize the solution from its initial pH,
39 which gives an additional advantage to PC system.

40 In general, either iron or steel can be used as anode for PC process, while a
41 carbonaceous cathode should be required for the electrolytic generation of H_2O_2 (**Eq. 1**).
42 Ferrous ions are generated in this electrolytic system via electro-dissolution of iron or stainless
43 steel anode. With the continuous iron dissolution and pH neutralization, floc is formed and the
44 pollutants (including byproducts generated by the attack of radicals) in the electrolytic system
45 will be removed either via adsorption and charge neutralization mechanism or enmeshment in
46 precipitate mechanism. To improve the mineralization efficiency of PC process, pH regulated
47 PC process is also proposed (Nidheesh and Gandhimathi, 2014; Venu et al., 2014).

48 The roadmap of PC process is shown in **Fig. 2**. PC process was initially reported by Prof.
49 Enric Brillas' group in 1997 (Brillas et al., 1997). After that, researchers (Mainly from Brillas

50 group) explored the performance of PC process for the removal of various targeted compounds
51 including aniline (Brillas and Casado, 2002), 4-chlorophenoxyacetic acid (Brillas et al.,
52 2003b), 4-chlorophenoxyacetic acid (Brillas et al., 2003a), 4-chloro-2-methylphenoxyacetic
53 acid (Boye et al., 2003a), 2,4,5-trichlorophenoxyacetic acid (Boye et al., 2003b), 3,6-dichloro-
54 2-methoxybenzoic acid (Brillas et al., 2003a), and basic yellow 2 (Salari et al., 2009). This can
55 be considered as the first stage of PC process and meanwhile, a review describing PC process
56 was published in 2009 (Brillas et al., 2009). Further in 2014, Gandhimathi's group reported the
57 PC process application for the treatment of real wastewater including leachate (Venu et al.,
58 2014) and textile wastewater (Nidheesh and Gandhimathi, 2014). A detailed review exclusively
59 describing PC systems was published in 2018 (Nidheesh, 2018), pointing out the end of the
60 second stage (2014-2018), in which researchers focused on the treatment of real wastewater,
61 in addition to the targeted pollutants.

62 The present review is focusing on the improvements made in PC technologies since
63 2018. Various advancements, including emerging applications such as disinfection and
64 removal of inorganic ions, various modified anodes and cathodes used as well as various
65 reactor designs are presented in detail. The performance of PC system in combination with
66 other processes is also discussed.

67

68 **2. Performance of PC process**

69 In recent years, PC process has emerged as a viable method for the removal of water
70 pollutants such as organic contaminants (do Vale-Júnior et al., 2018; Kumar et al., 2018; Ren
71 et al., 2018; Sandhwar and Prasad, 2018; Treviño-Reséndez et al., 2023), landfill leachate (Liu
72 et al., 2022), industry wastewater (Zazou et al., 2019; Zhou et al., 2020a, 2020b) and laundry
73 wastewater (Nayir et al., 2020). Degradation performance of PC was compared with single

74 process such as EF, EC or anodic oxidation. The results highlighted the higher efficiency of
75 Fenton's based process due to the higher amount of $\cdot\text{OH}$ present in EF and PC (do Vale-Júnior
76 et al., 2018; Liu et al., 2022). In addition, PC requires less energy consumption per pollutant
77 removal compared to the single process (Zazou et al., 2019). Based on the efficiency level and
78 economic reasons such as operating cost, the PC process can be considered as a promising and
79 appropriate technology for water and wastewater treatment that allows the reuse of treated
80 water for other purposes.

81 The efficiency of $\cdot\text{OH}$ and coagulant electrochemical production depend on various
82 factors, including pH, current density, supporting electrolytes, wastewater characteristics,
83 operating time, etc (do Vale-Júnior et al., 2018). Several investigations have been carried out
84 to increase the efficiency by optimizing the operating parameters to facilitate the application
85 of this process at the industrial level. Among these factors, pH is one of the most important
86 parameters governing the production of reactive oxygen species and hydrolyzed metal species
87 and hence determines the degradation and coagulation mechanisms (Nayir et al., 2020). In
88 reported works, performance is expressed in terms of initial pH because pH tends to change
89 throughout the PC process. The influence of pH depends on the type of pollutants due to the
90 competition of oxidation and coagulation. Many reports have confirmed that $\cdot\text{OH}$ and iron
91 hydroxides are highly produced at acid and neutral pH, respectively (Nayir et al., 2020;
92 Sandhwar and Prasad, 2018). Almost all studies reported that pH 3.0 is the optimal solution pH
93 for the degradation of organic pollutants in PC process (do Vale-Júnior et al., 2018; Kumar et
94 al., 2018; Zazou et al., 2019; Zhou et al., 2020a). However, Ren et al. reported a different
95 optimum pH showing the importance of the type of pollutants in PC process (Ren et al., 2018).
96 pH 7.0 was selected as the optimum for the removal of acrylonitrile and pH 5 for the removal
97 of TOC in leachate concentrate, suggesting PC had a wider range of pH compared to other
98 electrochemical technologies (Ren et al., 2018).

99 In the PC process, the amount of hydroxyl radical and dissolved metal ions produced
100 depends also on the applied current density. By increasing the current density up to a certain
101 value, the removal efficiency increases due to the formation of more iron hydroxide and the
102 production of more hydrogen peroxide leading to the formation of more $\cdot\text{OH}$ radical (Treviño-
103 Reséndez et al., 2023). However, the increase of current density above the optimum value led
104 to the decrease of removal efficiency due to the side parasitic reactions such as the reaction of
105 hydroxyl radical with an excess of Fe^{2+} (**Eq. 3**) and the reaction of H_2O_2 with Fe^{3+} produced in
106 previous reactions (**Eq. 4**) (do Vale-Júnior et al., 2018; Nayir et al., 2020). Therefore, current
107 density may enhance or disfavor PC process and the proper selection of current density depends
108 on the removal efficiency and energy cost (Zhou et al., 2020a). Lui et al. reported an increase
109 in energy consumption per unit TOC mass removal from $5.8 \pm 0.9 \text{ kWh (g TOC)}^{-1}$ to $64.4 \pm$
110 $1.20 \text{ kWh (g TOC)}^{-1}$ by increasing the current density from 2.5 mA cm^{-2} to 15 mA cm^{-2} for
111 almost the same TOC removal (Liu et al., 2022). Thus, the optimal current density depends on
112 the removal rate and energy cost.

113 Another important parameter is the initial pollutant concentration which provides the
114 range of pollutants concentration that can be efficiently treated by PC. The increase of initial
115 pollutant concentration in PC led to a decrease in removal efficiency (do Vale-Júnior et al.,
116 2018; Ren et al., 2018). Compared to other processes, PC can remove more pollutants due to
117 the combined action of generated $\cdot\text{OH}$ and formed $\text{Fe}(\text{OH})_3$ (Ren et al., 2018). Therefore, the
118 PC process can be a potential candidate to be used as the pretreatment of highly concentrated
119 pollutants.



