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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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Abstract

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

Keywords: Dye removal, Electrochemical advanced oxidation, Decolorization, Mineralization, Hydroxyl radicals, Wastewater treatment
1. Introduction

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

The effluents containing dyes are one of the major threats to environment. Even in low concentrations, the dyes are highly visible (esthetic pollution) and affect the aquatic life and food chain (chemical pollution) (Namasivayam and Kavitha, 2002; Malik, 2003). However, the average concentration of dyes in a textile wastewater is around 300 mg L\(^{-1}\) (Couto, 2009). Disposal of this highly colored wastewater into natural water bodies hamper light penetration,
distress biological process in the water medium and provide an aesthetically displeasing appearance (Arivoli et al., 2009). Reduced light penetration with the introduction of colored wastewater reduces the photosynthetic activity within the water body and this also affect the symbiotic process (Ju et al., 2008).

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

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

The hazardous, toxic and carcinogenic natures of dyes are also well known. Physiological disorders in aquatic organisms happen by the consumption of dyes in textile effluents via food chain (Karthikeyan et al., 2006). Some of the azo dyes are responsible for causing bladder cancer in humans and chromosomal aberration in mammalian cells (Mendevedev, 1988; Percy et. al., 1989). Cytotoxicity of reactive dyes (three monochlorotriazinyl dyes: yellow, red and blue with different concentrations) using human keratinocyte HaCaT cells in vitro was investigated by Klemola et al. (2007) and the mean inhibitory concentration values after 72 h of exposure was measured as 237 µg mL$^{-1}$ for yellow dye, 155 µg mL$^{-1}$ for red dye and 278 µg mL$^{-1}$ for blue dye. Similarly, spermatozoa
motility inhibition test of these dyes showed the mean inhibitory concentration values after 24 h of exposure as 135 µg mL\(^{-1}\) for yellow dye, µg mL\(^{-1}\) for red dye and 127 µg mL\(^{-1}\) for blue dye (Klemola et al., 2006). Frame-shift mutation and base pair substitution in Salmonella in the presence of CI disperse blue was observed by Umbuzeiro et al. (2005). Experimental investigations of Bae and Freeman (2007) reported that C.I. Direct Blue 218 is very toxic to daphnids. The 50% of mortality of daphnids was observed for concentrations of 1-10 mg L\(^{-1}\) of C.I. Direct Blue 218 after 48 h. Impact of textile effluents on a proteinous edible fresh water fish Mastacembelus Armatus was examined by Karthikeyan et al. (2006) and they observed a decrease in Na\(^+\) and Cl\(^-\) concentrations and increase in K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) concentrations after 35 d of Acid Blue 92 exposure. The toxicity of the textile dye industry effluent on freshwater female crab, Spiralothelphusa hydrodroma was investigated by Sekar et al. (2009). The authors observed a decrease in protein, carbohydrate and lipid contents in ovary, spermatheca, muscle, hepatopancreas, gill, brain, thoracic ganglia and eyestalks at 30 d of sublethal (69.66 ppm) concentration of textile dye industry effluent exposure. Mathur et al. (2005) tested the mutagenic activity of seven dyes by Ames assay, using strain TA 100 of Salmonella typhimurium and reported that except violet dye, all are mutagenic. Among these mutagenic dyes, Congo red and royal blue dyes are moderately mutagenic while bordeaux is highly mutagenic or extremely mutagenic. Similarly, effect of malachite green on immune and reproductive systems was observed by Srivastava et al. (2004). The authors also observed the potential genotoxic and carcinogenic nature of the mentioned basic dye.

These non-exhaustive examples highlight how much the presence of the dyes in water is harmful to the aquatic environment. Therefore, removal of dyes from aqueous medium is an important environmental issue in the environmental safety point of view.
2. Electrochemical advanced oxidation processes for dye removal

Various treatment techniques such as adsorption, coagulation, filtration, electrocoagulation, photolysis, sonolysis, biodegradation, wet land treatment, ozonation, photocatalysis, membrane filtration etc. have been used for removing synthetic dyes from aqueous solution. Advantages and disadvantages of dye removal methods have been discussed in detail (Crini, 2006; Martinez-Huitl and Brillas, 2009; Nidheesh et al., 2013).

