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► **To cite this version:**

P Nidheesh, Minghua Zhou, Mehmet A. Oturan. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes.. Chemosphere, Elsevier, 2018, 197 (210-227.), <10.1016/j.chemosphere.2017.12.195>. <hal-01721053>

**HAL Id: hal-01721053**

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Submitted on 1 Mar 2018

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# **An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes**

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**Paper submitted for publication in SI: EAOPs-POPs, Chemosphere**

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1 **Abstract**

2 Wastewater containing dyes are one of the major threats to our environment. Conventional  
3 methods are insufficient for the removal of these persistent organic pollutants. Recently much  
4 attention has been received for the oxidative removal of various organic pollutants by  
5 electrochemically generated hydroxyl radical. This review article aims to provide the recent  
6 trends in the field of various electrochemical advanced oxidation processes (EAOPs) used for  
7 removing dyes from water medium. The characteristics, fundamentals and recent advances in  
8 each processes namely anodic oxidation, electro-Fenton, peroxicoagulation, fered Fenton,  
9 anodic Fenton, photoelectro-Fenton, sonoelectro-Fenton, bioelectro-Fenton etc. have been  
10 examined in detail. These processes have great potential to destroy persistent organic  
11 pollutants in aqueous medium and most of the studies reported complete removal of dyes  
12 from water. The great capacity of these processes indicates that EAOPs constitute a  
13 promising technology for the treatment of the dye contaminated effluents.

14

15 **Keywords:** Dye removal, Electrochemical advanced oxidation, Decolorization,  
16 Mineralization, Hydroxyl radicals, Wastewater treatment

17

## 18 **1. Introduction**

19 Water pollution due to various industrial effluents is a global environmental problem.  
20 Due to the rapid industrialization, the use of coloring chemicals like dyes also increases day  
21 by day. Overall, 40,000 dyes and pigments with more than 7,000 different chemical  
22 structures have been reported recently (Demirbas, 2009). Production of dyestuff and  
23 pigments annually across the world is more than 700,000 tonnes and in India itself it is close  
24 to 80,000 tonnes (Mathur et al., 2005; Gong et al., 2007; Mane et al., 2007). Among this  
25 10,000 different types of dyes and pigments are being manufactured annually across the  
26 world (Ponnusami et al., 2008). These dyes are chemically, photolytically and biologically  
27 highly stable and are highly persistent in nature (Suteu and Bilba, 2005). Various industries  
28 like textile, leather, food, cosmetic, paper, pharmaceutical etc. are using variety of synthetic  
29 dyes. Among these industries, textile industries are the largest consumer of dyeing stuffs and  
30 pigments and produces large amount effluents after dyeing process. For example, 1.5 million  
31 liters per day of effluent are discharging into natural water bodies from an average mill  
32 producing  $60 \times 10^4$  m of fabric (COINDS, 2000). This wastewater contains various kinds of  
33 pollutants apart from dyes and most of them are hazardous. Depending on the textile  
34 processes, effluents generated from the industry contains various types of solvents, salts,  
35 detergents etc. apart from many types of dyes (Barredo-Damas et al., 2006). Typical  
36 characteristics of the effluent generated from textile industries are given in Table 1. Among  
37 these contaminants, removal of dyes from the wastewater needs to be a special attention.

38 The effluents containing dyes are one of the major threats to environment. Even in low  
39 concentrations, the dyes are highly visible (esthetic pollution) and affect the aquatic life and  
40 food chain (chemical pollution) (Namasivayam and Kavitha, 2002; Malik, 2003). However,  
41 the average concentration of dyes in a textile wastewater is around  $300 \text{ mg L}^{-1}$  (Couto, 2009).  
42 Disposal of this highly colored wastewater into natural water bodies hamper light penetration,

43 distress biological process in the water medium and provide an aesthetically displeasing  
44 appearance (Arivoli et al., 2009). Reduced light penetration with the introduction of colored  
45 wastewater reduces the photosynthetic activity within the water body and this also affect the  
46 symbiotic process (Ju et al., 2008).

47 **Table 1** Characteristics of textile wastewater. Reprinted with permission from Sandya et al.  
48 (2008), Copyright 2007, Elsevier.

Parameters	Concentration
Solution pH	9.5-12.5
Total Suspended Solids (mg L <sup>-1</sup> )	60-416
Total Dissolved Solids (mg L <sup>-1</sup> )	4500-12800
Total Organic Carbon (mg L <sup>-1</sup> )	26390-73190
Biochemical Oxygen Demand (mg L <sup>-1</sup> )	25-433
Chemical Oxygen Demand (mg L <sup>-1</sup> )	1835-3828
Aromatic Amines (mg L <sup>-1</sup> )	20-75
Ammonia (mg L <sup>-1</sup> )	2-3
Chloride (mg L <sup>-1</sup> )	1200-1375
Sulphate (mg L <sup>-1</sup> )	700-2400

49  
50 The hazardous, toxic and carcinogenic natures of dyes are also well known.  
51 Physiological disorders in aquatic organisms happen by the consumption of dyes in textile  
52 effluents via food chain (Karthikeyan et al., 2006). Some of the azo dyes are responsible for  
53 causing bladder cancer in humans and chromosomal aberration in mammalian cells  
54 (Mendevedev, 1988; Percy et. al., 1989). Cytotoxicity of reactive dyes (three  
55 monochlorotriazinyl dyes: yellow, red and blue with different concentrations) using human  
56 keratinocyte HaCaT cells in vitro was investigated by Klemola et al. (2007) and the mean  
57 inhibitory concentration values after 72 h of exposure was measured as 237 µg mL<sup>-1</sup> for  
58 yellow dye, 155 µg mL<sup>-1</sup> for red dye and 278 µg mL<sup>-1</sup> for blue dye. Similarly, spermatozoa

59 motility inhibition test of these dyes showed the mean inhibitory concentration values after  
60 24 h of exposure as  $135 \mu\text{g mL}^{-1}$  for yellow dye,  $\mu\text{g mL}^{-1}$  for red dye and  $127 \mu\text{g mL}^{-1}$  for  
61 blue dye (Klemola et al., 2006). Frame-shift mutation and base pair substitution in  
62 Salmonella in the presence of CI disperse blue was observed by Umbuzeiro et al. (2005).  
63 Experimental investigations of Bae and Freeman (2007) reported that C.I. Direct Blue 218 is  
64 very toxic to daphnids. The 50% of mortality of daphnids was observed for concentrations of  
65  $1\text{-}10 \text{ mg L}^{-1}$  of C.I. Direct Blue 218 after 48 h. Impact of textile effluents on a proteinous  
66 edible fresh water fish Mastacembelus Armatus was examined by Karthikeyan et al. (2006)  
67 and they observed a decrease in  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations and increase in  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  
68  $\text{Ca}^{2+}$  concentrations after 35 d of Acid Blue 92 exposure. The toxicity of the textile dye  
69 industry effluent on freshwater female crab, *Spiralothelphusa hydrodroma* was investigated  
70 by Sekar et al. (2009). The authors observed a decrease in protein, carbohydrate and lipid  
71 contents in ovary, spermatheca, muscle, hepatopancreas, gill, brain, thoracic ganglia and  
72 eyestalks at 30 d of sublethal (69.66 ppm) concentration of textile dye industry effluent  
73 exposure. Mathur et al. (2005) tested the mutagenic activity of seven dyes by Ames assay,  
74 using strain TA 100 of Salmonella typhimurium and reported that except violet dye, all are  
75 mutagenic. Among these mutagenic dyes, Congo red and royal blue dyes are moderately  
76 mutagenic while bordeaux is highly mutagenic or extremely mutagenic. Similarly, effect of  
77 malachite green on immune and reproductive systems was observed by Srivastava et al.  
78 (2004). The authors also observed the potential genotoxic and carcinogenic nature of the  
79 mentioned basic dye.

80         These non-exhaustive examples highlight how much the presence of the dyes in water  
81 is harmful to the aquatic environment. Therefore, removal of dyes from aqueous medium is  
82 an important environmental issue in the environmental safety point of view.

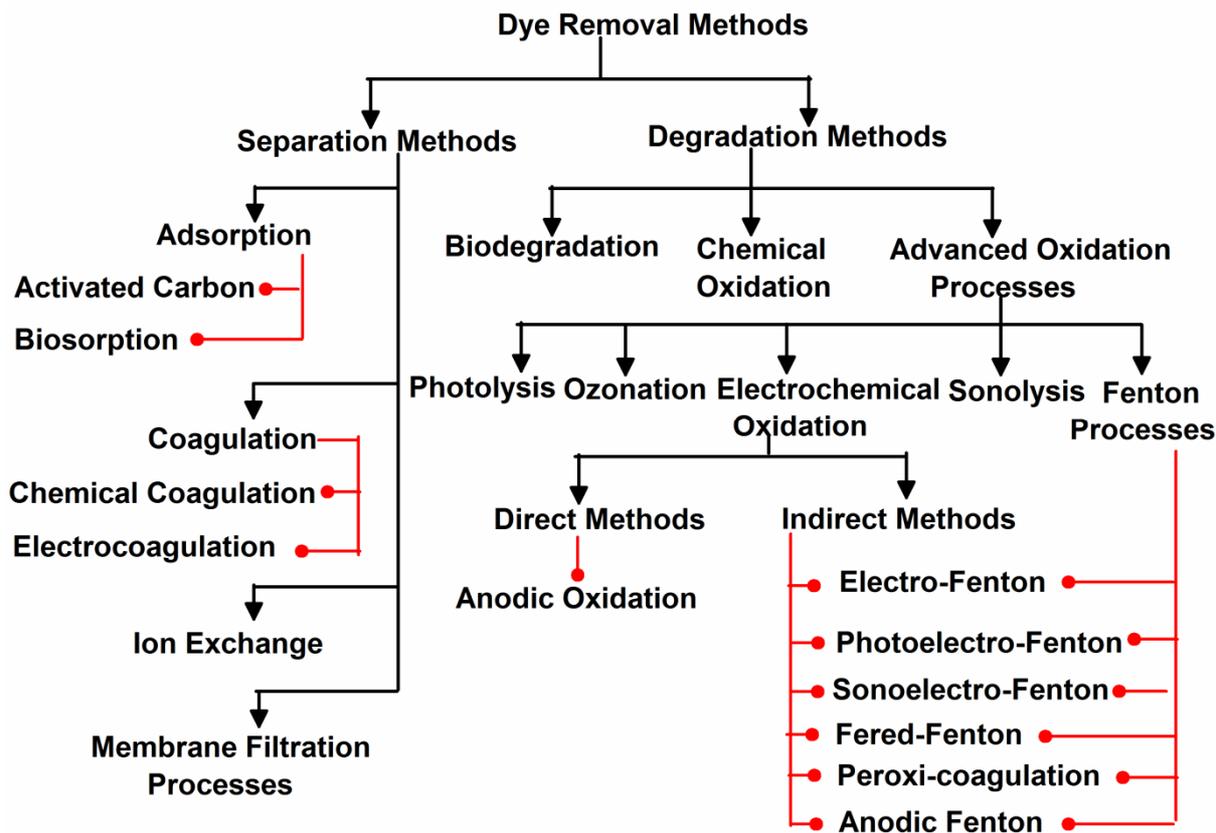
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## 85 **2. Electrochemical advanced oxidation processes for dye removal**

86 Various treatment techniques such as adsorption, coagulation, filtration,  
87 electrocoagulation, photolysis, sonolysis, biodegradation, wet land treatment, ozonation,  
88 photocatalysis, membrane filtration etc. have been used for removing synthetic dyes from  
89 aqueous solution. Advantages and disadvantages of dye removal methods have been  
90 discussed in detail (Crini, 2006; Martinez-Huitle and Brillas, 2009; Nidheesh et al., 2013).  
91 Based on the principle mechanism behind the removal of dyes, these processes can be  
92 divided into two broad classes: Separative (physical, and physicochemical) methods, and  
93 degradative (chemical and biological) methods. The schematic diagram of the various  
94 methods used for the dye removal is shown in Fig. 1. Most of the methods used for dye  
95 removal are separation process and the main disadvantage of these processes is the disposal  
96 of dye containing sludge as in coagulation process, dye sorbed adsorbents and concentrated  
97 dye solution as in membrane processes. In contrary to this, complex dye compounds undergo  
98 a series of degradation in chemical degradation methods. In the case of use of advanced  
99 oxidation processes, degradation procedure advance until ultimate oxidation degree, i.e.  
100 mineralization of organic pollutants. These methods produce carbon dioxide, water and  
101 various inorganic ions (following heteroatoms presents at the starting organic pollutants) as  
102 the final products.