122 As expected, PC performance has been boosted by the synergetic effects, which allow
123 efficient treatment of complex and refractory wastewater. Notwithstanding, improvement in
124 the following points is needed for its application at the industrial level: (i) explore the involved
125 mechanisms in the synergetic effects in PC process based on experimental and theoretical
126 methods to clarify the predominant mechanism for its optimization and (ii) the problem of
127 sludge disposal and high operational cost need to be reduced due to its great significance.

128

129 **3. Technical updates**

130 **3.1. Ferryl ion formation**

131 Ferryl ion formation during PC process was reported recently during the removal of
132 arsenic from water medium (Bandaru et al., 2020; Nidheesh et al., 2020; Si et al., 2017). Even
133 though ferryl ion is more selective and weaker than $\cdot\text{OH}$, this oxidant is able to oxidize organic
134 compounds through one-electron and two-electron pathways such as electron transfer,
135 hydrogen atom transfer, oxygen atom transfer, and hybrid transfer (He et al., 2016; Mártire et
136 al., 2002). Fenton reaction is one of the routes of ferryl ion generation. It has been observed in
137 heterogeneous Fenton process through the reaction between surface-bounded ferrous ion and
138 hydrogen peroxide (Gonzalez-Olmos et al., 2011). Ferryl ion production during Fenton
139 reactions was first proposed by Bray and Gorin (Bray and Gorin, 1932) (**Eqs. 5 and 6**). Bandaru
140 et al. (Bandaru et al., 2020) and Si et al. (Si et al., 2017) proposed similar reactions for the
141 generation of ferryl ions during PC process. These reactions occur in PC system at acidic
142 conditions as *in-situ* H_2O_2 generation is also depending on proton ion concentration. However,
143 Nidheesh et al. (Nidheesh et al., 2020) observed oxidation of arsenite even at alkaline pH, at
144 which formation of hydrogen peroxide and hydroxyl radicals is negligible. The authors
145 proposed the formation of ferryl ions by the reactions between ferrous ion and oxygen, as in

146 the case of aerated iron EC process (Syam Babu et al., 2021). However, the contribution of
147 ferryl ions during PC oxidation of organic pollutants is not yet checked.



150 **3.2. Importance of dissolved oxygen and initial pH**

151 Solution pH plays an important role in the performance of all electrochemical
152 processes. Pollutant removal mechanism of PC process is also depending on the solution pH
153 as particularly highlighted experimentally by Venu et al. (Venu et al., 2016). EF process
154 dominates in acidic conditions and the pollutants are degraded in these conditions during PC
155 oxidation (Nidheesh and Gandhimathi, 2014). In neutral and alkaline conditions, EC process
156 is predominant in PC process and the pollutants are removed from water medium by
157 separation. Similar results were observed by Leng et al. (Leng et al., 2022) for the removal of
158 coumarin. Production of 7-hydroxycoumarin, the hydroxylated product of coumarin, is higher
159 in solution pH below 4 and was significantly lesser at pH higher than 4. The 7-
160 hydroxycoumarin production is also enhanced with an increase in dissolved oxygen content,
161 which indicates the importance of aeration during PC process.

162 The effects of dissolved oxygen and pH on $\cdot OH$ production and floc generations during
163 PC process are displayed in **Fig. 3** (Leng et al., 2022). It was found that EF to EC conversion
164 takes place at pH between 3 and 4, while the conversion rate is also depending on the dissolved
165 oxygen conditions. For example, even at pH 3-4, EC predominates in PC process at anaerobic
166 conditions. However, EC predominates in PC process at pH above 4 whatever the dissolved
167 oxygen content. At the same time, the oxygen levels during PC system also affect the type of
168 floc generation. At higher dissolved oxygen concentrations ($> 22 \text{ mg L}^{-1}$), FeOOH formation
169 predominates, while magnetite and green rust formations are predominant at medium content

170 and anaerobic conditions, respectively (Leng et al., 2022). These observations are in
171 agreement with the observations made by Dubrawski et al. (Dubrawski et al., 2015) for aerated
172 iron EC process. However, it was reported by Dubrawski and co-workers that magnetite
173 formation is predominant in the absence of dissolved oxygen. Magnetite synthesis methods
174 like sol–gel, thermal decomposition, co-precipitation, microemulsion etc. are promoted under
175 anaerobic conditions (Niculescu et al., 2022), which validates the observations made by
176 Dubrawski et al. (Dubrawski et al., 2015). Another contradictory observation in the article
177 reported by Leng and co-workers (Leng et al., 2022) is related to the dissolved oxygen
178 concentration. It was reported to keep dissolved oxygen levels above 22 mg L⁻¹ for the
179 production of FeOOH flocs. At standard conditions and at 0 °C, the saturated dissolved
180 oxygen level is found to be around 15 mg L⁻¹ and it decreases with the temperature. However,
181 the procedure to keep the dissolved oxygen levels in PC process above 22 mg L⁻¹ is not
182 described in the article.

183 **3.3 Modifications in anode**

184 As previously explained in this review, the anode material plays a significant role since
185 it represents the source of iron for EC implementation (Alagesan et al., 2021; Garcia-Segura et
186 al., 2017) as well as for subsequent reaction with H₂O₂ electrogenerated at the cathode (i.e.
187 Fenton reaction). Most of the time iron plate materials have been used as anode materials in
188 PC processes (Casado, 2019; Nidheesh, 2018; Ren et al., 2018). Recently, more advanced
189 anode materials have been proposed based on the magnetically assembled electrodes (MAEs)
190 concept (Rao et al., 2022). It is made up of microscale zero-valent iron particles (mZVI)
191 (auxiliary electrode) tightly bonded to a conductive substrate (main electrode) by a magnetic
192 field. Three kinds of substrates have been tested, namely graphite, dimensionally stable anode
193 (DSA), and boron-doped diamond (BDD) plates (Rao et al., 2022). DSA is known to favor
194 chlorine evolution and therefore the formation of Cl[•] and active chlorine radical (ClO[•]) that

195 could enhance the COD removal efficiency (65% removed after 2 h) during PC (PC-
196 mZVI/DSA) process, as shown in **Fig. 4a**. In a similar way, BDD is known to favor the $\cdot\text{OH}$
197 generation due to the high O_2 evolution overvoltage (Mousset, 2022), which could outperform
198 during PC (PC-mZVI/BDD) in terms of COD decay (90% removed after 2 h) compared with
199 the other anode materials (**Fig. 4a**). Comparatively, typical iron plates underachieved for both
200 COD elimination (**Fig. 4a**) and total iron consumption (**Fig. 4b**).

201 For a more global comparison, it is also important to consider the costs of electrode
202 materials and energy consumption (Mousset et al., 2021). BDD-based PC process was
203 downgraded due to the high cost of BDD material compared to DSA, graphite, and iron plate
204 (**Fig. 4b**). PC-mZVI/DSA was finally identified as the most cost-effective process for the
205 simultaneous removal of COD, ammonia, and phosphates (Rao et al., 2022). The material
206 stability remains to be tested, knowing that the high anode potential required for radicals
207 generation could drastically reduce the lifetime of modified electrodes.