Based on the principle mechanism behind the removal of dyes, these processes can be divided into two broad classes: Separative (physical, and physicochemical) methods, and degradative (chemical and biological) methods. The schematic diagram of the various methods used for the dye removal is shown in Fig. 1. Most of the methods used for dye removal are separation process and the main disadvantage of these processes is the disposal of dye containing sludge as in coagulation process, dye sorbed adsorbents and concentrated dye solution as in membrane processes. In contrary to this, complex dye compounds undergo a series of degradation in chemical degradation methods. In the case of use of advanced oxidation processes, degradation procedure advance until ultimate oxidation degree, i.e. mineralization of organic pollutants. These methods produce carbon dioxide, water and various inorganic ions (following heteroatoms presents at the starting organic pollutants) as the final products.
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 (·OH). This radical is the second most powerful oxidizing agent (after fluorine) with a redox potential of $E^\circ (\cdot \text{OH}/\text{H}_2\text{O}) = 2.8$ 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
generated oxidizing agents (’OH, HO$_2^\cdot$, H$_2$O$_2$...) until the complete mineralization of organic pollutants.

\[ \cdot \text{OH} + \text{RX} \rightarrow \text{RX}^{\cdot \cdot} + \text{OH}^- \]  
(1)

\[ \cdot \text{OH} + \text{RH} \rightarrow \text{R}^{\cdot} + \text{H}_2\text{O} \]  
(2)

\[ \cdot \text{OH} + \text{PhX} \rightarrow \text{PhX(OH)}^{\cdot} \]  
(3)

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

\[ \text{M} + \text{H}_2\text{O} \rightarrow \text{M(}^{\cdot}\text{OH}) + \text{H}^{\cdot} + \text{e}^- \]  
(4)

with M: anode material. The production rate and extent depend on the nature (catalytic activity) of anode material, diffusion rate of organic pollutants on the active sites of anode and applied current density (Panizza and Cerisola 2009; Miled et al., 2010). The great advantage of this process is to not require the external addition of reagents for the production of hydroxyl radicals. In the case of indirect EAOPs, the generation of hydroxyl radicals is based on the Fenton chemistry including in situ electrochemical generation (electro-Fenton) or externally addition of the one of the reagent (H$_2$O$_2$ or ferrous iron) (fered-Fenton). Mostly H$_2$O$_2$ is in situ produced at the cathode thanks to the use of an adequate electrode material. Hydroxyl radicals are produced by the reaction between electrolytically generated or externally added H$_2$O$_2$ and anodically generated or externally added ferrous iron (Brillas et
Electro Fenton process constitutes an excellent example of indirect EAOPs, in which hydroxyl radicals are produced by the reaction between electrochemically *in situ* generated H$_2$O$_2$ and electrocatalytically regenerated ferrous ion.

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

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

3. **Direct EAOPs**

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

3.1 **Anodic Oxidation**

Anodic oxidation (AO) is the most popular direct EAOPs; it works based on the hydroxyl radical production at the anode surface (Panizza and Cerisola, 2009). The process is heterogeneous and hydroxyl radicals formed are adsorbed on the anode surface. They are
chemisorbed in the case of active anode like Pt or DSA and are less available. The production of hydroxyl radicals is promoted by high O₂ evolution overvoltage anodes such as boron-doped diamond (BDD) thin film anodes. In these latter cases, hydroxyl radicals are physisorbed and consequently more available for oxidation of organics. Various researchers well explained the organic pollutant degradation mechanism in AO process in the case of metal oxide (MOₓ) anodes (Comninellis, 1994; Scialdone, 2009). Heterogeneous hydroxyl radicals MOₓ(HO•) are mainly formed by the oxidation of water (Eq. (5)). The adsorbed radicals result in the production of chemisorbed oxygen (Eq. (6)) or oxygen evolution (Eq. (7)). The chemisorbed oxygen also undergoes further reaction and produces oxygen as in Eq. (8). The MOₓ(HO•) and oxygen oxidize the organic pollutant as in Eqs. (9) and (10). The surface of the anode is catalytically regenerated according to Eqs. (7)-(10).