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**Fig. 1** Schematic representation of method used in dye removal from water

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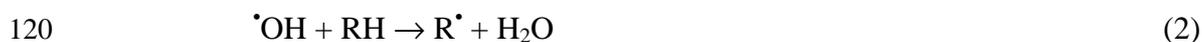
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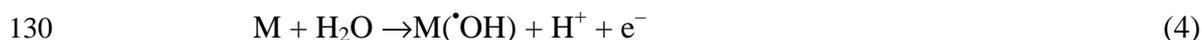
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Among various degradation techniques, advanced oxidation processes (AOPs) received great attention for the efficient degradation of dyes, during recent years (Martinez-Huitle et al., 2009, Oturan and Aaron, 2014). These processes are based on the production of highly reactive oxidants, mainly hydroxyl radical ( $\cdot\text{OH}$ ). This radical is the second most powerful oxidizing agent (after fluorine) with a redox potential of  $E^\circ (\cdot\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$ . Once these radicals are produced in situ, they attack organic pollutants with high reaction rates through following three different ways (Oturan, 2000; Brillas et al., 2009; Sirés et al., 2014): electron transfer (redox reaction) (Eq. (1)), H atom abstraction (dehydrogenation) (Eq. (2)), and electrophilic addition to  $\pi$  systems (hydroxylation) (Eq. (3)). These reactions produce organic radicals and start a radical chain including reactions with oxygen (formation of peroxy radicals) and formed reaction intermediates undergo further oxidation reactions with

117 generated oxidizing agents ( $\cdot\text{OH}$ ,  $\text{HO}_2\cdot$ ,  $\text{H}_2\text{O}_2\dots$ ) until the complete mineralization of organic  
118 pollutants.



122 Among the AOPs, electrochemical advanced oxidation processes (EAOPs) that have  
123 been developed during the last decade have generated great interest for the abatement of  
124 various persistent organic pollutants including synthetic dyes. EAOPs use electrolytically  
125 produced hydroxyl radicals for the mineralization of organic pollutants. Based on the  
126 production of hydroxyl radicals in the electrolytic system, EAOPs can be divided into two  
127 categories: direct and indirect EAOPs as shown in Fig. 1. In the case of direct EAOPs,  
128 hydroxyl radicals are produced on the anode surface by direct oxidation of water according to  
129 the Eq. (4):



131 with M: anode material. The production rate and extent depend on the nature (catalytic  
132 activity) of anode material, diffusion rate of organic pollutants on the active sites of anode  
133 and applied current density (Panizza and Cerisola 2009; Miled et al., 2010). The great  
134 advantage of this process is to not require the external addition of reagents for the production  
135 of hydroxyl radicals. In the case of indirect EAOPs, the generation of hydroxyl radicals is  
136 based on the Fenton chemistry including *in situ* electrochemical generation (electro-Fenton)  
137 or externally addition of the one of the reagent ( $\text{H}_2\text{O}_2$  or ferrous iron) (ferred-Fenton). Mostly  
138  $\text{H}_2\text{O}_2$  is *in situ* produced at the cathode thanks to the use of an adequate electrode material.  
139 Hydroxyl radicals are produced by the reaction between electrolytically generated or  
140 externally added  $\text{H}_2\text{O}_2$  and anodically generated or externally added ferrous iron (Brillas et

141 [al., 2009](#)). Electro Fenton process constitutes an excellent example of indirect EAOPs, in  
142 which hydroxyl radicals are produced by the reaction between electrochemically *in situ*  
143 generated H<sub>2</sub>O<sub>2</sub> and electrocatalytically regenerated ferrous ion.

144 EAOPs have several advantages over conventional treatment techniques. The main  
145 advantage of the EAOPs is environmental compatibility as the main reagent for all the  
146 EAOPs is electron, which is an inbuilt clean species ([Peralta-Hernández et al., 2009](#)). Other  
147 advantages are related to their versatile nature, higher pollutant removal efficiency,  
148 operational safety and amenability of automation ([Jüttner et al., 2000](#); [Anglada et al., 2009](#),  
149 [Sirés et al., 2014](#)). In addition, the presence of salt (e.g., NaCl) in wastewater could help to  
150 improve process efficiency and reduce energy consumption ([Zhou et al., 2011a, 2011b](#)).

151 The main aim of this review is to present a general review on the application of EAOPs  
152 for the removal of dyes from aqueous solution. Special attention is made on fundamental  
153 reactions involved of each EAOP to provide clear idea on its characteristics and oxidation  
154 capacity.

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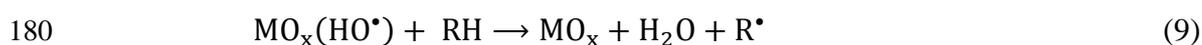
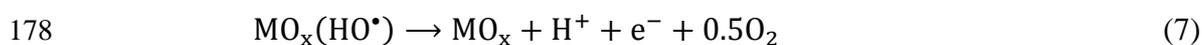
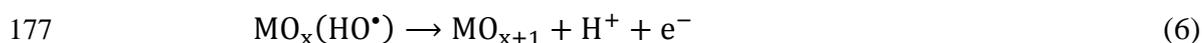
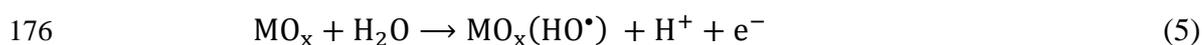
### 156 **3. Direct EAOPs**

157 Direct EAOPs produces hydroxyl radicals in the electrochemical reactor without the  
158 external addition of chemicals. Anodic oxidation (called also electrooxidation) is the best  
159 example of direct EAOPs. The following section explains the recent trends in dye removal by  
160 anodic oxidation process.

#### 161 **3.1 Anodic Oxidation**

162 Anodic oxidation (AO) is the most popular direct EAOPs; it works based on the  
163 hydroxyl radical production at the anode surface ([Panizza and Cerisola, 2009](#)). The process is  
164 heterogeneous and hydroxyl radicals formed are adsorbed on the anode surface. They are

165 chemisorbed in the case of active anode like Pt or DSA and are less available. The production  
 166 of hydroxyl radicals is promoted by high O<sub>2</sub> evolution overvoltage anodes such as boron-  
 167 doped diamond (BDD) thin film anodes. In these latter cases, hydroxyl radicals are  
 168 physisorbed and consequently more available for oxidation of organics. Various researchers  
 169 well explained the organic pollutant degradation mechanism in AO process in the case of  
 170 metal oxide (MO<sub>x</sub>) anodes (Comninellis, 1994; Scialdone, 2009). Heterogeneous hydroxyl  
 171 radicals MO<sub>x</sub>(HO•) are mainly formed by the oxidation of water (Eq. (5)). The adsorbed  
 172 radicals result in the production of chemisorbed oxygen (Eq. (6)) or oxygen evolution (Eq.  
 173 (7)). The chemisorbed oxygen also undergoes further reaction and produces oxygen as in Eq.  
 174 (8). The MO<sub>x</sub>(HO•) and oxygen oxidize the organic pollutant as in Eqs. (9) and (10). The  
 175 surface of the anode is catalytically regenerated according to Eqs. (7)-(10).



182 There are two ways of pollutant degradation mechanism in AO process (Comninellis  
 183 and Battisti, 1996): electrochemical conversion: degradation of persistent organic pollutants  
 184 into biodegradable byproducts such as short-chain carboxylic acids, and electrochemical  
 185 combustion or incineration (complete mineralization of organic pollutants into CO<sub>2</sub>, H<sub>2</sub>O and  
 186 inorganic ions). Between the oxidants produced in AO electrolytic cell, MO<sub>x</sub>(HO•) causes the  
 187 complete mineralization of the organic pollutants and the chemisorbed oxygen  
 188 (MO<sub>x</sub>(HO•)) causes the selective oxidation of organic pollutants (Chen, 2004). This

189 difference in the oxidation ability of these two oxidants is mainly due to their different  
190 oxidation potentials. Overall, AO process can be defined as the direct EAOPs in which the  
191 degradation of the organic pollutants occurs mainly by the adsorbed hydroxyl radicals  
192 produced by the water oxidation in the presence of high O<sub>2</sub> overvoltage anodes.

193 Compared with other treatment processes, AO process has several advantages. The  
194 major three advantages of AO process are (Chen et al., 2003): rapid degradation of pollutants,  
195 elevated removal efficiency, and easy operation. Apart from this, high efficiency at various  
196 solution pH is also promotes the practical implementation of AO process. In general hydroxyl  
197 radical formation is better in acidic media but the difference is not significant. Thus it was  
198 reported that heterogeneous hydroxyl radicals are also formed at pH  $\geq 10$  (Sirés et al., 2006;  
199 Özcan et al., 2008a). Even though complete mineralization of clofibric acid (Sirés et al.,  
200 2006) and 4,6-dinitro-o-cresol (Flox et al., 2005) at pH 12 was reported.

201 In AO, selection of anode affects significantly the efficiency of the process. There are  
202 two types of anodes in AO process: active and non-active anodes. This differentiation is  
203 mainly based on the reaction of anode material with adsorbed hydroxyl radicals. In the case  
204 of active anodes, formation of higher oxides or super oxides occurs by the reaction of anode  
205 with hydroxyl radicals. This reaction happens when the anode has higher oxidation potential  
206 above the standard potential required for the oxygen evolution (Migliorini et al., 2011). The  
207 anodes like Pt, IrO<sub>2</sub>, SnO<sub>2</sub> and RuO<sub>2</sub> are the examples of active anodes. On the other hand,  
208 hydroxyl radicals are physically sorbed on the non-active anodes and the mineralization of  
209 organic pollutants occurs mainly by the direct reaction of physisorbed hydroxyl radicals.  
210 These electrodes do not contribute any direct anodic reaction of organic pollutants and do not  
211 impart any catalytic site for the effective pollutant sorption (Migliorini et al., 2011). BDD  
212 electrode is the best example of non-active anodes.

213 Compared to active electrodes, non-active electrodes have high mineralization capacity.  
214 For example, BDD anode was found to be the best electrode for the mineralization of various  
215 persistent organic pollutants. This is mainly due to its greater O<sub>2</sub> overvoltage (which  
216 increases the hydroxyl radical production rate), its wide potential window, low background  
217 current and very low activity for O<sub>2</sub> evolution reaction (Braga et al., 2010; Migliorini et al.,  
218 2011; Oturan et al., 2012; Haidar et al., 2013). The removal of adsorbed organics on the BDD  
219 surface is also easy. In most of the cases, rinsing with appropriate solvent is required for the  
220 effective cleaning of BDD surface (Migliorini et al., 2011). The degradation of carboxylic  
221 acids by Pt is also very difficult. But the degradation of these acids is feasible with BDD  
222 anode, thanks to the efficiency of BDD(<sup>•</sup>OH) and also the strong oxidants such as  
223 peroxodisulfate and O<sub>3</sub> formed during oxidation process according to the following reactions  
224 (Muruganathan et al., 2007; Flox et al., 2009; Li et al., 2010a).



228 Recently a great attention has been paid to improve the efficiency of anodes by using  
229 appropriate substrate (Wang et al., 2013; Hu et al., 2014). The selection of suitable substrate  
230 is also an important parameter. A substrate should have good electrical conductivity,  
231 sufficient mechanical strength, and electrochemical inertness or easy formation of protective  
232 films on substrate surfaces by passivation (Chen et al., 2003). For example, various substrates  
233 like Si, Ti, Nb etc. were used as substrate for BDD anode. The substrate used for the BDD  
234 anode has been classically Si. But, Si is difficult to use as a substrate for electrode due to its  
235 fragile nature and its conductivity is strongly dependent on the experimental environments  
236 (Sun et al., 2011). Among the various substrates, the suitable substrate for the BDD anode

237 was found as Ti (Chen et al., 2003; Sun et al., 2011). Also, the O<sub>2</sub> overvoltage potential of  
238 Ti/BDD is higher than that of Si/BDD anode (Chen, 2004).