208 **3.4 Modifications in cathode**

209 The cathode material has a primordial role in PC process to provide H_2O_2 for
210 subsequent reaction with iron(II) for $\cdot\text{OH}$ generation. New recent cathodes have been proposed
211 to improve the PC efficiency, based on modifications of carbon substrate materials that are
212 typically used due to their low H_2 evolution overvoltage (Adnan et al., 2022; Brillas et al.,
213 2009; Mousset et al., 2016a). Thus, graphite felt modified with carbon black and
214 polytetrafluoroethylene (PTFE) (M-GF) (Ren et al., 2018), graphene-coated on graphite felt
215 (Ren et al., 2019), graphite felt doped with carbon (C) powder, nitrogen (N) and boron (B)
216 (Ding et al., 2020), and natural air diffusion electrode (NADE) (Li et al., 2021b) could
217 effectively remove acrylonitrile, organics in coking wastewater, dimethyl phthalate and 2,4-
218 dichlorophenoxyacetic acid, respectively. The graphene-doped graphite material could increase
219 the O_2 reduction activity towards H_2O_2 production by reaching 160 mg L^{-1} of H_2O_2 , while

220 removing around 70% of COD in coking wastewater (**Fig. 5a**) (Ren et al., 2019). As a 2D
221 material, graphene is known to increase the active surface area of the material as well as its
222 conductivity, which can raise the H₂O₂ yield (Du et al., 2021; Le et al., 2015; Mousset et al.,
223 2016b). This led to lower specific energy requirements using graphene-based material (0.15
224 kWh kg-COD⁻¹) compared to EC (3.4 kWh kg-COD⁻¹), EF (6.9 kWh kg-COD⁻¹), and ozonation
225 (7.5 kWh kg-COD⁻¹) (Ren et al., 2019).

226 The modification of graphite with N and B was further shown to favor the catalytic
227 activity towards the H₂O₂ electrogeneration (**Fig. 5b**) and therefore the PC efficiency to
228 completely eliminate dimethyl phthalate in 60 min (Ding et al., 2020). N and B are known to
229 involve a dipole with C, which increases the O₂ adsorption onto the cathode for its subsequent
230 reduction (Ding et al., 2020; Du et al., 2021; Mousset et al., 2017). N can also promote the
231 charge redistribution to increase O₂ adsorption, while B can favor the O-O bond cleavage for
232 H₂O₂ electrogeneration (Ding et al., 2020).

233 An alternative material, namely NADE, was recently proposed to overcome the need
234 for air/O₂ supply to generate H₂O₂ (Li et al., 2021b). This cathode has a superhydrophobic
235 three-phase interface which permits the natural diffusion of oxygen without external energy
236 requirement typically used to pump air through the gas diffusion layer (Zhang et al., 2020).
237 This led to a high H₂O₂ production rate (102 mg h⁻¹ cm⁻²) (Zhang et al., 2020). It has been
238 shown that NADE implemented in PC could outperform the M-GF material, with 79% (12
239 kWh kg-TOC⁻¹) against 65% (20 kWh kg-TOC⁻¹) of TOC removal respectively (**Fig. 5c**), due
240 to higher O₂ transfer and adsorption (Li et al., 2021b). By considering the fact that no aeration
241 device is required with NADE, it was 36 times more cost-efficient than the PC operated with
242 modified graphite felt.

243 Though a few cathode lifetime tests have been proposed in the literature (Ren et al.,
244 2019), there is a need for accelerated lifetime test development for a more accurate estimation
245 for real applications, while this should be applied systematically to all new materials proposed.

246 **3.5 Modifications in reactor design**

247 In hybrid systems like PC, the reactor design is particularly important (Mousset and
248 Hatton, 2022). There is a need to favor both electro-separation (EC) and electro-conversion
249 (electro-oxidation/reduction) within the same reactor (Mousset and Hatton, 2022). Recently,
250 the multi-stage flow-through PC system (Ren et al., 2019), the dual-cathode PC process (Zhang
251 et al., 2022), and the self-powered PC combined with fuel cell (PCFC) (Ni et al., 2020) have
252 been suggested in the literature.

253 The successive stages implemented in PC system could increase the removal yield, with
254 COD effluent decreasing from 1800-1900 mg-O₂ L⁻¹ (first stage) to 1200-1300 mg-O₂ L⁻¹ in
255 second stage and 800-900 mg-O₂ L⁻¹ at the third step (**Fig. 6a**). This corroborates the
256 electrochemical engineering theory that highlights the rise of conversion yield with the increase
257 of the number of reactors in series (Coeuret and Storck, 1984; Newman and Balsara, 2021;
258 Walsh and Ponce de León, 2018).

259 For reducing the iron sludge formation and enhancing the degradation of organic
260 contaminants, the possibility to set up a dual-cathode system has been recently explored (Zhang
261 et al., 2022). It consisted of the following cathode/anode combinations: NADE/DSA for H₂O₂
262 electrogeneration and modified carbon felt (MCF)/Fe for iron source regeneration. This novel
263 configuration could increase drastically the kinetics of sulfamethazine removal, with a quasi-
264 complete removal after 60 min, while only around 5% was degraded at the equivalent treatment
265 time with a single system (i.e., NADE/DSA or MCF/Fe) (**Fig. 6b**) (Zhang et al., 2022).

266 The energy requirement in electrolytic technologies can hamper their development at
267 an industrial scale. Therefore, many efforts have been made to develop self-powered devices
268 to drastically decrease global energy consumption (Ganiyu and Martínez-Huitle, 2020). The
269 combination of PCFC combination is a recent solution proposed that permit to use the power
270 generated in a fuel cell (from 50 (pH 6) to 100 mW m⁻² (pH 3) (**Fig. 6c**)) in the PC process. At
271 maximum power density, the quasi-complete removal of p-arsanilic acid could be reached in
272 15 min, against 40 min in EC process (Ni et al., 2020).

273 An alternative to decrease the energy requirement while reducing the consumption of
274 iron coagulant is the pulsed switching method. This technique consists of alternating on-off the
275 power supply at a given frequency. A pulsed switching frequency of 1:0.3 s ratio (i.e., H₂O₂
276 generation:Fe²⁺ production) gave the minimal specific energy (around 140 kWh kg⁻¹ •OH) (**Fig.**
277 **6d**), leading to two-times lower residual TOC compared to conventional PC after 4 h of
278 treatment (Lu et al., 2018).

279 A flexible design, namely a reactive electro-mixing system, could be further tested, as
280 it combines the advantages of micro-reactors (lower energy requirement, increase of redox
281 kinetics, intensification of mass and charge transfers) with macro-reactor (higher treatment
282 capacity) (Mousset, 2020). This permit to involve multiple electro-processes simultaneously
283 within the same reactor, which could give synergy for electro-separation/conversion hybrid
284 systems such as PC.