\[
\text{MO}_x + H_2O \rightarrow \text{MO}_x(\text{HO}^\bullet) + H^+ + e^- \quad (5)
\]

\[
\text{MO}_x(\text{HO}^\bullet) \rightarrow \text{MO}_{x+1} + H^+ + e^- \quad (6)
\]

\[
\text{MO}_x(\text{HO}^\bullet) \rightarrow \text{MO}_x + H^+ + e^- + 0.5O_2 \quad (7)
\]

\[
\text{MO}_{x+1} \rightarrow \text{MO}_x + 0.5O_2 \quad (8)
\]

\[
\text{MO}_x(\text{HO}^\bullet) + RH \rightarrow \text{MO}_x + H_2O + R^\bullet \quad (9)
\]

\[
\text{MO}_{x+1} + RH \rightarrow \text{MO}_x + \text{RHO} \quad (10)
\]

There are two ways of pollutant degradation mechanism in AO process (Comninellis and Battisti, 1996): electrochemical conversion: degradation of persistent organic pollutants into biodegradable byproducts such as short-chain carboxylic acids, and electrochemical combustion or incineration (complete mineralization of organic pollutants into CO₂, H₂O and inorganic ions). Between the oxidants produced in AO electrolytic cell, MOₓ(HO•) causes the complete mineralization of the organic pollutants and the chemisorbed oxygen (MOₓ(\text{HO}•)) causes the selective oxidation of organic pollutants (Chen, 2004). This
difference in the oxidation ability of these two oxidants is mainly due to their different oxidation potentials. Overall, AO process can be defined as the direct EAOPs in which the degradation of the organic pollutants occurs mainly by the adsorbed hydroxyl radicals produced by the water oxidation in the presence of high $O_2$ overvoltage anodes.

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

In AO, selection of anode affects significantly the efficiency of the process. There are two types of anodes in AO process: active and non-active anodes. This differentiation is mainly based on the reaction of anode material with adsorbed hydroxyl radicals. In the case of active anodes, formation of higher oxides or super oxides occurs by the reaction of anode with hydroxyl radicals. This reaction happens when the anode has higher oxidation potential above the standard potential required for the oxygen evolution (Migliorini et al., 2011). The anodes like Pt, IrO$_2$, SnO$_2$ and RuO$_2$ are the examples of active anodes. On the other hand, hydroxyl radicals are physically sorbed on the non-active anodes and the mineralization of organic pollutants occurs mainly by the direct reaction of physisorbed hydroxyl radicals. These electrodes do not contribute any direct anodic reaction of organic pollutants and do not impart any catalytic site for the effective pollutant sorption (Migliorini et al., 2011). BDD electrode is the best example of non-active anodes.
Compared to active electrodes, non-active electrodes have high mineralization capacity. For example, BDD anode was found to be the best electrode for the mineralization of various persistent organic pollutants. This is mainly due to its greater $O_2$ overvoltage (which increases the hydroxyl radical production rate), its wide potential window, low background current and very low activity for $O_2$ evolution reaction (Braga et al., 2010; Migliorini et al., 2011; Oturan et al., 2012; Haidar et al., 2013). The removal of adsorbed organics on the BDD surface is also easy. In most of the cases, rinsing with appropriate solvent is required for the effective cleaning of BDD surface (Migliorini et al., 2011). The degradation of carboxylic acids by Pt is also very difficult. But the degradation of these acids is feasible with BDD anode, thanks to the efficiency of BDD($^•$OH) and also the strong oxidants such as peroxodisulfate and $O_3$ formed during oxidation process according to the following reactions (Murugananthan et al., 2007; Flox et al., 2009; Li et al., 2010a).

\[
2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (11)
\]

\[
2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad (12)
\]

\[
3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad (13)
\]

Recently a great attention has been paid to improve the efficiency of anodes by using appropriate substrate (Wang et al., 2013; Hu et al., 2014). The selection of suitable substrate is also an important parameter. A substrate should have good electrical conductivity, sufficient mechanical strength, and electrochemical inertness or easy formation of protective films on substrate surfaces by passivation (Chen et al., 2003). For example, various substrates like Si, Ti, Nb etc. were used as substrate for BDD anode. The substrate used for the BDD anode has been classically Si. But, Si is difficult to use as a substrate for electrode due to its fragile nature and its conductivity is strongly dependent on the experimental environments (Sun et al., 2011). Among the various substrates, the suitable substrate for the BDD anode
was found as Ti (Chen et al., 2003; Sun et al., 2011). Also, the O\textsubscript{2} overvoltage potential of Ti/BDD is higher than that of Si/BDD anode (Chen, 2004).