239 Dye removal from aqueous solution using the AO process has been studied by various  
240 researchers. Faouzi et al. (2007) reported a total degradation and mineralization of alizarin  
241 red S by AO process using BDD anode. Similarly, complete mineralization of methyl orange  
242 in the presence of *in situ* microwave activated Pt was observed by Zhao et al. (2009). Color  
243 and COD removals from real textile effluents using BDD anode was studied by Martínez-  
244 Huitle et al. (2012) and they observed an effective reduction in color and COD after 15 h of  
245 electrolysis. Yavuz and Shahbazi (2012) used bipolar trickle tower reactor containing BDD  
246 anode for the removal of reactive black 5 in a continuous flow mode operation and achieved  
247 97% color, ~51% COD and 29.3% TOC removal at the optimal conditions, along with the  
248 reduction in toxicity. The oxidation of methyl orange using BDD anode in a 3 L capacity  
249 electrolytic cell was studied by Ramírez et al. (2013) and obtained a 94% decolorization and  
250 63.3% TOC removal efficiencies at the optimal conditions. Complete color and COD  
251 removals from an aqueous solution containing methylene blue in the presence of BDD anode  
252 was observed by Panizza et al. (2007). Degradation of three azoic dyes, Congo red, methyl  
253 orange, and eriochrome black T, using conductive-diamond anodes was investigated by  
254 Canizares et al. (2006) and concluded that the efficiency of the system depends only on the  
255 initial concentration of dye.

256 Nava et al. (2008) compared the color and COD removal efficiencies of various  
257 electrode materials for the abatement of alphazurine A dye and observed almost complete  
258 mineralization of dye with Pb/PbO<sub>2</sub> and Si/BDD electrodes, while Ti/IrO<sub>2</sub> disfavored such  
259 process. Similarly complete removal of color and COD induced by the alphazurine A using  
260 BDD anode was observed by Bensalah et al. (2009). Aquino et al. (2013) used Si/BDD anode  
261 for the degradation of reactive red 141 in a filter-press flow cell and applied response surface

262 methodology to determine the effects of different operating parameters on color, COD and  
263 TOC removals. The performances of Ti–Pt/ $\beta$ -PbO<sub>2</sub> and BDD anodes on the removal of  
264 reactive orange 16 in a filter press reactor were investigated by [Andrade et al. \(2009\)](#). The  
265 study concluded that even though complete dye removal is achieved by both the electrodes,  
266 BDD provided better results than Ti–Pt/ $\beta$ -PbO<sub>2</sub> due to less energy consumption. [Abdessamad  
267 et al. \(2013\)](#) compared the efficiency of monopolar and bipolar BDD electrodes for the  
268 removal of alizarin blue black B and concluded that the dye degradation efficiency of bipolar  
269 AO system is 1.2 times higher than that of monopolar AO system. [Chen et al. \(2003\)](#) were  
270 found that dye removal efficiency of Ti/BDD anode was higher than that of Ti/Sb<sub>2</sub>O<sub>5</sub>–SnO<sub>2</sub>  
271 anode. Also, Ti/BDD anode has higher dye removal efficiency in the cases of alizarin red S  
272 ([Sun et al., 2011](#)), orange II and reactive red HE-3B ([Chen et al., 2003](#)). The dye removal  
273 efficiencies of BDD and PbO<sub>2</sub> electrodes were compared by [Panizza and Cerisola \(2008\)](#) and  
274 observed a higher oxidation rate and higher current efficiency in the case of BDD anode than  
275 that of PbO<sub>2</sub> anode. At the same time, methyl orange degradation efficiency of TiRuSnO<sub>2</sub> is  
276 very much less than that of BDD and PbO<sub>2</sub> anode ([Labiadh et al., 2016](#)). Partial removal of  
277 the dye was achieved by using TiRuSnO<sub>2</sub> anode, but complete dye removal was also  
278 observed with other anodes. Even though, both anodes are efficient for the complete dye  
279 removal, complete mineralization was occurred only in the presence of BDD anode.

280 [Yao et al. \(2013\)](#) prepared PbO<sub>2</sub>-ZrO<sub>2</sub> nanocomposite electrodes by pulse  
281 electrodeposition and used it for the removal of methylene blue. The authors observed a  
282 100% dye and 72.7% COD removal after 120 min of electrolysis. Similarly, [An et al. \(2012\)](#)  
283 synthesized TiO<sub>2</sub>-NTs/Sb–SnO<sub>2</sub>/PbO<sub>2</sub> anode for the abatement of C.I. reactive blue 194 and  
284 reported that the prepared electrode has a high decolorization and mineralization ability.  
285 Recent study by [do Vale-Júnior et al. \(2016\)](#) demonstrates that Sn-Cu-Sb alloy anode  
286 prepared by cold gas spray is very efficient for the degradation of dyes from water medium.

287 The authors observed complete acid blue-29 removal and mineralization after 300 min and  
288 600 min of electrolysis, respectively.

289 Effect of boron doping in BDD anode on dye removal was investigated by [Migliorini et al. \(2011\)](#)  
290 and reported that highly boron doped electrodes has the higher reactive orange 16  
291 removal efficiency. Similar result has been observed by [Bogdanowicz et al. \(2013\)](#).

292 [Rodriguez et al. \(2009\)](#) observed two different oxidation mechanisms for acid yellow 1  
293 in the presence of BDD anodes. The oxidation of dye depends more on its initial  
294 concentration. At the lower dye concentration, the oxidation process followed pseudo first  
295 order kinetics and under the control of mass transport. While, at the higher dye  
296 concentrations, the degradation of acid yellow 1 followed zero order kinetics and reaction  
297 kinetics was controlled by charge transfer.

298 [Panizza and Cerisola \(2008\)](#) observed the pH independent methyl red oxidation in the  
299 range of 3 to 7. Similarly, insignificant effect of initial solution pH on dye removal by AO  
300 process using Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> was observed by [Song et al. \(2010\)](#). Similar result has been  
301 reported by [Petrucci and Montanaro \(2011\)](#). The authors observed that even though the color  
302 removal was affected by the change in pH, the mineralization ability of BDD anode was not  
303 altered with the solution pH.

304 Supporting electrolyte also plays an important role on the dye removal mechanism.  
305 [Aquino et al. \(2012\)](#) studied the effects of the salt (supporting electrolyte) addition for the  
306 removal of acid blue 62, reactive red 141, direct black 22, and disperse orange 29 using  
307 conductive-diamond anodes. The authors observed a mediated electrooxidation of dyes in the  
308 presence of chloride addition. At the same time, the removal of dyes by the addition of  
309 sulphate as supporting electrolyte is mainly by the attack of hydroxyl radicals, generated from  
310 BDD anode. [Zhou et al. \(2011a\)](#) compared the methyl orange degradation by electrochemical

311 oxidation using BDD and mixed metal oxide anodes and found enhanced dye removal in the  
312 presence of NaCl, which is mainly attributed to the co-action of mediated oxidation from  
313 active chlorine species.

314 The functional groups presents in the dyes also affects the efficiency of the electrolytic  
315 system. [Saez et al. \(2007\)](#) compared the alizarin red and eriochrome black T removals in the  
316 presence of BDD anode. The authors reported two different oxidation mechanisms for dye  
317 removals, even though complete COD and color removals from both dye wastewaters were  
318 observed. The removal of alizarin red was mainly due to hydroxyl radical mediated oxidation  
319 and controlled by mass transfer process, while the removal of eriochrome black T was mainly  
320 due to electrolytically generated reagents like peroxodisulphate.

321

#### 322 **4. Indirect EAOPs**

323 Production of hydroxyl radicals in indirect EAOPs is accomplished by the in situ  
324 production or external addition of chemicals. Fenton based EAOPs are the best examples of  
325 indirect EAOPs. The following sections discuss the applications and recent advances in these  
326 processes for the removal of dyes from aqueous medium.

##### 327 **4.1 Electro-Fenton (EF) process**

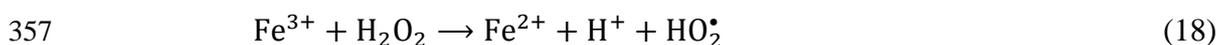
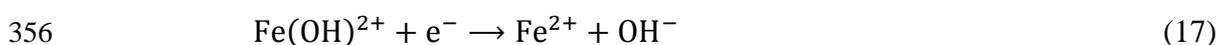
328 During the last decade EF process received much attraction among other processes.  
329 This is an economically and environmentally friendly process to remove efficiently toxic  
330 and/or persistent organic pollutants from water. Oturan and Brillas groups reported the  
331 principles of the EF process in the starting of 2000 ([Oturan and Pinson 1995](#); [Brillas et al., 1996](#);  
332 [Oturan, 2000](#); [Brillas et al., 2000](#)). EF process is an attractive tool and its interest is  
333 mainly due to its high degrading effectiveness of persistent organic pollutants, fast pollutant

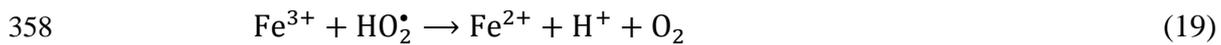
334 removal rate and environmental compatibility (Oturán et al., 2000; Brillas et al., 2009;  
335 Nidheesh et al., 2013; Sirés et al., 2014; Vasudevan and Oturan 2014).

336 EF process works based on the *in situ* electrogeneration of Fenton's reagent, a mixture  
337 of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> which is the origin of the Fenton's reaction (Eq. (15)) to generate hydroxyl  
338 radicals. Hydrogen peroxide is generated continuously at the cathode surface from the two  
339 electron reduction of O<sub>2</sub> in the acidic medium (Eq. (14)) (Oturán et al., 2008a; Özcan et al.,  
340 2009a; Nidheesh and Gandhimathi, 2012). Supply of oxygen near the cathode during EF  
341 treatment is required for fulfilling the continuous production of hydrogen peroxide in the  
342 electrolytic system. The addition of a catalytic amount of a ferrous salt (to produce Fe<sup>2+</sup> ions)  
343 into the solution leads to production of •OH according to Fenton's reaction (Eq. (15)).



346 Catalysis of the Fenton's reaction by electrochemical regeneration of ferrous ion is an  
347 important advantage of EF process compared to conventional Fenton process (Oturán et al.,  
348 2011; Moreira et al., 2013). Indeed, the optimal pH value for Fenton's reaction and Fenton  
349 related processes is about 3 (Brillas et al., 2009). At this pH, the predominant species of iron  
350 is Fe(OH)<sup>2+</sup> (Eq. 16) (Özcan et al., 2013). The Fe<sup>3+</sup> produced by Fenton's reaction remains  
351 under the form of Fe(OH)<sup>2+</sup> and undergoes cathodic reduction to produce ferrous ion  
352 according to Eq. (17) (Özcan et al., 2008b). Apart from this main source, ferrous ions are  
353 regenerated in the EF process via Fenton's chain reactions as in Eqs. (18-20) (Oturán et al.,  
354 2004; Oturan et al., 2010a).





360 where  $\text{R}^{\bullet}$  is organic radical.

361 Also, in overall, EF process results the production of two moles of hydroxyl radicals from 0.5  
362 moles of oxygen as in Eq. (21) (Oturán et al., 2001) showing the catalytic behavior of the  
363 process.



365 An insignificant change in solution pH with electrolysis time is the other advantage of  
366 EF process. This is mainly due to the counterbalancing of proton consumed during the Fenton  
367 reaction by the protons produced via water oxidation at the anode (El-Desoky et al., 2010)  
368 and carboxylic acids generated during the oxidation process (Oturán and Aaron, 2014).