285

286 **4. Recent applications**

287 **4.1. Removal of inorganic ions**

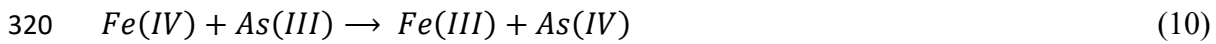
288 EAOPs are famous for removing recalcitrant organic compounds through its
289 mineralization. PC technology featured an additional advantage because it is able to remove

290 inorganic ions present in the water mainly through EC process. It is well known that EC is
291 more efficient for the removal of inorganic ions through adsorption and charge neutralization
292 as well as sweep floc coagulation mechanisms (Nidheesh et al., 2022b). At the same time,
293 inorganic ion removal efficiency of PC process from landfill leachate is found much better than
294 EC process (Liu et al., 2022). The authors tested the heavy metal and metalloid removal
295 efficiencies of PC, EC, and EF by considering five heavy metals (Ni, Cr, Mn, Pb, and Cu) and
296 two metalloids (As and Sb) present in the landfill leachate. The efficiencies of electrochemical
297 treatments were compared at pH 3 and 8. The EF performance was found significantly lower
298 than PC and EC in most of the tested conditions. In the meantime, PC performs better than EC
299 in 10 out of 14 cases, while both have similar efficiencies in the remaining 4 cases. The superior
300 performance of PC system may remain in the higher production of ferric hydroxides in the
301 presence of oxidants such as $\cdot\text{OH}$ and H_2O_2 (Si et al., 2018).

302 The solution pH also plays a crucial role in heavy metal removal efficiency during PC.
303 In general, heavy metal removal is predominant in alkaline conditions and the same trend was
304 followed in the case of PC process. However, Cr removal was found better in acidic conditions
305 due to the reduction of Cr(VI) to Cr(III), which rise remarkably the kinetics of elimination (Liu
306 et al., 2022). The authors didn't find any significant difference in the metalloid removal
307 efficiencies of PC process at pH 3 and 8 (Liu et al., 2022).

308 Removal of arsenite is a challenging task as it will be in its non-ionic form at pH less
309 than 8 and its oxidation is essential for its effective removal (Nidheesh et al., 2022a). Anodic
310 oxidation and EF are effective for the oxidation of arsenite, while both processes are not able
311 to remove arsenate from water (Nidheesh et al., 2020). Contrastingly, PC is able to oxidize
312 arsenite and is able to remove arsenate from water at pH in the range of 3 to 11 (Nidheesh et
313 al., 2020). *In-situ* generated oxidants such as H_2O_2 , ferryl ion and $\cdot\text{OH}$ are responsible for the
314 oxidation of arsenite (**Eqs. 7-10**), while ferryl ion is the superior oxidant responsible for

315 arsenite oxidation at pH above 6. This is because protons are required for the generation of
316 H₂O₂ and •OH in the electrolytic system, while its concentration is negligible at pH above 6.



321

322 **4.2. Disinfection**

323 Electrochemical disinfection is an emerging field in the area of water and wastewater
324 treatments (Bruguera-Casamada et al., 2019; Martínez-Huitle and Brillas, 2021; Srivastava et
325 al., 2021). EF and electro-PC processes (H₂O₂ added externally) are found effective for the
326 inactivation and degradation of *E. coli*. (Kourdali et al., 2018). The efficiency of both processes
327 is much better than that of the EC process. Reactive oxidants are the main agents responsible
328 for the degradation of microorganisms. This is further improved by the addition of NaCl and
329 Na₂SO₄ as supporting electrolytes, due to the additional radical generation (i.e., sulfate and
330 chloride radicals, respectively). Microbial inactivation by electrochemical methods is due to
331 (Gheraout et al., 2019; Martínez-Huitle and Brillas, 2021): (1) oxidative stress and cell loss
332 caused by reactive oxygen species; (2) irreversible permeabilization of cell membranes by the
333 applied electric field; (3) adsorption of microorganisms on anode surface (microorganisms are
334 negatively charged) and direct electron transfer reaction; and (4) vital cellular constituents
335 damage caused by the electric field. Even though electrochemical disinfection is effective, it is
336 not advisable for water treatment as the process is not able to provide residual protection. Apart
337 from that, disinfection is generally the last process in water treatment and the use of PC as
338 disinfection system may impart excess of iron generated from the anode in the drinking water.

339

340

341 **5. Performance of PC process in combination with other processes**

342 As all technologies, PC has its own limitations such as the increase in disposal cost due
343 to the huge sludge generation that restricts its application at the industrial level (Li et al.,
344 2021a). To make this process more sustainable, efficient, and economical, various integrated
345 and hybrid processes with PC were developed for their applications in the treatment of a vast
346 variety of water and wastewater sources (Nordin et al., 2019). To improve the performance of
347 integrated PC, hybridization with other advanced or conventional wastewater treatment
348 technologies must be selected properly to take the advantage of each one. The integration of
349 PC with other processes is indeed beneficial to increase its performance and avoid the
350 shortcomings in the application at the industrial level. In recent years, many studies have
351 demonstrated the synergetic effect in the integrated PC with advanced and conventional
352 processes to treat water and wastewater (Jayashree et al., 2019; Li et al., 2023).

353 In order to increase the hybrid PC performance, the key is how to balance the synergetic
354 effect of oxidation and coagulation, while avoiding the formation of huge amounts of sludge.
355 This can be achieved by connecting EF and PC in parallel in the same system, which allows
356 allocating the current into the stable anode in EF system and iron sacrificial anode in PC system
357 (**Fig. 7a**). In a representative example, Li et al. reported the hybrid PC with EF to achieve the
358 goal of effective removal of organic pollutants by using NADE as cathode and DSA and iron
359 as anode for EF and PC, respectively (Li et al., 2021a). In this system, a slide rheostat was
360 applied to adjust the current of the parallel circuit to facilitate the setup of optimum current,
361 which is different for EF and PC (**Fig. 7b**). Authors performed the removal of 2,4-
362 dichlorophenoxyacetic acid (2,4-D) at 100 mA as setting total current for both DSA and iron.

363 By varying the resistance of sliding rheostat, the optimum condition was found at 50 Ω (30 mA
364 for the iron anode), which allows for achieving complete 2,4-D removal and 70% TOC removal
365 with 19.59 kWh (kg TOC)⁻¹ and 73% sludge reduction. In summary, the hybrid process allows
366 enhancing the single PC with energy and sludge reduction.

367 Differently, the photo-assisted PC (PPC) hybrid process is simpler. Hybrid PPC can be
368 considered as a combination of namely photoelectro-Fenton process and EC. The introduction
369 of UV or solar irradiation could boost the production of $\cdot\text{OH}$ and improve the degradation and
370 mineralization process by the photodegradation of iron complexes (Brillas et al., 2003b). As a
371 result, Jorfi et al. reported an improvement in the removal of COD from high-salinity
372 petrochemical wastewater, up to 90% COD removal is achieved (Jorfi et al., 2018). The high
373 COD removal in PPC can be attributed to the photodegradation of Fe(III)-oxalate complexes
374 and the production of more $\cdot\text{OH}$.