Dye removal from aqueous solution using the AO process has been studied by various researchers. Faouzi et al. (2007) reported a total degradation and mineralization of alizarin red S by AO process using BDD anode. Similarly, complete mineralization of methyl orange in the presence of \textit{in situ} microwave activated Pt was observed by Zhao et al. (2009). Color and COD removals from real textile effluents using BDD anode was studied by Martínez-Huitle et al. (2012) and they observed an effective reduction in color and COD after 15 h of electrolysis. Yavuz and Shahbazi (2012) used bipolar trickle tower reactor containing BDD anode for the removal of reactive black 5 in a continuous flow mode operation and achieved 97\% color, \sim51\% COD and 29.3\% TOC removal at the optimal conditions, along with the reduction in toxicity. The oxidation of methyl orange using BDD anode in a 3 L capacity electrolytic cell was studied by Ramírez et al. (2013) and obtained a 94\% decolorization and 63.3\% TOC removal efficiencies at the optimal conditions. Complete color and COD removals from an aqueous solution containing methylene blue in the presence of BDD anode was observed by Panizza et al. (2007). Degradation of three azoic dyes, Congo red, methyl orange, and eriochrome black T, using conductive-diamond anodes was investigated by Canizares et al. (2006) and concluded that the efficiency of the system depends only on the initial concentration of dye.

Nava et al. (2008) compared the color and COD removal efficiencies of various electrode materials for the abatement of alphazurine A dye and observed almost complete mineralization of dye with Pb/PbO\textsubscript{2} and Si/BDD electrodes, while Ti/IrO\textsubscript{2} disfavored such process. Similarly complete removal of color and COD induced by the alphazurine A using BDD anode was observed by Bensalah et al. (2009). Aquino et al. (2013) used Si/BDD anode for the degradation of reactive red 141 in a filter-press flow cell and applied response surface
methodology to determine the effects of different operating parameters on color, COD and TOC removals. The performances of Ti–Pt/β-PbO$_2$ and BDD anodes on the removal of reactive orange 16 in a filter press reactor were investigated by Andrade et al. (2009). The study concluded that even though complete dye removal is achieved by both the electrodes, BDD provided better results than Ti–Pt/β-PbO$_2$ due to less energy consumption. Abdessamad et al. (2013) compared the efficiency of monopolar and bipolar BDD electrodes for the removal of alizarin blue black B and concluded that the dye degradation efficiency of bipolar AO system is 1.2 times higher than that of monopolar AO system. Chen et al. (2003) were found that dye removal efficiency of Ti/BDD anode was higher than that of Ti/Sb$_2$O$_5$–SnO$_2$ anode. Also, Ti/BDD anode has higher dye removal efficiency in the cases of alizarin red S (Sun et al., 2011), orange II and reactive red HE-3B (Chen et al., 2003). The dye removal efficiencies of BDD and PbO$_2$ electrodes were compared by Panizza and Cerisola (2008) and observed a higher oxidation rate and higher current efficiency in the case of BDD anode than that of PbO$_2$ anode. At the same time, methyl orange degradation efficiency of TiRuSnO$_2$ is very much less than that of BDD and PbO$_2$ anode (Labiadh et al., 2016). Partial removal of the dye was achieved by using TiRuSnO$_2$ anode, but complete dye removal was also observed with other anodes. Even though, both anodes are efficient for the complete dye removal, complete mineralization was occurred only in the presence of BDD anode.

Yao et al. (2013) prepared PbO$_2$-ZrO$_2$ nanocomposite electrodes by pulse electrodeposition and used it for the removal of methylene blue. The authors observed a 100% dye and 72.7% COD removal after 120 min of electrolysis. Similarly, An et al. (2012) synthesized TiO$_2$-NTs/Sb–SnO$_2$/PbO$_2$ anode for the abatement of C.I. reactive blue 194 and reported that the prepared electrode has a high decolorization and mineralization ability. Recent study by do Vale-Júnior et al. (2016) demonstrates that Sn-Cu-Sb alloy anode prepared by cold gas spray is very efficient for the degradation of dyes from water medium.
The authors observed complete acid blue-29 removal and mineralization after 300 min and 600 min of electrolysis, respectively.

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

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

Panizza and Cerisola (2008) observed the pH independent methyl red oxidation in the range of 3 to 7. Similarly, insignificant effect of initial solution pH on dye removal by AO process using Ti/SnO$_2$–Sb/PbO$_2$ was observed by Song et al. (2010). Similar result has been reported by Petrucci and Montanaro (2011). The authors observed that even though the color removal was affected by the change in pH, the mineralization ability of BDD anode was not altered with the solution pH.