369 Carbonaceous materials are widely used as the cathode, which is the working electrode  
370 of EF process. This is mainly due to its wide range of electrochemical activity for  $\text{O}_2$   
371 reduction and low catalytic activity for  $\text{H}_2\text{O}_2$  decomposition (Panizza and Cerisola, 2001).  
372 Also, the porosity of carbonaceous material is very high, in particular 3D carbon materials  
373 like carbon felt or graphite felt are of high porosity. These pores are useful for the sorption of  
374 oxygen gas supplied near the cathode surface and consequently results in higher amount of  
375 hydrogen peroxide generation. Various carbonaceous materials like carbon-felt (Oturán,  
376 2000; Murati et al., 2012), reticulated vitreous carbon sheet (El-Desoky et al., 2010; Ghoneim  
377 et al., 2011), activated carbon fiber (Wang et al., 2010), graphite (George et al., 2013, 2016;  
378 Nidheesh et al., 2014a), commercial graphite-felt (Khataee et al., 2009; Panizza and Oturan,  
379 2011) and chemically or electrochemically modified graphite felt (Zhou et al., 2013; 2014),  
380 carbon sponge (Özcan et al., 2008c) etc. were used as the cathode material for the efficient  
381 electrogeneration of hydrogen peroxide in EF cell. Özcan et al. (2008c) compared the dye

382 degradation efficiency of carbon sponge and carbon-felt for the abatement of acidified basic  
383 blue 3 solutions and found that carbon sponge is the effective cathode than carbon felt for EF  
384 process. By analyzing the reported literatures, various forms of Pt have been used frequently  
385 as anode in EF cell for the degradation of various organic pollutants (Nidheesh and  
386 Gandhimathi, 2012; Sopaj et al., 2015, 2016).

387 The efficiency of EF process increases by combining AO and EF processes. This can be  
388 achieved by the use of an O<sub>2</sub> overvoltage anode in the EF process along with the  
389 carbonaceous cathode. Oturan et al. (2012) showed that this process was able to mineralize  
390 quasi-completely the herbicide atrazine and its by-product cyanuric acid which already  
391 reported many times to be recalcitrant to hydroxyl radicals.

392 EF process has been proved as an efficient tool for the abatement of dyes from water  
393 medium. Nidheesh and Gandhimathi (2014a) used graphite-graphite electrolytic system for  
394 the abatement of rhodamine B (RhB) at pH 3. The authors reported that with the increase in  
395 electrode immersion depth the efficiency of the electrolytic system also increases. This is  
396 mainly due to the increased contact between cathode surface and air bubbles and the authors  
397 recommended to use bubble column reactor with lengthy electrode for the efficient removal  
398 of organic pollutants. Similarly, complete destruction of azure B and 95% TOC abatement at  
399 the end of 8 h EF treatment was observed by Olvera-Vargas et al. (2014). Almomani and  
400 Baranova (2013) analyzed the dye removal efficiencies of single and two compartment cells  
401 in the presence of stainless steel cathode and BDD anode and observed that two compartment  
402 cell is better than single cell for the removal of dyes from aqueous medium. Lakhimi et al.  
403 (2007) investigated the depollution of methylene blue, Congo red and yellow drimaren using  
404 carbon felt cathode and Pt sheet anode and observed a rapid degradation of dyes in their  
405 single and mixture solution. Almost complete mineralization of dyes also observed by  
406 Guivarch et al. (2003) and Guivarch and Oturan (2004). Similarly, 95% of the initial TOC

407 caused by alizarin red (Panizza and Oturan, 2011) and acid red 97 (Kayan et al., 2010) was  
408 removed effectively using the graphite-felt and carbon-felt cathodes, respectively. Diagne et  
409 al. (2014) compared the efficiencies of AO and EF processes for the removal of indigo dye  
410 and observed higher mineralization efficiency for EF process. Complete mineralization of the  
411 dye was observed within 2 h of electrolysis. Yu et al. (2015) modified graphite felt by using  
412 carbon black and PTFE; and observed 10.7 times higher H<sub>2</sub>O<sub>2</sub> production compared to  
413 unmodified electrode. EF process using this modified graphite felt cathode is efficient for  
414 complete removal of 50 mg L<sup>-1</sup> methyl orange within 15 min and 95.7% TOC removal at 2 h  
415 electrolysis; this efficiencies being more than 4 times that of EF process operated with raw  
416 graphite felt cathode.

417         Apart from, solution pH, catalyst dosage, initial pollutant concentration, electrode area,  
418 applied current and inner electrode spacing; the hardness in the water also affects the  
419 efficiency of EF process significantly (dos Santos et al., 2016). The presence of magnesium  
420 and calcium in water medium reduced the dye removal efficiency of EF process for the dye  
421 eriochrome black T. This reduction in the performance of EF process is mainly related to the  
422 difficulty to break the divalent cation- eriochrome black T complex by •OH.

423         Xu et al. (2014) prepared graphene doped gas diffusion electrode using modified  
424 Hummers' method and used for the removal of reactive brilliant blue in a three electrode  
425 undivided cell of volume 200 mL. The study concluded that under the optimal conditions,  
426 80% of the dye and 33% of TOC were removed after 180 min of electrolysis by the novel  
427 electrode. Ghoneim et al. (2011) observed a complete dye removal and 97% of mineralization  
428 by EF process in an electrolytic cell of 600 mL capacity containing reticulated vitreous  
429 carbon cathode, platinum gauze anode and 0.2 mM sunset yellow FCF azo dye. Sirés et al.  
430 (2008) compared the dye removal efficiency of EF cell with carbon-felt cathode for the  
431 degradation of crystal violet (CV), fast green FCF (FCF), methyl green (MeG) and malachite

432 green (MG). In this study, it was observed that the absolute rate constant for their reaction  
433 with hydroxyl radicals increases in the order MeG < FCF < CV < MG. Total depollution of a  
434 dye mixture containing the above four dyes with a COD of 1000 mg L<sup>-1</sup> was also observed.  
435 Complete decolorization and approximately 85–90% mineralization of levafix red CA and  
436 levafix blue CA was observed by [El-Desoky et al. \(2010\)](#). Similar results were obtained in the  
437 cases of real dyeing wastewater ([Wang et al., 2010](#)), reactive blue 4 ([Gözmen et al., 2009](#)),  
438 direct orange 61 ([Hammami et al., 2007](#)), etc.

439 [Lin et al. \(2014\)](#) studied orange II removal behavior of EF process in a divided cell and  
440 reported that dye removal rate in cathodic compartment was much faster than that in anodic  
441 compartment. [Scialdone et al. \(2013\)](#) performed the abatement of acid orange 7 in a  
442 microfluidic reactor and reported that the process is efficient for the usage of cheaper and  
443 easier to handle graphite as cathodic material, mainly due to the sufficient oxygen production  
444 from the anode. Therefore, external addition of air or oxygen is not required for this type of  
445 reactor. [Iglesias et al. \(2013a\)](#) used airlift continuous reactor for the removal of reactive black  
446 5 and lissamine green B and accomplished high decolorization percentages at high residence  
447 times. Methyl orange removal in a 3 L capacity pilot flow plant was studied by [Isarain-  
448 Chávez et al. \(2013\)](#) and obtained 80% of decolorization efficiency at the optimal conditions.  
449 Nanostructured ZnO-TiO<sub>2</sub> thin films deposited on graphite felt anode ([El-Kacemi et al.,  
450 2016](#)) exhibited higher dye removal and mineralization efficiency. Within 60 min of  
451 electrolysis Amido black 10B dye was discolored and the mineralization efficiency of the EF  
452 process reached 91% after 6 h of electrolysis. Application of graphene based electrode  
453 material improves the efficiency of EF process in a noticeable manner ([Yang et al., 2017](#)).  
454 Graphene ([Zhao et al., 2016](#)), graphene doped graphite-PTFE ([Xu et al., 2014](#)), reduced  
455 graphene oxide coated carbon felt ([Le et al., 2015](#)), graphite felt modified with

456 electrochemically exfoliated graphene (Yang et al., 2017) electrodes exhibited excellent  
457 hydrogen peroxide generation potential and subsequent dye removal efficiency.

458 Ferrous ion is the worldwide accepted Fenton catalyst for the generation of hydroxyl  
459 radical (Oturán and Aaron, 2014). Apart from this, other forms iron like zero-valent iron  
460 ( $\text{Fe}^0$ ) and ferric ions ( $\text{Fe}^{3+}$ ) can be used as Fenton catalyst. Addition of  $\text{Fe}^{3+}$  instead of  $\text{Fe}^{2+}$   
461 undergoes the ferrous ion regeneration reaction prior to Fenton reaction.  $\text{Fe}^0$  addition leads to  
462 the production of  $\text{Fe}^{2+}$  by the reaction between hydrogen peroxide as in Eq. (22) (Fu et al.  
463 2010a). Oturan et al. (2008a) used ferric ion instead of ferrous ion for the degradation of  
464 malachite green in Pt/CF cell at pH 3. The authors observed a total decolorization within 22  
465 min and total mineralization within 540 min of electrolysis at an applied current of 200 mA.  
466 Özcan et al. (2009b) investigated the acid orange 7 removal by EF process using ferric ions  
467 and 92% of TOC removal was reported. Nidheesh and Gandhimathi (2014b) compared the  
468 RhB) removal efficiencies of  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in graphite-graphite EF system. The rate of  
469 dye removal at the optimal conditions follows the order of  $\text{Fe}^0 > \text{Fe}^{3+} > \text{Fe}^{2+}$ . But the optimum  
470 amount of Fenton's reagent followed the order of  $\text{Fe}^0 \sim \text{Fe}^{2+} > \text{Fe}^{3+}$ .

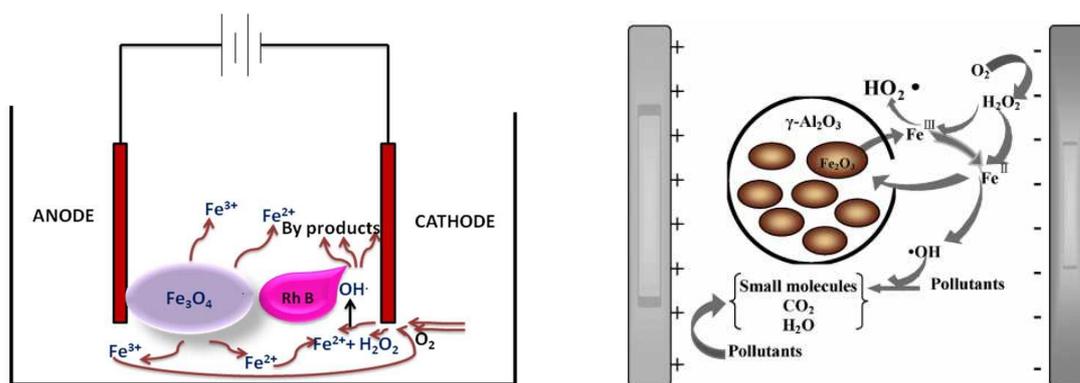


472 Persistent organic pollutant abatement using EF like process also received a great  
473 attention in recent years. The transition metals having more than one oxidation states and  
474 having a difference of unity in oxidation states can undergo Fenton like reactions as shown in  
475 Eq. (23). Various transition metals like Mn (Balci et al., 2009; George et al., 2014; Nidheesh  
476 and Gandhimathi, 2014b), Cu (Oturán et al., 2010b; George et al., 2013b; Nidheesh and  
477 Gandhimathi, 2014b), Co (Oturán et al., 2010b), Ag (Oturán et al., 2010b), Ni (George et al.,  
478 2014) etc. have been used as EF like catalyst for the abatement of various pollutants.