375 New photo-assisted system with energy self-power has been proposed to improve the
376 efficiency of PPC (Ba et al., 2021). Simulated solar light-mediated PC process sustained by the
377 iron-air fuel cell (PPC-IAFC) was developed for the oxidation of ethylene diamine
378 tetra(methylene phosphonic acid) (EDTMP). PPC-IAFC achieved 96% EDTMP removal with
379 generation of electricity simultaneously (2459 mW m⁻²). Good driving force for spontaneous
380 energy production is obtained due to the high positive potential of the oxygen reduction
381 reaction compared to the standard potential of anodic iron oxidation (Si et al., 2018). Therefore,
382 a beneficial situation is created to carry out a sustainable PPC process.

383 To improve self-power generation, new photoanodes have been developed for the
384 removal of pollutants by hybrid PC. TiO₂, ZnO, and $\alpha\text{-Fe}_2\text{O}_3$ immobilized on carbon cloth (CC)
385 have been proposed as photoanodes in the hybrid system of photocatalytic fuel cell and peroxi-
386 coagulation (PFC-PC) (Nordin et al., 2019). For the power generation, the highest power
387 density was achieved using ZnO/CC (117 mW m⁻²), which can be due to higher electron

388 mobility and electrical conductivity. As for the pollutant removal, the best performance
389 (93.8%) was obtained using Zn/CC photoanode. The increase in removal efficiency compared
390 to PC (86.9%) can be attributed to the additional contribution of the generated electron-hole
391 pair. High removal efficiency (94.1%) and power generation (314 mW m^{-2}) have been also
392 reported using ZnO immobilized in carbon plate (Nordin et al., 2020). In the PFC-PC process,
393 it is important to optimize the recombination rate and band gap energy to the photoanode which
394 could affect the performance of the process.

395 The synergetic effect of hybrid PC was also demonstrated by integrating PC with
396 microbial fuel cells (MFC), which allows energy production by degrading the organic
397 pollutants present in the wastewater (Jayashree et al., 2019). This hybrid process was
398 performed in two stages. First, MFC process is carried out to remove organic pollutants and
399 generate electricity. Then, the optimized MFC is used in the second stage, in which generated
400 electricity is used to carry out PC for the removal of pollutants. Jayashree et al. reported the
401 degradation of various real-life wastewaters using dual-chamber H-type MFC. The highest
402 COD removal efficiency (94%) was achieved using dairy wastewater with 5.2 mA current
403 output compared to 90% and 61% COD removal and 2.6 and 1.9 mA current output using
404 municipal and cassava wastewater, respectively (Jayashree et al., 2019). Then, the integration
405 of MFC with PC was performed using the highest generated current in MFC, which allowed
406 98% color removal of Rhodamine B solution. The integrated MFC-PC process is a promising
407 energy efficient as well as cost-effective technique for wastewater treatment.

408 In addition to the application of the hybrid technologies mentioned above, the
409 synergistic effects of oxidation, coagulation, and adsorption have also been demonstrated in
410 the integration of PC with ozone (Li et al., 2023), ultrasound-assisted (Eslami et al., 2021), and
411 electrosorption (Yang et al., 2021). Li et al. developed a hybrid PC/ozonation process (PCO),
412 in which authors demonstrated excellent performance in the mineralization and degradation of

413 phenol (Li et al., 2023). Hybrid PCO allowed until 45-fold improvement compared to a single
414 process. Eslami et al. evaluated the treatment of pulp and paper wastewater by ultrasound-
415 assisted PC (SPC) (Eslami et al., 2021). An improvement of SPC was observed compared with
416 single PC, EF, and EC with 81.7% COD removal. Yang et al. reported a high capacity for
417 integrated PC and electrosorption (PCES) for the removal of orange II (Yang et al., 2021).
418 PCES improved 10-folds ES process and allowed 93% removal with $31.9 \text{ kWh m}^{-3} \text{ order}^{-1}$. All
419 these hybrid processes have demonstrated to be an efficient and applicable technology for the
420 treatment of wastewater.

421 In summary, hybrid PC has benefited the most performance parameters boosting
422 removal efficiency, reducing sludge production, and allowing self-power generation, which
423 decrease the operating cost of the process. Some mentioned shortcomings of PC in the section
424 2 have been overcome in the hybrid PC processes. However, there is a lack of information on
425 how these technologies work synergically and their effectiveness in treating complex real
426 wastewater. Therefore, it is necessary to undertake additional studies for the development of a
427 fundamental understanding of the new hybrid PC process in complex actual wastewater. It is
428 also necessary to focus future studies on the optimization of operational parameters and
429 developing new self-power systems to face the high electricity consumption, which has a direct
430 impact on operational expenses. Since the hybrid system has been successfully demonstrated
431 to be promising in lab-scale systems, the next steps should focus on their scale-up to translate
432 hybrid PC systems to a higher technology readiness level and accelerate their implementation
433 at the industrial level.

434

435 **6. Conclusions and Future Perspectives**

436 PC process is found more effective for treating various pollutants in water and
437 wastewater and its efficacy is improved with modifications in electrodes and cells. The process
438 is also able to remove inorganic ions as well as arsenite after oxidation. Formation of ferryl
439 ions in the system along with hydroxyl radicals and hydrogen peroxide made this process more
440 attractive as ferryl ion is able to degrade pollutant in the absence of hydroxyl radicals,
441 especially in alkaline pH conditions. The oxidation and separation properties of PC process are
442 useful for handling complex wastewater as the pollutant will be oxidized at the initial stages of
443 the process and recalcitrant by-products will be removed at the EC phase.

444 Application of PC process is drawing attention as it will not produce harmful compounds,
445 as in the case of conventional chlorination. However, its inability to provide residual protection
446 for treated drinking water is a concern for real-field applications. At the same time, this process
447 can be used for the disinfection of sewage or similar contaminated water, where residual
448 protection of treated water is not a major concern.

449 Controlling of increase in solution pH with electrolysis time is always a challenging task
450 of PC process. With the increase in solution pH, the production of hydroxyl radicals in the
451 system decreases, which ultimately reduces the oxidation potential of PC process. This problem
452 can be controlled by intermittent acid addition. However, it will increase the cost of treatment.
453 At the same time, the production of ferryl ions is an advantage of the system as it can oxidize
454 pollutants at wide pH conditions.

455 An increase in solution pH with electrolysis time will not be a major issue in the
456 continuous flow studies. However, such studies are not yet conducted. Further research should
457 be focused more on the scale-up of this electrolytic system. In the higher scales, the experiment
458 can be conducted in a continuous flow manner and the initial pH of the wastewater can be
459 adjusted to the optimal pH, which is near 3. The reactor can be designed in such a way that the
460 effluent pH should be reached near neutral along with optimal pollutant removal.

461 Passivation of the cathode is also a concern of PC process in real-field implementation.
462 Being a carbonaceous material, the cathode is able to adsorb more ions, which ultimately
463 reduces its efficiency. Pulsed power supply is able to tackle this issue to some extent. However,
464 more research is needed for the reduction of passivation in PC process. Successful
465 hybridization and integration of PC with advanced or conventional processes have been
466 performed for the removal of wastewater, but the synergetic action of integrated processes is
467 not fully understood. Reactor design and several water matrices can play an important role,
468 while involving the production of different oxidants that contribute to the effective removal of
469 wastewater. Therefore, studies that complete the missing pieces will contribute to the
470 improvement and overcome of the mentioned shortcoming of PC for its future application.