Supporting electrolyte also plays an important role on the dye removal mechanism. Aquino et al. (2012) studied the effects of the salt (supporting electrolyte) addition for the removal of acid blue 62, reactive red 141, direct black 22, and disperse orange 29 using conductive-diamond anodes. The authors observed a mediated electrooxidation of dyes in the presence of chloride addition. At the same time, the removal of dyes by the addition of sulphate as supporting electrolyte is mainly by the attack of hydroxyl radicals, generated from BDD anode. Zhou et al. (2011a) compared the methyl orange degradation by electrochemical
oxidation using BDD and mixed metal oxide anodes and found enhanced dye removal in the
presence of NaCl, which is mainly attributed to the co-action of mediated oxidation from
active chlorine species.

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

4. Indirect EAOPs

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

4.1 Electro-Fenton (EF) process

During the last decade EF process received much attraction among other processes.
This is an economically and environmentally friendly process to remove efficiently toxic
and/or persistent organic pollutants from water. Oturan and Brillas groups reported the
principles of the EF process in the starting of 2000 (Oturan and Pinson 1995; Brillas et al.,
1996; Oturan, 2000; Brillas et al., 2000). EF process is an attractive tool and its interest is
mainly due to its high degrading effectiveness of persistent organic pollutants, fast pollutant
removal rate and environmental compatibility (Oturan et al., 2000; Brillas et al., 2009; Nidheesh et al., 2013; Sirés et al., 2014; Vasudevan and Oturan 2014).

EF process works based on the in situ electrogeneration of Fenton’s reagent, a mixture of H$_2$O$_2$ and Fe$^{2+}$ which is the origin of the Fenton's reaction (Eq. (15)) to generate hydroxyl radicals. Hydrogen peroxide is generated continuously at the cathode surface from the two electron reduction of O$_2$ in the acidic medium (Eq. (14)) (Oturan et al., 2008a; Özcan et al., 2009a; Nidheesh and Gandhimathi, 2012). Supply of oxygen near the cathode during EF treatment is required for fulfilling the continuous production of hydrogen peroxide in the electrolytic system. The addition of a catalytic amount of a ferrous salt (to produce Fe$^{2+}$ions) into the solution leads to production of $^\cdot$OH according to Fenton's reaction (Eq. (15)).

$$\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$$  \hspace{1cm} (14)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^\cdot$$ \hspace{1cm} (15)

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

$$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}({\text{OH}})^{2+} + \text{H}^+$$ \hspace{1cm} (16)

$$\text{Fe}({\text{OH}})^{2+} + e^- \rightarrow \text{Fe}^{2+} + \text{OH}^-$$ \hspace{1cm} (17)

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^\cdot$$ \hspace{1cm} (18)
(19) \[ \text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \]

(20) \[ \text{Fe}^{3+} + \text{R}^* \rightarrow \text{Fe}^{2+} + \text{R}^+ \]

where R’ is organic radical.

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

(21) \[ \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{HO}^* \]

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

Carbonaceous materials are widely used as the cathode, which is the working electrode of EF process. This is mainly due to its wide range of electrochemical activity for $\text{O}_2$ reduction and low catalytic activity for $\text{H}_2\text{O}_2$ decomposition (Panizza and Cerisola, 2001). Also, the porosity of carbonaceous material is very high, in particular 3D carbon materials like carbon felt or graphite felt are of high porosity. These pores are useful for the sorption of oxygen gas supplied near the cathode surface and consequently results in higher amount of hydrogen peroxide generation. Various carbonaceous materials like carbon-felt (Oturán, 2000; Murati et al., 2012), reticulated vitreous carbon sheet (El-Desoky et al., 2010; Ghoneim et al., 2011), activated carbon fiber (Wang et al., 2010), graphite (George et al., 2013, 2016; Nidheesh et al., 2014a), commercial graphite-felt (Khataee et al., 2009; Panizza and Oturan, 2011) and chemically or electrochemically modified graphite felt (Zhou et al., 2013, 2014), carbon sponge (Özcan et al., 2008c) etc. were used as the cathode material for the efficient electrogeneration of hydrogen peroxide in EF cell. Özcan et al. (2008c) compared the dye
degradation efficiency of carbon sponge and carbon-felt for the abatement of acidified basic blue 3 solutions and found that carbon sponge is the effective cathode than carbon felt for EF process. By analyzing the reported literatures, various forms of Pt have been used frequently as anode in EF cell for the degradation of various organic pollutants (Nidheesh and Gandhimathi, 2012; Sopaj et al., 2015, 2016).