480 Recently, the EF related researches focused on the heterogeneous EF system (Nidheesh,  
481 2015). In this process, solid catalysts containing iron species are used as the iron source  
482 instead of ferrous salts. Heterogeneous catalyst can be reused several times for the  
483 degradation of organic pollutants. Recently Oturan and co-workers proposed EF-pyrite  
484 process and found it to be very efficient for the mineralization of various organic pollutants  
485 (Amar et al., 2015; Barhoumi et al., 2015; 2016). Labiadh et al. (2015) used this technology  
486 for the removal of 4-amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid, an azo dye  
487 from water medium and found complete mineralization of 175 mg L<sup>-1</sup> dye within 8 h of  
488 electrolysis. Nidheesh et al. (2014a) prepared magnetite by the chemical precipitation method  
489 and used for the decolorization of RhB. The authors used magnetite containing various  
490 concentrations of ferrous and ferric ions and found that the magnetite with Fe(II)/Fe(III) ratio  
491 2:1 and 1:2 has good dye removal efficiency than other catalysts. At the optimal conditions,  
492 97% of RhB was removed effectively by the heterogeneous EF process. Similarly EF  
493 oxidation of acid red 3R in the presence of Fe<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was investigated by Yue et al.  
494 (2014) and it was reported 77% dye removal within 100 min of electrolysis. Rosales et al.  
495 (2012) used Fe alginate gel beads for the removal of azure B and lissamine green B; and  
496 obtained almost complete removal of dyes from aqueous solution. Iglesias et al. (2013a) used  
497 the same catalyst for the decolorization of reactive black and lissamine green B 5 in an airlift  
498 continuous reactor. Iron loaded sepiolite was used as a heterogeneous EF catalyst for the  
499 removal of reactive black 5 in a continuous flow mode of operation (Iglesias et al., 2013b)  
500 and obtained 80 to 100% dye removal at the optimal conditions. Liang et al. (2016)  
501 investigated the effect of five metals (Cu, Ce, Mn, Fe and Co) and their loading contents on  
502 methyl orange degradation, observing the highest activity on Co/GDE and good stability  
503 toward wide pH ranges (3–9).

504 The dye removal mechanism of heterogeneous EF process is illustrated in Fig. 2. Iron  
 505 species from the heterogeneous catalyst are released into the solution and reacts with the  
 506 hydrogen peroxide produced at the cathode surface as in conventional Fenton process. In  
 507 some of the cases, the Fenton reactions may occurs at the solid catalyst surface, without the  
 508 dissolution of iron species. At these conditions the catalyst should be in suspension or  
 509 efficient mixing should be there for the effective removal of organic pollutants.

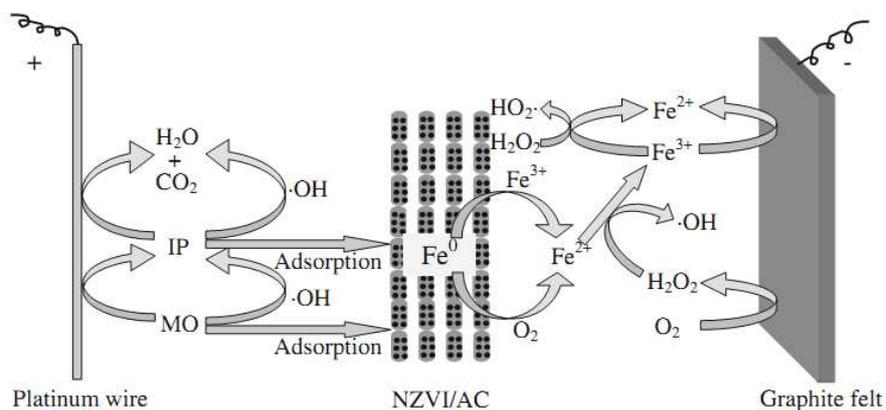


510 **Fig. 2** Dye removal mechanism of heterogeneous EF process using (a) magnetite (Nidheesh  
 511 et al., 2014d), (b)  $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  (Yue et al., 2014). Reprinted with permission from *RSC Adv.*,  
 512 Copyright 2014 RSC and *J. Ind. Eng. Chem.*, Copyright The Korean Society of Industrial and  
 513 Engineering Chemistry and Elsevier 2013, respectively.

514 Another trend in EF process is the application of three dimensional (3D) electrolytic  
 515 cells for the abatement of persistent organic pollutants. 3D EF process is similar to the  
 516 conventional two electrode system. But it contains particle electrode as the third electrode.  
 517 Particle electrode is generally a granular material, which may contain iron oxides and filled  
 518 between anode and cathode. Iron loaded inert substances and iron oxides can be used as the  
 519 particle electrode for the EF system. Polarization of the particle electrode occurs during the  
 520 electrolysis. Due to the polarization, these particles converts as a large numbers of charged  
 521 microelectrodes with anode in one surface and cathode in other surface (Zhang et al., 2013).

522 These electrodes reduce the pollutant concentration by the sorption process, increasing the  
 523 ionic strength of the electrolytic cell and supplying additional iron species in the system. In  
 524 EF process, the particle electrodes predominately act as a heterogeneous EF catalyst (Wang et  
 525 al., 2014a). Thus the efficiency of 3D EF system is higher than conventional EF system due  
 526 to its large electrode surface and higher mass transfer (Wang et al., 2008a). The COD  
 527 removal efficiency of 3D system should be 10-15% higher than that of conventional EF  
 528 system (Zhang et al., 2013).

529 Zhang et al. (2014) used nanoscale zero-valent iron/activated carbon (NZVI/AC) as a  
 530 heterogeneous Fenton catalyst in 3D EF system for the removal of methyl orange (MO). 20-  
 531 30% of methyl orange mineralization efficiency increment was observed with the addition of  
 532 the heterogeneous Fenton catalyst. More than 80% of dye removal efficiency after 10 min of  
 533 electrolysis and 40% of TOC after 2 h of electrolysis were observed. Based on the  
 534 experimental results, the authors proposed the degradation mechanism of MO in 3D EF  
 535 system as in Fig. 3.



536  
 537 **Fig. 3** Methyl orange degradation mechanism in a 3D EF system (where, MO is methyl  
 538 orange, NZVI/AC is nanoscale zero-valent iron/activated carbon and IP is intermediate  
 539 products). Reprinted from Zhang et al. (2014), Copyright 2014, Springer-Verlag Berlin  
 540 Heidelberg.

541 [Wang et al. \(2014b\)](#) used catalytic particle electrodes derived from steel slag and  
542 manganese loaded on the particle electrodes by ultrasound impregnation calcinations  
543 approach for the removal of RhB from aqueous solution by 3D EF process containing Pt  
544 anode and stainless steel cathode. The authors observed a complete removal of dye within 50  
545 min of electrolysis. Electrolysis of real dyeing wastewater in the presence of graphite raschig  
546 rings particle electrode, Pt/Ti plate anode and graphite cathode was carried out by [Wang et al.](#)  
547 [\(2008a\)](#). The authors attained a 70.6% color removal under specific operation conditions in  
548 150 min. [Wang et al. \(2014a\)](#) used particle electrode prepared from steel slag for the removal  
549 of RhB and obtained 82.4% and 65.45% of RhB removal with and without of air supply  
550 within 60 min of electrolysis.

551 Removal of dyes from water medium using EF process under continuous flow mode  
552 was tested by [Nidheesh and Gandhimathi \(2015a, b\)](#). The authors used bubble column reactor  
553 (BCR) of capacity 3L for the removal of RhB from aqueous solution. They studied the effects  
554 of applied voltage, solution pH, catalyst concentration and inlet flow rate on the removal of  
555 dyes in continuous flow mode. At the optimal conditions, 98% of the RhB solution having an  
556 initial concentration of 50 mg L<sup>-1</sup> was removed effectively using the BCR under continuous  
557 flow mode. Similarly, EF process operated in BCR is highly efficient for the treatment of real  
558 textile wastewater ([Nidheesh and Gandhimathi, 2015b](#)). Due to the increased mass and  
559 electron transfer, flow-through EF reactor (in which solution is flow through anode and  
560 cathode) was found more energy-efficient and more pollutant removal efficiency than  
561 conventional EF reactor ([Ma et al., 2016; Ren et al., 2016](#)).

562 Even EF or related processes are very efficient for the abatement of various persistent  
563 organic pollutants from water medium; the incomplete mineralization of these pollutants may  
564 cause further environmental pollution. Some of the intermediate compounds are more toxic  
565 than their parent compounds. For example, [Le et al. \(2016\)](#) carried out the toxicity analysis

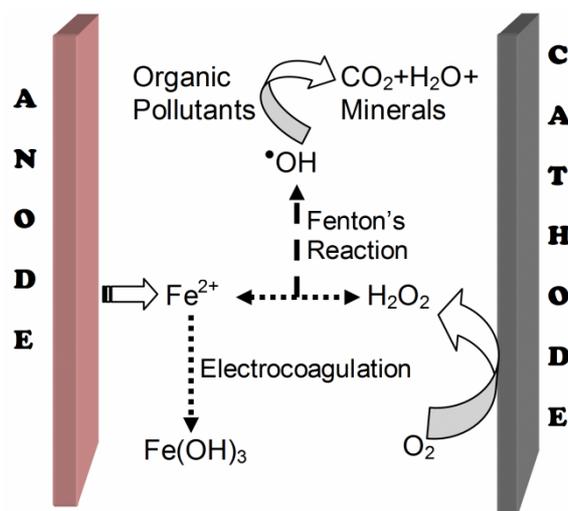
566 during the acid orange 7 degradation via EF process. In the initial periods of electrolysis, the  
567 toxicity values increased abruptly and are very much higher than that of acid orange 7. This is  
568 mainly due to the generation of more toxic intermediate products such as 1,2-naphthaquinone  
569 and 1,4-benzoquinone. The subsequent degradation of these compounds resulted in the  
570 production of carboxylic acids and decreased the toxicity values significantly. But,  
571 phytotoxicity and microbial toxicity of real textile wastewater has been reduced significantly  
572 after 1 h EF treatment (Roshini et al., 2017).

573

#### 574 **4.2 Peroxi-coagulation**

575 Peroxi-coagulation is a modified EF process which use iron or stainless steel as anode  
576 for supplying ferrous ions in water medium, instead of external ferrous ion addition as in EF  
577 process. Ferrous ions continuously generated from anode by oxidation of a sacrificial anode  
578 according to Eq. (24). In the case of use an appropriate cathode able to generate H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>  
579 supply, Fenton's reaction takes place to form <sup>•</sup>OH. With the increase in electrolysis time,  
580 ferric ions accumulates in the aqueous medium leads to the formation of Fe(OH)<sub>3</sub> precipitate.  
581 Thus, peroxi-coagulation process is a combination of EF and electrocoagulation, in which  
582 organic pollutants are removed by the attack of hydroxyl radicals (degradation process) and  
583 coagulation with iron precipitates (Brillas and Casado, 2002). This process was firstly applied  
584 for the removal of aniline from aqueous medium (Brillas et al., 1997). The overall reactions  
585 occurring in a peroxi-coagulation cell along with organic pollutants removal mechanism are  
586 shown in Fig. 4.





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**Fig. 4** Working principles of peroxi-coagulation process

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Increase in solution pH with electrolysis time is the difference in peroxi-coagulation with EF process (Venu et al., 2014, 2016). Hydrogen evolution reaction by the water reduction at the cathode surface (Eq. (25)) is the main reason behind the raise in solution pH (Drogui et al., 2008). This increase in pH increases also the rate  $\text{Fe}(\text{OH})_3$  formation and causes electrocoagulative removal of pollutants along with oxidative action Fenton's reaction. This results in a higher amount of sludge production in the electrolytic cell. Brillas and Casado (2002) observed higher pollutant removal efficiency for peroxi-coagulation than EF process for currents  $\geq 10$  A and this is mainly attributed to the effective removal of intermediate compounds formed (by the attack of hydroxyl radicals) and by coagulation (adsorption or imprisonment in  $\text{Fe}(\text{OH})_3$ ). The sludge formation in the peroxi-coagulation cell can be reduced by maintaining the solution pH to 3. At these conditions, the iron (III) concentration in the system is less than that of ferrous or ferric ions, results in Fenton's reaction to take place more efficiently.

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604

605

A few studies have been reported for the dye removal by peroxi-coagulation process. Zarei et al. (2010a) used peroxi-coagulation process for the removal of four dyes namely C.I.