471

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Figure 1

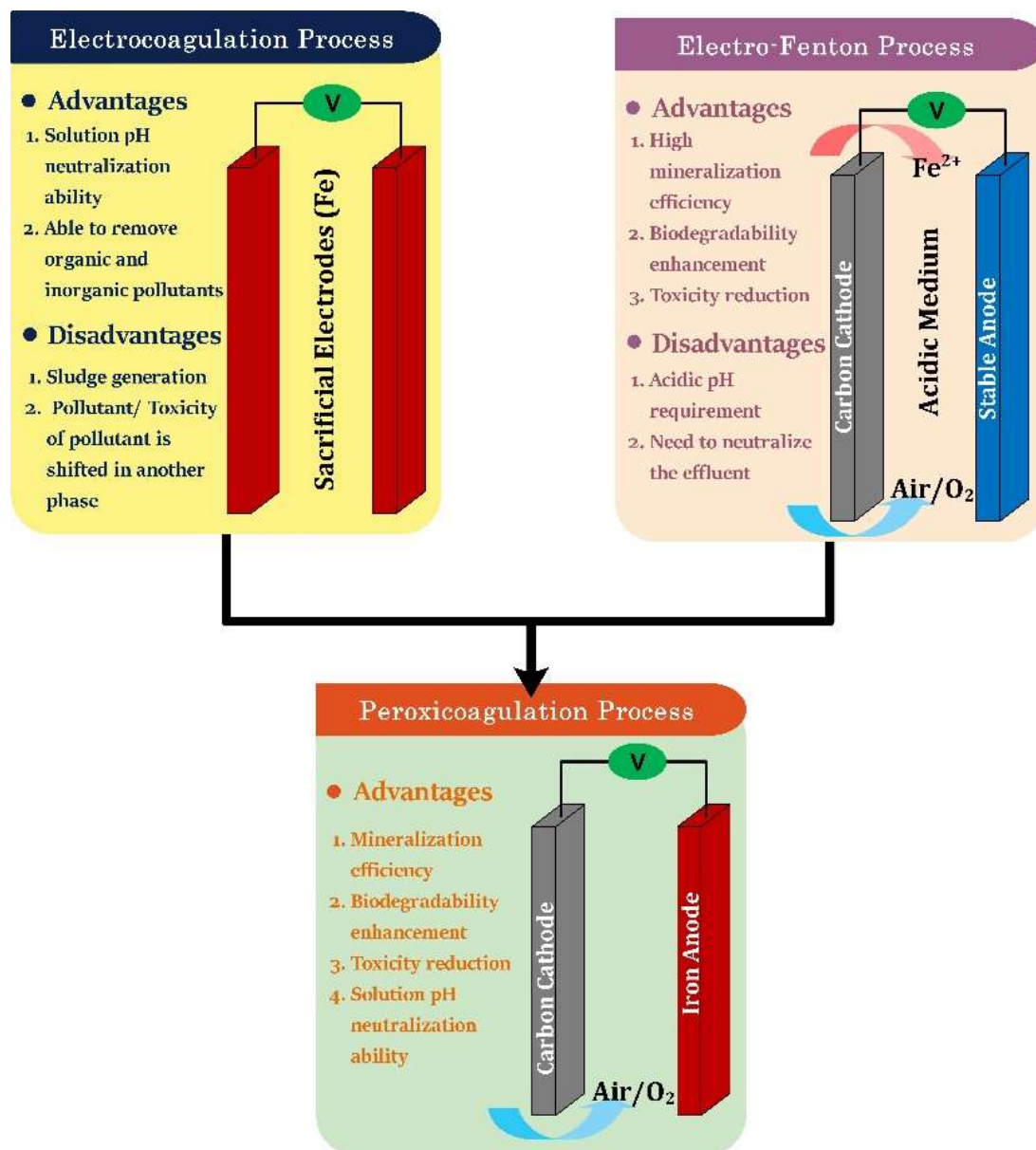


Figure 2

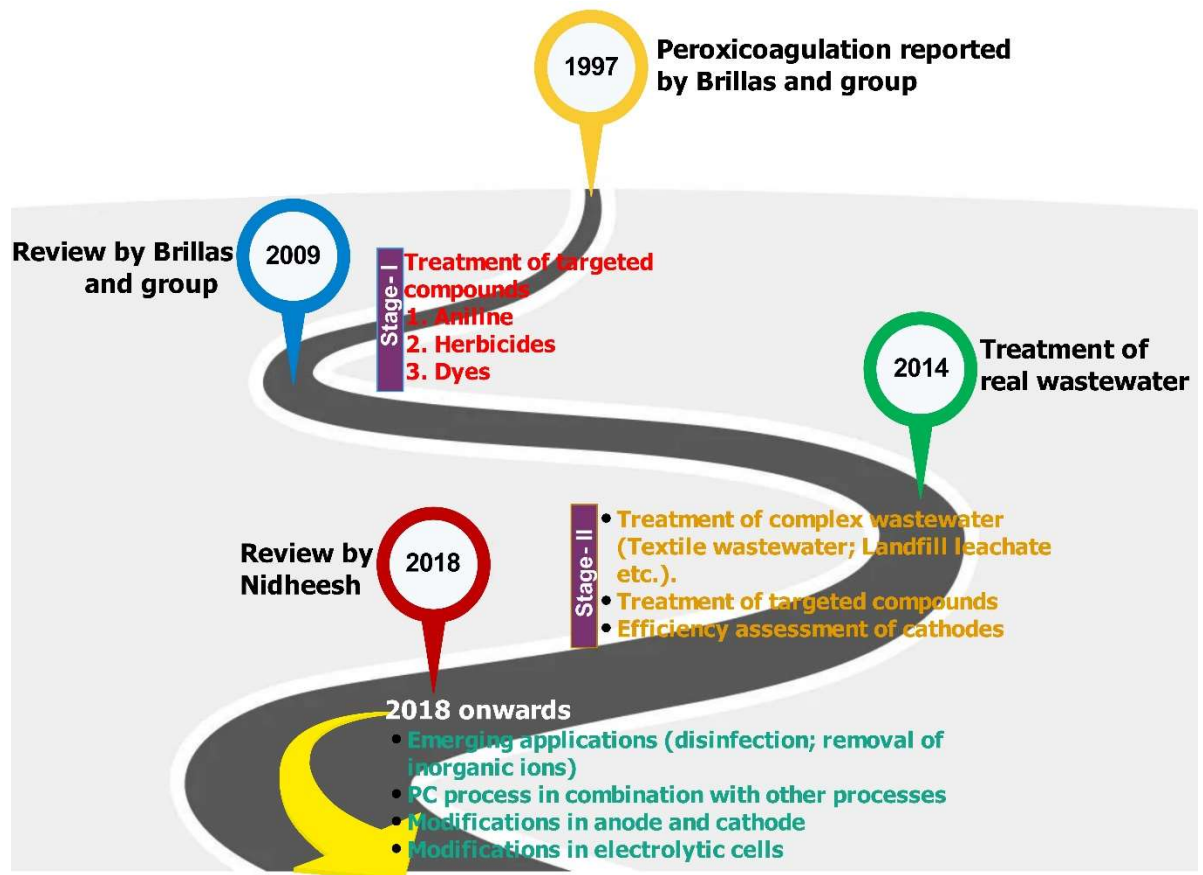