The efficiency of EF process increases by combining AO and EF processes. This can be achieved by the use of an O$_2$ overvoltage anode in the EF process along with the carbonaceous cathode. Oturan et al. (2012) showed that this process was able to mineralize quasi-completely the herbicide atrazine and its by-product cyanuric acid which already reported many times to be recalcitrant to hydroxyl radicals.

EF process has been proved as an efficient tool for the abatement of dyes from water medium. Nidheesh and Gandhimathi (2014a) used graphite-graphite electrolytic system for the abatement of rhodamine B (RhB) at pH 3. The authors reported that with the increase in electrode immersion depth the efficiency of the electrolytic system also increases. This is mainly due to the increased contact between cathode surface and air bubbles and the authors recommended to use bubble column reactor with lengthy electrode for the efficient removal of organic pollutants. Similarly, complete destruction of azure B and 95% TOC abatement at the end of 8 h EF treatment was observed by Olvera-Vargas et al. (2014). Almomani and Baranova (2013) analyzed the dye removal efficiencies of single and two compartment cells in the presence of stainless steel cathode and BDD anode and observed that two compartment cell is better than single cell for the removal of dyes from aqueous medium. Lahkimi et al. (2007) investigated the depollution of methylene blue, Congo red and yellow drimaren using carbon felt cathode and Pt sheet anode and observed a rapid degradation of dyes in their single and mixture solution. Almost complete mineralization of dyes also observed by Guivarch et al. (2003) and Guivarch and Oturan (2004). Similarly, 95% of the initial TOC
caused by alizarin red (Panizza and Oturan, 2011) and acid red 97 (Kayan et al., 2010) was removed effectively using the graphite-felt and carbon-felt cathodes, respectively. Diagne et al. (2014) compared the efficiencies of AO and EF processes for the removal of indigo dye and observed higher mineralization efficiency for EF process. Complete mineralization of the dye was observed within 2 h of electrolysis. Yu et al. (2015) modified graphite felt by using carbon black and PTFE; and observed 10.7 times higher H$_2$O$_2$ production compared to unmodified electrode. EF process using this modified graphite felt cathode is efficient for complete removal of 50 mg L$^{-1}$ methyl orange within 15 min and 95.7% TOC removal at 2 h electrolysis; this efficiencies being more than 4 times that of EF process operated with raw graphite felt cathode.

Apart from, solution pH, catalyst dosage, initial pollutant concentration, electrode area, applied current and inner electrode spacing; the hardness in the water also affects the efficiency of EF process significantly (dos Santos et al., 2016). The presence of magnesium and calcium in water medium reduced the dye removal efficiency of EF process for the dye ericochrome black T. This reduction in the performance of EF process is mainly related to the difficulty to break the divalent cation- ericochrome black T complex by 'OH.

Xu et al. (2014) prepared graphene doped gas diffusion electrode using modified Hummers' method and used for the removal of reactive brilliant blue in a three electrode undivided cell of volume 200 mL. The study concluded that under the optimal conditions, 80% of the dye and 33% of TOC were removed after 180 min of electrolysis by the novel electrode. Ghoneim et al. (2011) observed a complete dye removal and 97% of mineralization by EF process in an electrolytic cell of 600 mL capacity containing reticulated vitreous carbon cathode, platinum gauze anode and 0.2 mM sunset yellow FCF azo dye. Sirés et al. (2008) compared the dye removal efficiency of EF cell with carbon-felt cathode for the degradation of crystal violet (CV), fast green FCF (FCF), methyl green (MeG) and malachite
green (MG). In this study, it was observed that the absolute rate constant for their reaction with hydroxyl radicals increases in the order MeG < FCF < CV < MG. Total depollution of a dye mixture containing the above four dyes with a COD of 1000 mg L⁻¹ was also observed. Complete decolorization and approximately 85–90% mineralization of levafix red CA and levafix blue CA was observed by El-Desoky et al. (2010). Similar results were obtained in the cases of real dyeing wastewater (Wang et al., 2010), reactive blue 4 (Gözmen et al., 2009), direct orange 61 (Hammami et al., 2007), etc.