606 basic red 46, C.I. basic blue 3, C.I. basic yellow 2 and malachite green from aqueous solution  
607 at pH 3 and reported about 90% of dye removal within 10 min electrolysis. [Salari et al.](#)  
608 [\(2009\)](#) reported that peroxi-coagulation process has the ability to decolorize 90% of the dye  
609 in less than 30 min and 81% mineralization of dye at 6 h. Similar results were reported by  
610 [Zarei et al. \(2009\)](#).

611 Sludge formation in peroxi-coagulation process can be reduced by regulating the  
612 solution pH to 3. [Nidheesh and Gandhimathi \(2014 d\)](#) reported that pH regulated peroxi-  
613 coagulation has higher dye removal efficiency than that of pH unregulated peroxi-coagulation  
614 process. But the authors observed scavenging effects by the addition of sodium salts  
615 containing chloride, bicarbonate, carbonate and sulphate. For maintaining the pH, the authors  
616 used sulphuric acid and regulated the solution pH to 3 at every 15 min interval. This  
617 increased the concentration of sulphate ions in the cell. By the addition of sodium salts,  
618 higher amount of sulphate salts precipitate produces (as per common ion effect according to  
619 Le Chatelier's principle) and form a layer at the cathode surface. The authors observed a  
620 white layer formation on the cathode surface after the electrolysis, and this layer contains  
621 higher amount of sodium sulphates. This layer was removed with the insertion of cathode in  
622 an acid solution. Due to this layer formation, the volume of active pores at cathode surface  
623 reduces and results in lesser hydrogen peroxide formation. This causes a reduction in dye  
624 removal efficiency by the addition of sodium salts.

625 [Nidheesh and Gandhimathi \(2014c\)](#) compared the decolorization and degradation  
626 efficiencies of EF, peroxi-coagulation (PC) and pH-regulated peroxi-coagulation (PC-pH)  
627 processes from real textile wastewater. Based on the experimental results, the authors  
628 concluded that the color and COD removal efficiency of EF process is mainly by the  
629 oxidation of pollutants and the efficiency of peroxi-coagulation is mainly by the combination  
630 of oxidation and separation processes. The authors observed a higher sludge production for

631 PC and PC-pH processes at higher pH values and concluded that the higher removal  
632 efficiencies at higher pH values is mainly by electrocoagulation process. The sludge  
633 produced from PC process was reused as a heterogeneous EF catalyst for the abatement of  
634 same real textile wastewater and observed 97% of color, 47% of COD and 33.2% TOC  
635 reductions.

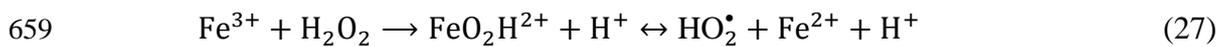
636

### 637 **4.3 Fered-Fenton and Anodic Fenton processes**

638 Fered-Fenton process is a modified form of Fenton process, in which hydrogen  
639 peroxide and ferrous ions are added externally to the electrolytic cell and then ferrous iron  
640 regenerated electrochemically from reduction of  $\text{Fe}^{3+}$  formed in Fenton's reaction (Eq. 15) for  
641 the improvement of process efficiency (Brillas et al., 2009). This process is also known as  
642 EF-Fere and is suitable for the abatement of organic pollutants with high TOC value and  
643 lower biodegradability. With the addition of hydrogen peroxide and ferrous iron salt,  
644 conventional Fenton's reaction occurs between ferrous ion and hydrogen peroxide and  $\cdot\text{OH}$   
645 produced following Fenton's reaction (Eq. 15) results in the reduction of organic loading.  
646 Further reduction of organic pollutant can be attributed to conventional Fenton process  
647 assisted by electrochemistry since Fenton's reaction is catalyzed by the regeneration of  
648 ferrous ions from the electrochemical reduction of ferric ions (Brillas et al., 2009).

649 Anodic Fenton process is a Fenton related electrochemical peroxidation process. It can  
650 be considered as a modified form of peroxi-coagulation process. One of the major  
651 disadvantages of peroxi-coagulation process is the sludge production due to the formation of  
652  $\text{Fe}(\text{OH})_3$  in excess of iron(III) in the solution. The main problem for this is the lack of  
653 sufficient quantity of hydrogen peroxide production at the cathode surface (As per  
654 conventional Fenton's reaction, the theoretical ratio of ferrous to hydrogen peroxide is 1. But

655 in peroxi-coagulation process, the concentration of ferrous ion increases and that of hydrogen  
656 peroxide comes to saturation or decreases with electrolysis time). This results in higher  
657 sludge formation and may cause scavenging reactions as given below (Brillas et al., 2009).



660 This can be reduced by the external addition of hydrogen peroxide, known as anodic Fenton  
661 process. Ghosh et al. (2012) studied the degradation of methylene blue and titan yellow dye  
662 solutions using this method (but authors mentioned it wrongly as EF process) and observed  
663 98% and 96% respective dyes removal after 60 min of electrolysis at pH 3, 1 mM of H<sub>2</sub>O<sub>2</sub>  
664 and current density of 4.31 mA cm<sup>-2</sup>. Eslami et al. (2013) compared the efficiencies of anodic  
665 Fenton process (but authors mentioned it wrongly as EF process) with conventional Fenton  
666 process for the removal of color and COD from real textile wastewater and higher removal  
667 efficiency for anodic Fenton process was observed. The decolorization and COD removal  
668 efficiencies of anodic Fenton process after 60 min of electrolysis were found as 72.9% and  
669 70.6%, respectively, within 350 mA current and externally added 1978 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>  
670 concentration. At the same time, 52.3% of color and 51.2% of COD were removed via  
671 Fenton process after 120 min of treatment at 1978 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> concentration and 250 mg L<sup>-1</sup>  
672 of ferrous ion concentration.

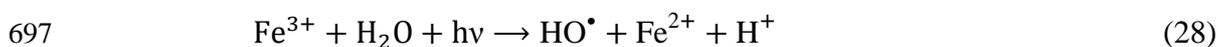
673 In order to improve the efficiency of anodic Fenton process and to reduce the negative  
674 effect of hydroxyl ions produced by the water reduction at cathode, Saltmiras and Lemley  
675 (2000) used divided electrolytic cell. Anode cell and cathode cell are connected with a salt  
676 bridge. Then the anode cell is enriched with the electrolytically generated ferrous ions and  
677 Fenton reactions occur with the external addition of hydrogen peroxide. Thus, anodic Fenton  
678 process reduces the external addition of large quantity of iron salts as in conventional Fenton

679 process and the effluent pH can be partially neutralized by combining the treated solutions  
680 from each cells (Wang and Lemley, 2002). But the scale up of anodic Fenton with a salt  
681 bridge is a little difficult task because the salt bridge requires frequent replacement of the  
682 saturated NaCl solution (Wang and Lemley, 2003). To overcome this, Lemley group  
683 developed membrane anodic Fenton process, in which an ion exchange membrane used  
684 between anode cell and cathode cell, instead of salt bridge.

685

#### 686 **4.4 Photoelectro-Fenton process**

687 A combination of UV radiation along with EF process, known as photoelectro-Fenton  
688 (PEF) process, produces more hydroxyl radicals than that in conventional EF process. This  
689 enhances the rate of dye degradation by the Fenton's reaction. The additional hydroxyl  
690 radicals are produced by the photochemical reduction of Fe<sup>3+</sup> ions from UV light irradiation  
691 as in Eq. 28 (Brillas et al., 1998 a, b; Muruganandham and Swaminathan, 2004). On the other  
692 hand the regeneration of Fe<sup>2+</sup> ions by this reaction (Eq. (28)) catalyzes also the Fenton's  
693 reaction (Eq. 15) to produce more <sup>•</sup>OH. The photolysis of *in situ* produced H<sub>2</sub>O<sub>2</sub> in the  
694 presence of UV light also produces additional <sup>•</sup>OH according to Eq. (29) (Brillas, 2014), but  
695 the amount of <sup>•</sup>OH produced by this reaction is not significant because of very low absorption  
696 coefficient of H<sub>2</sub>O<sub>2</sub>.



699 Production of hydroxyl radicals and regeneration of ferrous ions from the photodegradation  
700 of iron complexes and ferric carboxylates is another advantage of PEF over conventional EF  
701 process. The photo-reduction of ferric hydroxyl complexes especially Fe(OH)<sup>2+</sup> produces  
702 additional <sup>•</sup>OH as in Eq. 30 (Gogate and Pandit, 2004; Kavitha and Palanivelu, 2004; Brillas

703 2014). Similarly, photo-reactive ferric carboxylates also undergoes degradation process and  
704 produces additional ferrous ions and  $\cdot\text{OH}$  according to Eq. (31) (Brillas, 2014).

705 Many researchers put an interest on dye removal using PEF process. Khataee et al.  
706 (2014) compared the efficiency of EF and PEF processes for the abatement of C.I. Acid Blue  
707 5 under recirculation mode with a cathode containing multi walled carbon nanotubes. The  
708 authors observed dye removals of 98% after 60 min of electrolysis for PEF processes.  
709 Similarly, Bedolla-Guzman et al. (2016) compared the efficiencies of anodic oxidation, EF  
710 and PEF processes for the degradation of Reactive Yellow 160 dye, using BDD anode. The  
711 authors observed dye removal efficiency order as: PEF>EF>anodic oxidation. Similar results  
712 are reported by Solano et al. (2015) for the degradation of Congo red dye and El-Ghenymy et  
713 al. (2015) for the abatement of malachite green oxalate dye. Khataee et al. (2010a) used  
714 carbon nanotube-polytetrafluoroethylene cathode for the removal of C.I. basic red 46 by the  
715 oxalate catalyzed PEF process and compared its efficiency with the efficiencies of EF and  
716 PEF processes. The authors reported that oxalate catalyzed PEF process has higher dye  
717 removal efficiency than that of PEF and EF process. Abatement of  $244 \text{ mg L}^{-1}$  Acid Red 29  
718 by PEF process using BDD anode and carbon-PTFE cathode in an undivided cell was studied  
719 by Almeida et al. (2012) and observed an almost complete dye mineralization. Garcia-Segura  
720 et al. (2012) compared the Direct Yellow 4 degradation efficiencies of EF, PEF and photo-  
721 assisted EF process. Photo-assisted EF was performed by applying EF treatment for a  
722 particular time, followed by the photolysis of treated dye solution. They reported higher dye  
723 removal efficiency for PEF process (almost total mineralization). The authors also observed  
724 an equivalent dye removal capacity of PEF process for photo-assisted EF process after giving  
725 sufficient time for the EF process to produce intermediates that can be mineralized by the  
726 photolysis. Peralta-Hernández et al. (2008) compared the Orange II removal efficiencies of  
727 direct photolysis, EF and PEF processes and observed 31%, 63% and 83% of TOC removals,

728 respectively. Mineralization of Acid Red 14 by PEF process using an activated carbon fiber  
729 cathode was examined by Wang et al. (2008b) and compared its efficiency with EF process.  
730 The authors observed 60–70% mineralization efficiency for EF process and more than 94%  
731 mineralization efficiency for PEF process. Mineralization and decolorization of aqueous  
732 solution containing Acid Violet 7 and Reactive Black 5 by EF and PEF processes using a  
733 vitreous carbon electrode cathode was studied by Salazar and Ureta-Zañartu (2012) and  
734 observed more than 90% mineralization efficiency for PEF process.

735 The pseudo first order rate of dye removal by PEF process was modeled as a function  
736 of catalyst concentration, initial dye concentration, solution pH, applied current and flow rate  
737 by Khataee et al. (2014). The authors reported the rate constant as:

$$738 \quad k_{\text{app}} = 1310.4 \frac{[\text{CA}]^{0.48} I^{0.55}}{[\text{Dye}]^{1.07} \text{pH}^{1.75} Q^{0.84}} \quad (32)$$

739 where,  $k_{\text{app}}$  is the apparent rate constant following first order kinetic, CA is the catalyst  
740 concentration in mM,  $I$  is the applied current in A,  $Q$  is the flow rate in L h<sup>-1</sup>.