Figure 3

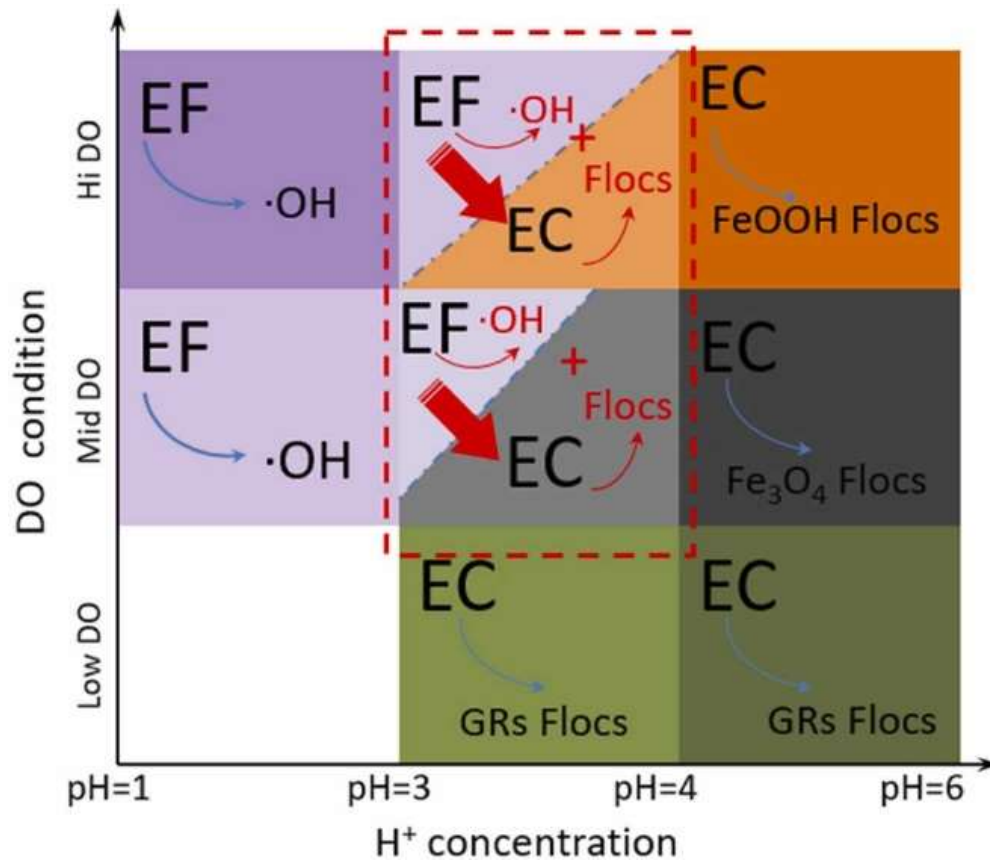


Figure 4

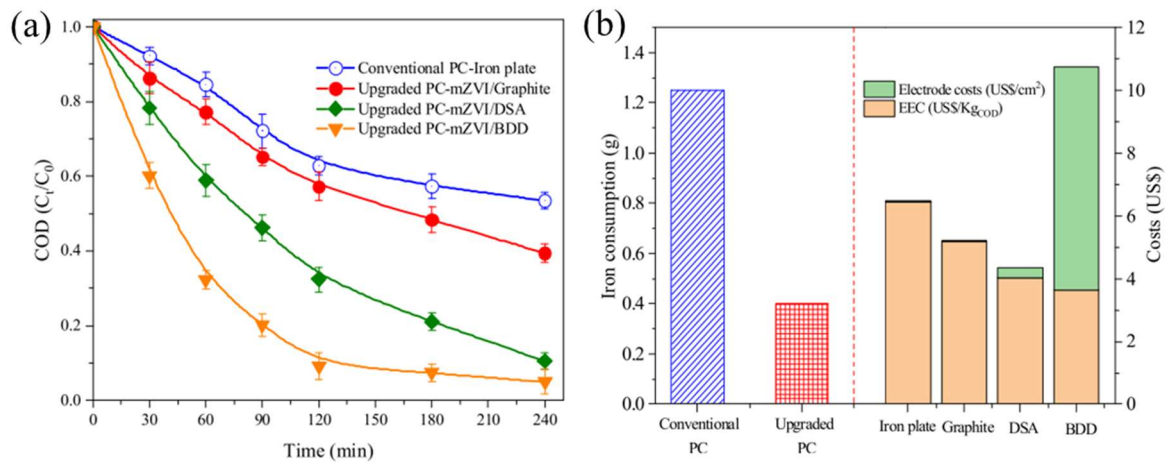


Figure 5

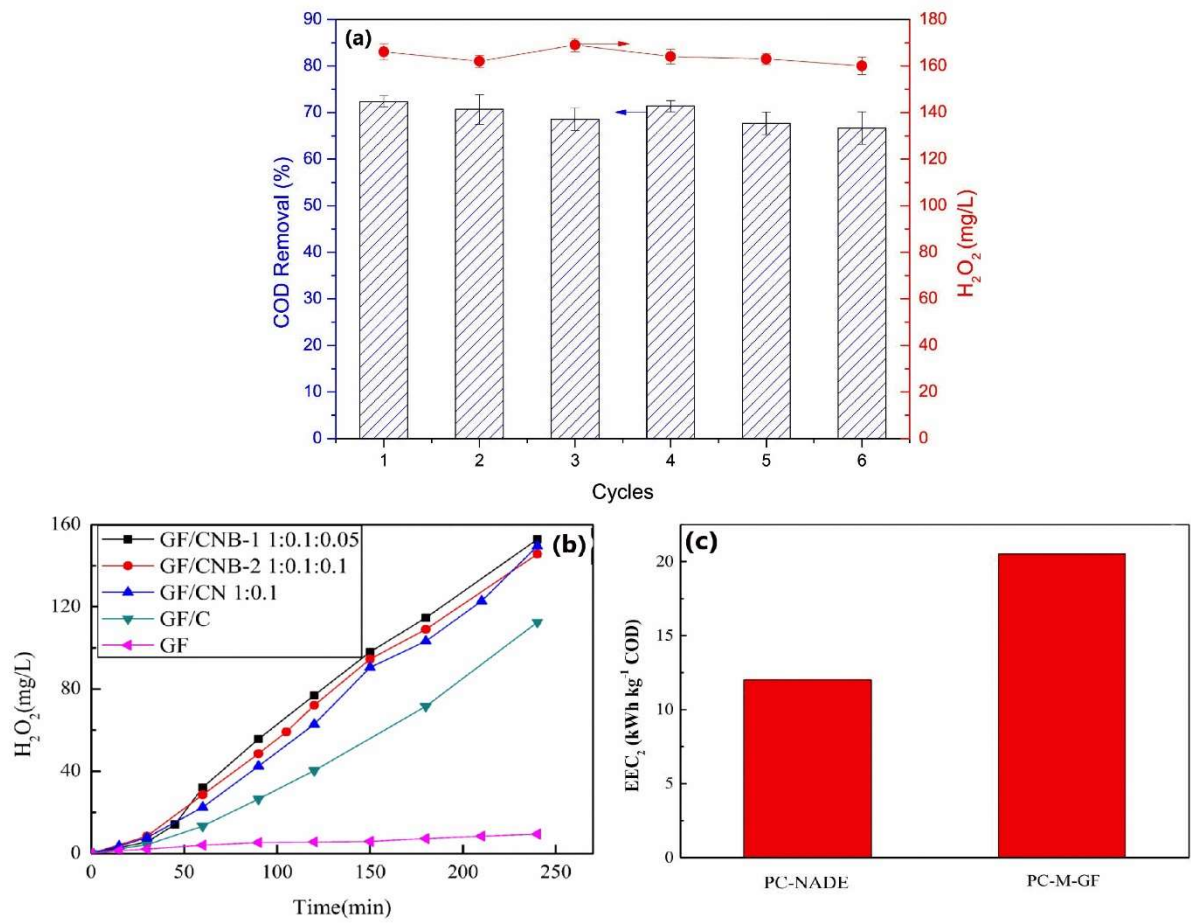