Lin et al. (2014) studied orange II removal behavior of EF process in a divided cell and reported that dye removal rate in cathodic compartment was much faster than that in anodic compartment. Scialdone et al. (2013) performed the abatement of acid orange 7 in a microfluidic reactor and reported that the process is efficient for the usage of cheaper and easier to handle graphite as cathodic material, mainly due to the sufficient oxygen production from the anode. Therefore, external addition of air or oxygen is not required for this type of reactor. Iglesias et al. (2013a) used airlift continuous reactor for the removal of reactive black 5 and lissamine green B and accomplished high decolorization percentages at high residence times. Methyl orange removal in a 3 L capacity pilot flow plant was studied by Isarain-Chávez et al. (2013) and obtained 80% of decolorization efficiency at the optimal conditions.

Nanostructured ZnO-TiO₂ thin films deposited on graphite felt anode (El-Kacemi et al., 2016) exhibited higher dye removal and mineralization efficiency. Within 60 min of electrolysis Amido black 10B dye was discolored and the mineralization efficiency of the EF process reached 91% after 6 h of electrolysis. Application of graphene based electrode material improves the efficiency of EF process in a noticeable manner (Yang et al., 2017). Graphene (Zhao et al., 2016), graphene doped graphite-PTFE (Xu et al., 2014), reduced graphene oxide coated carbon felt (Le et al., 2015), graphite felt modified with
electrochemically exfoliated graphene (Yang et al., 2017) electrodes exhibited excellent hydrogen peroxide generation potential and subsequent dye removal efficiency.

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

$$\text{Fe}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{OH}^- \quad (22)$$

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

$$\text{M}^{(n-1)} + \text{H}_2\text{O}_2 \rightarrow \text{M}^{n+} + \text{HO}^* + \text{OH}^- \quad (23)$$
Recently, the EF related researches focused on the heterogeneous EF system (Nidheesh, 2015). In this process, solid catalysts containing iron species are used as the iron source instead of ferrous salts. Heterogeneous catalyst can be reused several times for the degradation of organic pollutants. Recently Oturan and co-workers proposed EF-pyrite process and found it to be very efficient for the mineralization of various organic pollutants (Amar et al., 2015; Barhoumi et al., 2015; 2016). Labiadh et al. (2015) used this technology for the removal of 4-amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid, an azo dye from water medium and found complete mineralization of 175 mg L\(^{-1}\) dye within 8 h of electrolysis. Nidheesh et al. (2014a) prepared magnetite by the chemical precipitation method and used for the decolorization of RhB. The authors used magnetite containing various concentrations of ferrous and ferric ions and found that the magnetite with Fe(II)/Fe(III) ratio 2:1 and 1:2 has good dye removal efficiency than other catalysts. At the optimal conditions, 97\% of RhB was removed effectively by the heterogeneous EF process. Similarly EF oxidation of acid red 3R in the presence of Fe\(_2\)O\(_3\)/γ-Al\(_2\)O\(_3\) was investigated by Yue et al. (2014) and it was reported 77\% dye removal within 100 min of electrolysis. Rosales et al. (2012) used Fe alginate gel beads for the removal of azure B and lissamine green B; and obtained almost complete removal of dyes from aqueous solution. Iglesias et al. (2013a) used the same catalyst for the decolorization of reactive black and lissamine green B 5 in an airlift continuous reactor. Iron loaded sepiolite was used as a heterogeneous EF catalyst for the removal of reactive black 5 in a continuous flow mode of operation (Iglesias et al., 2013b) and obtained 80 to 100\% dye removal at the optimal conditions. Liang et al. (2016) investigated the effect of five metals (Cu, Ce, Mn, Fe and Co) and their loading contents on methyl orange degradation, observing the highest activity on Co/GDE and good stability toward wide pH ranges (3–9).
The dye removal mechanism of heterogeneous EF process is illustrated in Fig. 2. Iron species from the heterogeneous catalyst are released into the solution and reacts with the hydrogen peroxide produced at the cathode surface as in conventional Fenton process. In some of the cases, the Fenton reactions may occurs at the solid catalyst surface, without the dissolution of iron species. At these conditions the catalyst should be in suspension or efficient mixing should be there for the effective removal of organic pollutants.