741 Coupling of conventional photocatalysis with PEF process received great attention in  
742 recent years. The principles of photocatalysis were explained well by various researchers  
743 (Bahemann, 2004; Girish Kumar and Gomathi Devi, 2011; Rauf et al., 2011; Lam et al.,  
744 2012). Iranifam et al. (2011) used ZnO nanoparticles as the photo catalyst for the removal of  
745 C.I. Basic Yellow 28 from aqueous solution and compared the dye removal efficiencies of  
746 ultraviolet-C (UV-C), EF, UV/ZnO, PEF and PEF/ZnO processes. The authors found the  
747 decreasing color removal efficiency order as: PEF/ZnO > PEF > UV/ZnO > EF > UV-C.  
748 Similarly, Khataee and Zarei (2011) reported the C.I. Direct Yellow 12 removal efficiency  
749 order as: PEF/ZnO > PEF > EF > UV/ZnO. Photocatalytic treatment of C.I. Acid Red 17 using  
750 immobilized TiO<sub>2</sub> nanoparticles combined with PEF process was investigated by Khataee et  
751 al. (2010b) and it was observed the color removal decreasing order as: PEF/UV/TiO<sub>2</sub> > PEF >

752 EF > UV/TiO<sub>2</sub>. The authors observed 93.7%, 85.9%, 66.8% and 20% decolorization  
753 efficiencies for PEF/UV/TiO<sub>2</sub>, PEF, EF and UV/TiO<sub>2</sub> processes respectively. Similar order  
754 was reported by [Zarei et al. \(2010b\)](#) for the removal of C.I. Basic Red 46. The authors  
755 observed 98.8% mineralization of 20 mg L<sup>-1</sup> C.I. Basic Red 46 dye at 6 h of electrolysis using  
756 PEF/TiO<sub>2</sub> process.

757

#### 758 **4.5 Solar Photoelectro-Fenton**

759 PEF process has been found as an effective tool for the abatement of dyes from water  
760 medium. But the higher energy consumption of artificial UV light used in PEF process  
761 increases the operational cost of this process ([Brillas, 2014](#)). In order to solve this  
762 disadvantage of PEF process and to increase the chance of applying this process in the real  
763 field, [Brillas' group \(Flox et al., 2007a, 2007b\)](#) proposed a modified form of PEF process,  
764 known as solar photoelectro-Fenton (SPEF) process for the degradation and removal of  
765 various organic persistent pollutants. In this process, the EF treated wastewater is irradiated  
766 with sunlight ( $\lambda > 300$  nm), instead of artificial UV light as in PEF process. Therefore, SPEF  
767 method is cheap, uses renewable energy source, high energy efficient, amenable to  
768 automation, versatile and safe ([Martínez-Huitle and Brillas, 2009](#); [Brillas, 2014](#)). It is also  
769 found that the efficiency of SPEF is higher than that of PEF process due to the greater  
770 intensity of UVA and UVB lights of sunlight which can photolyze the ferric carboxylate  
771 complexes more rapidly ([Garcia-Segura et al., 2013](#); [Brillas, 2014](#)). Also, compared to EF  
772 process, SPEF process is more potent than EF, with higher mineralization efficiency, higher  
773 current efficiency and lower energy consumption ([Salazar et al., 2011](#)). [Garcia-Segura and](#)  
774 [Brillas \(2016\)](#) compared the performance of SPEF for the degradation of monoazo, diazo and  
775 triazo dyes in water medium. Acid Orange 7, Acid Red 151 and Disperse Blue 71 were  
776 considered as the model monoazo, diazo and triazo dyes, respectively. SPEF process is very

777 much efficient for the degradation of monoazo dye with almost complete mineralization after  
778 3 h of electrolysis. At the same time, the dye degradation efficiency of SPEF is high for triazo  
779 dye than diazo dye.

780 [Ruiz et al. \(2011a\)](#) used 2.5 L flow plant for the degradation of Acid Red and Acid  
781 Yellow from water medium. The electrolytic cell was equipped with carbon-PTFE cathode  
782 and BDD anode. The solar photo-reactor having irradiated volume of 600 mL and containing  
783 mirror at bottom with a horizontal inclination of 30<sup>0</sup>. The authors observed a rapid  
784 decolorization of both dyes by the EF process, but the mineralization rate was low. This low  
785 mineralization rate of EF process is mainly due to the higher concentration of persistent  
786 carboxylic acids and their iron-complexes. But the photolysis of this electrolyzed solution  
787 leads to almost total mineralization of dye wastewater. [Ruiz et al. \(2011b\)](#) used same reactor  
788 for the removal of Acid Yellow 36 from aqueous solution and observed the similar results as  
789 explained above. Degradation of Disperse Red 1 and Disperse Yellow 3 using SPEF process  
790 was examined by [Salazar et al. \(2011\)](#) and observed total mineralization of both dyes.

791

#### 792 **4.6 Sonoelectro-Fenton:**

793 Application of ultrasound for the treatment of water and wastewater received a great  
794 attention during the recent years ([Gogate et al., 2002](#); [Sivasankar and Moholkar, 2010](#); [Bagal  
795 and Gogate, 2014](#)). Acoustic cavitation is the forcing phenomenal for the degradation of  
796 organic pollutants in the presence of ultrasound in water medium. It is the process of  
797 formation, growth, and succeeding collapse of microbubbles or cavities due to ultrasound in a  
798 water medium ([Gogate and Pandit, 2004](#)). The collapse of bubbles occurs within 50 ns, and  
799 the process is almost adiabatic ([Chakma and Moholkar, 2013](#)), results in the generation of  
800 higher pressure (in the range of 500–5,000 bar) and temperature (in the range of 1,000–

801 15,000 K) in the reactor (Suslick, 1989). Due to this cavitation phenomenon, hydroxyl  
802 radicals are formed as given below (Li et al., 2010).



804 where U refers to the application of ultrasound.

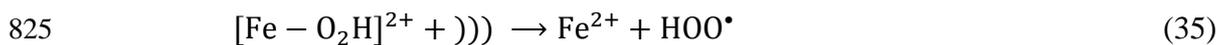
805 Addition of ultrasound in EF process, known as sonoelectro-Fenton (SEF) process  
806 (Oturán et al., 2008b), results in a higher amount of radicals in the water medium and thus  
807 higher removal efficiency than EF process. In the presence of ultrasound, the electrolytically  
808 produced hydrogen peroxide dissociated into hydroxyl radicals as:



810 Oturán et al. (2008b) reported the order of relevance of the enhancing factors in SEF  
811 process as: (1) enhanced production of hydroxyl radical and Fenton reaction kinetics by the  
812 improved mass transfer rate of both reactants (ferric ions and oxygen) towards the cathode  
813 surface for the electrochemical generation of Fenton's reagent and its transfer into the  
814 solution, (2) the additional hydroxyl radical generation by the sonolysis, and (3) pyrolysis of  
815 organics at the time of bubble explosion.

816 Li et al. (2010) observed an increased hydrogen peroxide production with the addition  
817 of ultrasound in EF cell. The hydrogen peroxide produced in SEF process is higher than the  
818 sum of hydrogen peroxide concentration produced from EF and sono Fenton processes. This  
819 improvement can be related to enhancement of mass transfer by sonolysis Oturán et al.  
820 (2008b).

821 In the presence of ultrasound, the regeneration of ferrous ions from intermediate  
822 complex produced via conventional Fenton process also occurs as in Eq. (35) (Pradhan and  
823 Gogate, 2010; Bagal and Gogate, 2014). This results in an enhancement of Fenton reactions  
824 in the electrolytic cell.



826 The arrangement of sono probe (one type of ultrasound source) and electrode also affects the  
827 efficiency of SEF process. There are three types of probe-electrode arrangement ([Compton et](#)  
828 [al., 1997](#)) in a sono-electrochemical reactor, namely face-on, side-on and sonotrode. Among  
829 this arrangement, face-on orientation has higher mass transfer capability and is depends on  
830 ultrasound power, electrode-horn distance and electrode area ([Ramachandran and Saraswathi,](#)  
831 [2011](#)). These authors also tested the efficiency of angular geometry and compared with that  
832 of face-on orientation. But the mass flux values of face-on orientation are two to three times  
833 higher than that of angular geometry. Thus, face-on geometry is the better probe-electrode  
834 arrangement in a SEF reactor. This arrangement reduces the layer formation on the cathode  
835 surface and enhances the efficiency of SEF process. Thus the enhancement in the efficiency  
836 of SEF process is mainly due to physical and chemical mechanisms ([Babuponnusami and](#)  
837 [Muthukumar, 2012](#)). Physical mechanism related to the high mixing and electrode surface  
838 cleaning by the addition of ultrasound in the EF reactor. This enhances the mass transfer  
839 between electrode and solution in addition to higher hydrogen peroxide production. The  
840 chemical mechanism is due to the additional radical formation in the cell as explained above.

841 SEF process has been found as an efficient tool for the abatement of dyes from aqueous  
842 solution. An enhancement in hydrogen peroxide production and dye removal rate with the  
843 addition of ultrasound in EF process was observed by [Li et al. \(2010b\)](#). Authors concluded  
844 that in SEF process, low frequency ultrasound has a positive effect on dye mineralization.  
845 The rate of dye removal by SEF process is 10 fold higher than that of sonolysis and 2 fold  
846 higher than that of conventional Fenton process ([Martínez and Uribe, 2012](#)). Abatement of  
847 reactive blue 19 dye using SEF process was investigated by [Siddique et al. \(2011\)](#). The  
848 authors observed an almost complete removal of dye and 56.47% of TOC from un-  
849 hydrolyzed reactive blue 19 dye solution at a frequency of 80 kHz. At the same time, 81% of

850 TOC removal was observed for hydrolyzed reactive blue 19 solution. Similar way, 85% of  
851 TOC and more than 90% of color introduced by azure B were removed efficiently by SEF  
852 process in the presence of reticulated vitreous carbon cathode and platinum gauze counter  
853 electrode (Martínez and Uribe, 2012). Oturan et al. (2008b) observed a synergistic effect in  
854 SEF process (compared to EF process) in degradation of azobenzene at low frequencies (i.e.  
855 20 and 60 80 kHz) and an improvement in degradation kinetics for early treatment times.  
856 Similarly, Şahinkaya (2013) observed a negligible increase in treatment efficiency of SEF  
857 process, when compared with the capital and operating costs of sonication. Lounis et al.  
858 (2016) examined the performance of SEF for the degradation of Orange G in various water  
859 mediums like pure water, natural water and seawater. The dye removal rate was very high in  
860 sea water medium followed by pure water and natural mineral water. Complete dye removal  
861 was observed for sea water and pure water medium, while 94% of dye removal was observed  
862 for natural mineral water medium.

863

#### 864 **4.7 Bioelectro Fenton**

865 Two versions of bioelectro-Fenton were reported: (i) bioelectro-Fenton (BEF) based on  
866 bio-electrochemical reactor proposed by Zhu and Ni (2009) consisting of two cells: microbial  
867 fuel cell (MFC) containing biodegradable organic substrates and anodic Fenton treatment  
868 (AFT) cell containing pollutants to be degraded by EF process, and (ii) BEF consisting of  
869 coupling between EF process and microbial degradation (Olvera-Vargas et al., 2016a, b). EF  
870 step being utilized as pre-treatment for mineralization of beta-blocker drug metoprolol: 1 h  
871 EF pre-treatment step followed by aerobic biodegradation allowed 90% mineralization at 4  
872 days. On the other hand, Ganzenko et al., (2017) investigated the use of BEF during  
873 treatment of a pharmaceutical wastewater treatment in two scenarios: EF as both pre-

874 treatment and post-treatment of biological step and found and found first scenario more  
875 efficient.

876 [Feng et al. \(2010b\)](#) used BEF system containing anaerobic anode chamber having  
877 *Shewanella decolorationis* S12 as microorganism for the generation of electricity and carbon  
878 nanotube (CNT)/ $\gamma$ -FeOOH composite cathode for the production of hydrogen peroxide. The  
879 authors used this system for the abatement of orange II and observed a complete  
880 decolorization and mineralization of dye. A maximum power output of  $230 \text{ mW m}^{-2}$  was also  
881 obtained from the BEF system. But modification of BEF system with  
882 polypyrrole/anthraquinone-2,6-disulfonate (PPy/AQDS) conductive film boosted the  
883 performance of the system. [Feng et al. \(2010a\)](#) observed a maximum power density of  $823$   
884  $\text{mW m}^{-2}$  by the use this conductive film.