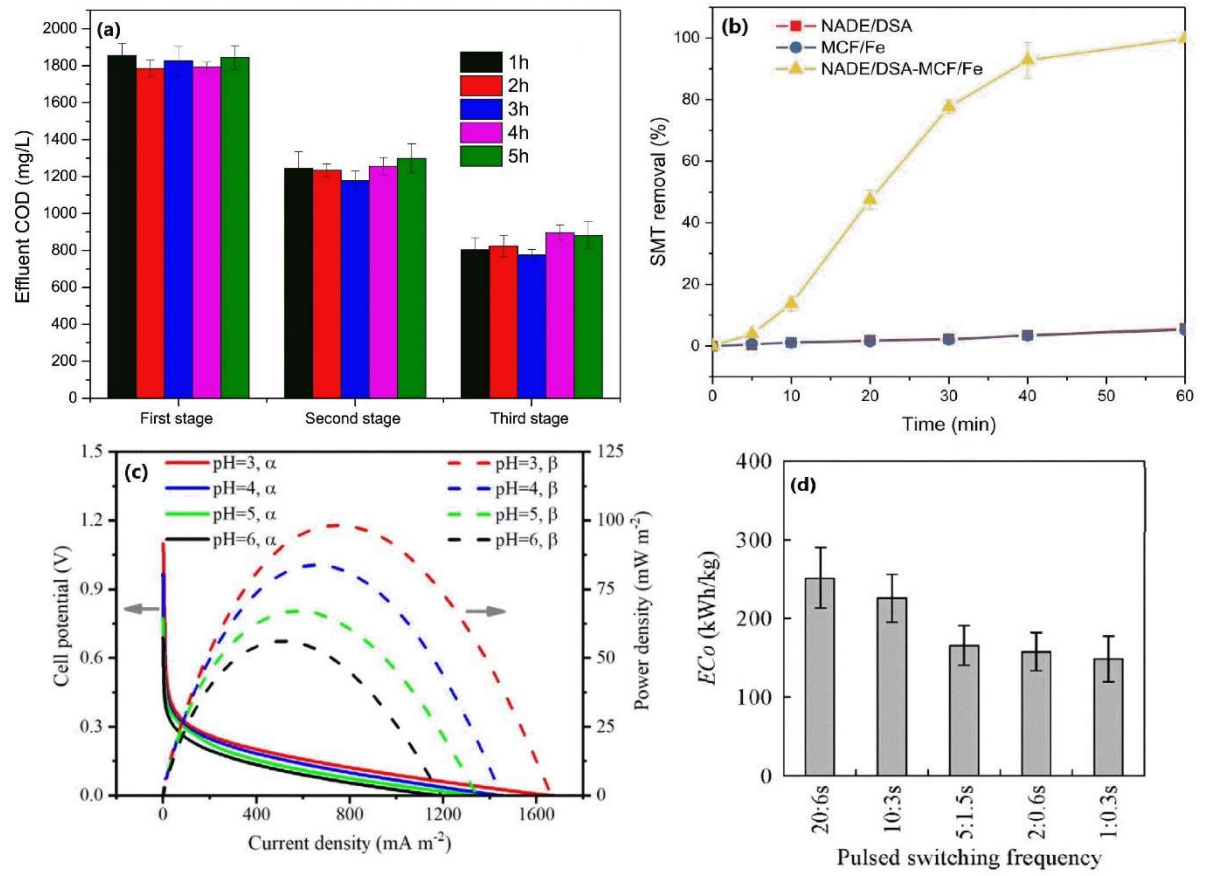
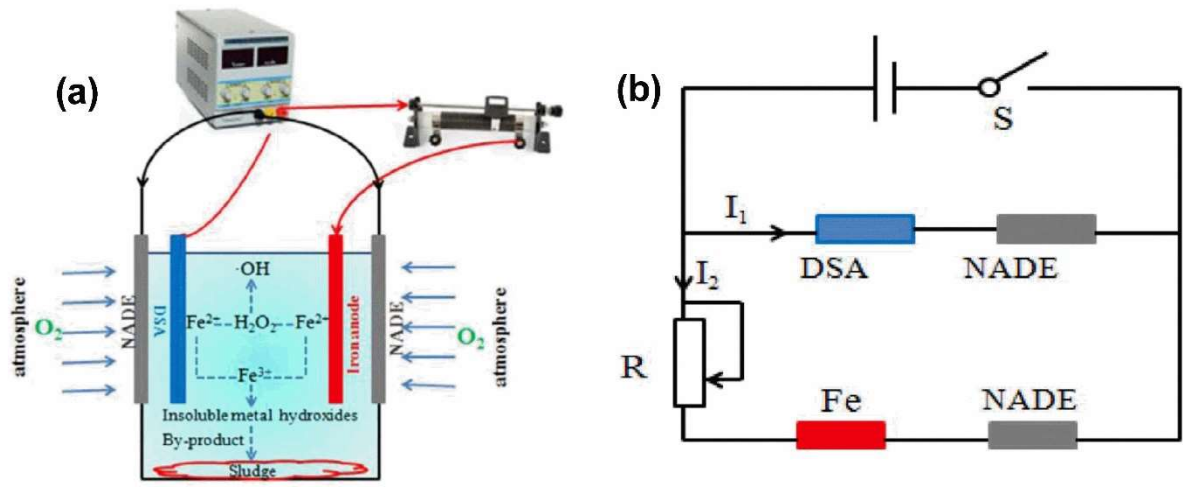


Figure 6



1 **Figure 7**



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