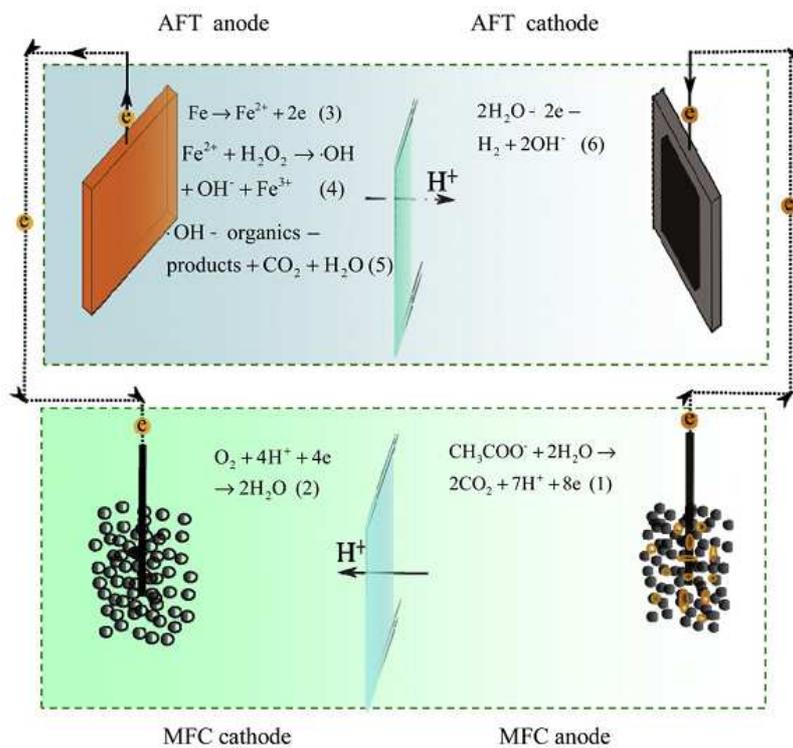
885 MFC is a “renewable energy device that converts energy available in organic  
886 compounds to electricity via the canalization of microorganisms” ([Feng et al., 2010a](#)). The  
887 biodegradable organic substance generally used in an MFC is glucose or acetate.  
888 Microorganisms present on the anode compartment oxidize these substrates and generates  
889 protons and electrons ([Zhu and Logan, 2013](#)). The electrons produced via this oxidation  
890 process flow through an external circuit to cathode. At the same time, the protons released  
891 into the solution. At the cathode surface, oxygen reacts with both proton and electron, forms  
892 water as in [Eq. \(36\)](#).



894 Besides the electricity generation, MFC have several other advantages. Self-regeneration  
895 capacity of microorganism reduces the catalyst cost in MFC compared to conventional  
896 chemical fuel cells ([Fernándezde Dios et al., 2013](#)). Absence of pollutant generation

897 (including all toxic substances) during any operations in MFC makes this cell as an  
 898 environmentally friendly energy system (Gong et al., 2011).

899 Rabaey and Rozendal, (2010) showed that a MFC can generate a voltage of 0.8 V to an  
 900 open circuit and this low-voltage electricity can be used for other electrolytic process like  
 901 hydrogen peroxide production in EF process. By this reaction, 78.85 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>  
 902 production in the cell after 12 h of electrolysis was observed by Fu et al. (2010b). This  
 903 hydrogen peroxide undergoes conventional Fenton's reaction and produces <sup>•</sup>OH. But in BEF,  
 904 the production of hydrogen peroxide requires only two-electron transfer. Thus a BEF system  
 905 generates electricity, produces <sup>•</sup>OH in cathodic compartment and causes degradation of  
 906 organic pollutants. The working principles of a BEF system are shown in Fig. 5.



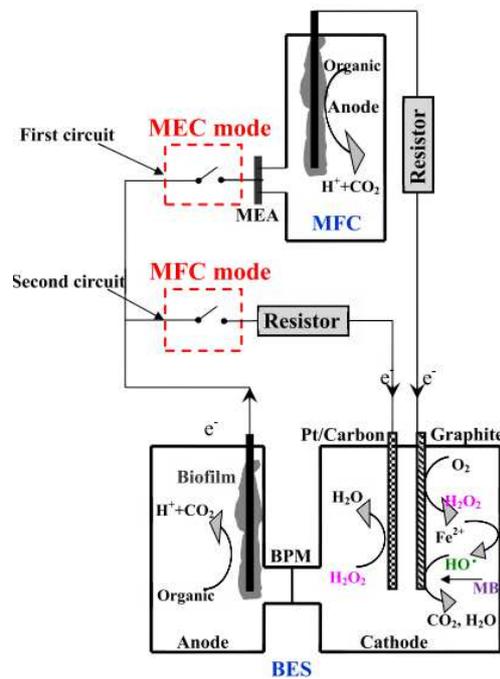
907  
 908 **Fig. 5** Energy generation and subsequent pollutant removal reactions in MFC assisted-AFT  
 909 system. Reprinted with permission from Liu et al., (2012). Copyright 2012, Elsevier.

910 Effect of MFC combined with *in situ* and *ex situ* EF processes on the abatement of dye  
911 was examined by [Fernández de Dios et al. \(2013\)](#). The authors carried out the experiments  
912 both in batch and continuous flow mode for the removal of lissamine green B and crystal  
913 violet from aqueous solution. 94% of lissamine green B and 83% of crystal violet removals  
914 were observed by the researchers after 9 h of electrolysis in MFC combined with *in situ* EF  
915 process. For this condition, respective TOC amounts of 82% and 70% were removed from the  
916 same BEF reactor respectively for lissamine green and crystal violet. At the same time more  
917 than 95% of dye removal and 85% of TOC removal were observed in a bubble column  
918 reactor used in MFC combined with *ex situ* EF process.

919 Recently, [Zhang et al. \(2015\)](#) developed a new BEF reactor capable of supplying  
920 hydrogen peroxide and eliminating its residual concentration ([Fig. 6](#)). The investigators  
921 achieved this by alternating switching between microbial electrolysis cell (MEC) and  
922 microbial fuel cell (MFC). In MEC mode of operation, degradation of pollutants occurs by  
923 the electrolytic generation of H<sub>2</sub>O<sub>2</sub> and subsequent generation of hydroxyl radicals by the  
924 reaction with ferrous ions. The residual hydrogen peroxide after the MEC mode of operation  
925 consumes during the MFC mode of operation, by using hydrogen peroxide as electron  
926 acceptor. The authors tested the efficiency of this BEF system for the abatement of 50 mg L<sup>-1</sup>  
927 methylene blue solution. Almost complete decolorization and mineralization of the dye  
928 solution were achieved after 8 h and 16 h in MEC mode of operation. The residual hydrogen  
929 peroxide concentration was observed as 180 mg L<sup>-1</sup> and this was consumed completely in  
930 MFC mode of operation within 39 h of operation.

931 Coupling EF and microbial oxidation process is effective for treating real textile  
932 wastewater ([Roshini et al., 2017](#)). Combined EF and aerobic-microaerophilic process is able  
933 to remove 86.4% COD, 85.8% color and 56.1% TOC of textile wastewater. Similarly, 82.5%

934 COD, 52.7% color and 41% TOC were removed by EF process followed by aerobic  
 935 microbial process..



936

937 **Fig. 6** BEF reactor with alternate switching, where MEC: microbial electrolysis cell; MFC:  
 938 microbial fuel cell; MEA: membrane electrode assembly; BES: bioelectrochemical system;  
 939 BPM: bipolar membrane. Reprinted with permission from Zhang et al. (2015). Copyright  
 940 2015, Elsevier

## 941 5. Scale up of EAOPs cells

942 Application of EAOPs for the abatement of dyes was largely investigated at lab scale.  
 943 A few studies were investigated even in continuous flow mode of operation, which resembles  
 944 the practical conditions for the dye wastewater treatment. The next step of investigation is  
 945 pilot scale studies for dye removal by EAOPs. The scale up of an electrolytic reactor depends  
 946 on its geometric, kinematic, current/potential and thermal similarity between the reactors  
 947 (Gupta and Oloman, 2006). Geometric similarity can be achieved by keeping the dimensional  
 948 ratios as constant. But it is not advisable to increase the inner electrode spacing. Because,  
 949 with increase in electrode spacing, the ohmic drop between electrodes increases, which

950 results in reduction in the efficiency of EAOPs. The increased spacing requires higher  
951 voltages for the optimal operation and this increases the energy consumption of the cell,  
952 consequently increases the cost of operation. Therefore, during scale up process of  
953 electrolytic reactors, geometric similarity is usually sacrificed in favor of current/potential  
954 similarity (Gupta and Oloman, 2006). Current/potential similarity is also known as electrical  
955 similarity; which can be achievable by keeping constant differences in electrode potential and  
956 current density (Goodridge and Scott, 1994). This can be achieved by keeping a constant  
957 inner electrode gap during scale up process. The kinematic similarity depends on the inlet  
958 flow rate and this similarity can be achievable by keeping same residence time or flow rate  
959 during the scale up process. Thermal similarity is another important parameter to be  
960 considered during the scale up process. Most of the lab scale works were carried out at the  
961 room temperature. But the effluents from the textile industry have the temperature near to the  
962 100 °C. Therefore, a mismatching between the lab scale efficiency and real field efficiency  
963 will occurs. Because in the case of Fenton based EAOPs, the elevated temperature decreases  
964 the stability of oxygen and hydrogen peroxide. This decreases the efficiency of EAOPs at  
965 elevated temperature.

966

## 967 **6. Conclusions and perspectives**

968 EAOPs have a great potential to remove dyes from water medium. Comparing to direct  
969 EAOPs, indirect EAOPs, especially that based on Fenton chemistry has received increased  
970 attention in the last decade. AO process, a well-known direct EAOPs, is also very efficient to  
971 remove dyes from aqueous solution. The higher cost of high oxygen over potential anode is  
972 one of the main drawbacks of this process. Various types of Fenton process based EAOPs,  
973 naming EF, PEF, SEF, peroxi-coagulation, fered Fenton, anodic Fenton etc. have been  
974 applied effectively for the removal of dyes. Total decolorization of dyes has been achieved in

975 most of the cases. But the mineralization efficiency is, in general, less than that of  
976 decolorization efficiency. This is mainly due to the less degradation rate of by-products in all  
977 the EAOPs. Ferrous ion is found as an efficient catalyst among various forms of iron for the  
978 removal of dyes in EF and related processes. EF like reactions, heterogeneous EF and 3D EF  
979 processes are the new trends in dye removal by EF based processes. The external addition of  
980 iron salt has been replaced with sacrificial iron anode in peroxi-coagulation process. But the  
981 sludge production and increased passivation rate of electrodes decreases the degradation  
982 efficiency of this process. The efficiency of EF process has been increased significantly by  
983 the addition of UV light (PEF) and ultrasound (SEF). The rate of removal of PEF and SEF  
984 processes are generally higher than that of EF process, but these latest processes are more  
985 costly because of coupling with highly energy consuming processes. The practical  
986 implementation of PEF process has been simplified by the introduction of solar energy  
987 (SPEF). Combined biological process and EAOPs is also a new trend in this field. In BEF,  
988 electricity produced from MFC has been used for the production of hydroxyl radicals. But the  
989 time taken for the removal of dyes by BEF is much higher than that of EF process.

990         Scale up of EAOPs is a global problem, even though these processes are very efficient  
991 and cheap. Electrical similarity is the major factor to be remembered during scale up  
992 operations. Since, this is very important for the real implementation of EAOPs, more works  
993 on dye removal by EAOPs in industrial scale is required. Overall, it can be concluded that  
994 EAOPs constitute a promising technology for the removal of dyes from aqueous solution.

995

996 **References**

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