![Fig. 2 Dye removal mechanism of heterogeneous EF process using (a) magnetite (Nidheesh et al., 2014d), (b) Fe$_2$O$_3$/γ-Al$_2$O$_3$ (Yue et al., 2014). Reprinted with permission from RSC Adv., Copyright 2014 RSC and J. Ind. Eng. Chem., Copyright The Korean Society of Industrial and Engineering Chemistry and Elsevier 2013, respectively.](image)

Another trend in EF process is the application of three dimensional (3D) electrolytic cells for the abatement of persistent organic pollutants. 3D EF process is similar to the conventional two electrode system. But it contains particle electrode as the third electrode. Particle electrode is generally a granular material, which may contain iron oxides and filled between anode and cathode. Iron loaded inert substances and iron oxides can be used as the particle electrode for the EF system. Polarization of the particle electrode occurs during the electrolysis. Due to the polarization, these particles converts as a large numbers of charged microelectrodes with anode in one surface and cathode in other surface (Zhang et al., 2013).
These electrodes reduce the pollutant concentration by the sorption process, increasing the ionic strength of the electrolytic cell and supplying additional iron species in the system. In EF process, the particle electrodes predominately act as a heterogeneous EF catalyst (Wang et al., 2014a). Thus the efficiency of 3D EF system is higher than conventional EF system due to its large electrode surface and higher mass transfer (Wang et al., 2008a). The COD removal efficiency of 3D system should be 10-15% higher than that of conventional EF system (Zhang et al., 2013).

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

![Fig. 3 Methyl orange degradation mechanism in a 3D EF system (where, MO is methyl orange, NZVI/AC is nanoscale zero-valent iron/activated carbon and IP is intermediate products). Reprinted from Zhang et al. (2014), Copyright 2014, Springer-Verlag Berlin Heidelberg.](image-url)
Wang et al. (2014b) used catalytic particle electrodes derived from steel slag and manganese loaded on the particle electrodes by ultrasound impregnation calcinations approach for the removal of RhB from aqueous solution by 3D EF process containing Pt anode and stainless steel cathode. The authors observed a complete removal of dye within 50 min of electrolysis. Electrolysis of real dyeing wastewater in the presence of graphite raschig rings particle electrode, Pt/Ti plate anode and graphite cathode was carried out by Wang et al. (2008a). The authors attained a 70.6% color removal under specific operation conditions in 150 min. Wang et al. (2014a) used particle electrode prepared from steel slag for the removal of RhB and obtained 82.4% and 65.45% of RhB removal with and without of air supply within 60 min of electrolysis.

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

Even EF or related processes are very efficient for the abatement of various persistent organic pollutants from water medium; the incomplete mineralization of these pollutants may cause further environmental pollution. Some of the intermediate compounds are more toxic than their parent compounds. For example, Le et al. (2016) carried out the toxicity analysis
during the acid orange 7 degradation via EF process. In the initial periods of electrolysis, the
toxicity values increased abruptly and are very much higher than that of acid orange 7. This is
mainly due to the generation of more toxic intermediate products such as 1,2-naphthaquinone
and 1,4-benzoquinone. The subsequent degradation of these compounds resulted in the
production of carboxylic acids and decreased the toxicity values significantly. But,
phytotoxicity and microbial toxicity of real textile wastewater has been reduced significantly
after 1 h EF treatment (Roshini et al., 2017).

4.2 Peroxi-coagulation

Peroxi-coagulation is a modified EF process which use iron or stainless steel as anode
for supplying ferrous ions in water medium, instead of external ferrous ion addition as in EF
process. Ferrous ions continuously generated from anode by oxidation of a sacrificial anode
according to Eq. (24). In the case of use an appropriate cathode able to generate H₂O₂ and O₂
supply, Fenton's reaction takes place to form •OH. With the increase in electrolysis time,
ferric ions accumulates in the aqueous medium leads to the formation of Fe(OH)₃ precipitate.
Thus, peroxi-coagulation process is a combination of EF and electrocoagulation, in which
organic pollutants are removed by the attack of hydroxyl radicals (degradation process) and
coagulation with iron precipitates (Brillas and Casado, 2002). This process was firstly applied
for the removal of aniline from aqueous medium (Brillas et al., 1997). The overall reactions
occurring in a peroxi-coagulation cell along with organic pollutants removal mechanism are
shown in Fig. 4.

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (24)
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 Fe(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$10 A and this is mainly attributed to the effective removal of intermediate compounds formed (by the attack of hydroxyl radicals) and by coagulation (adsorption or imprisonment in Fe(OH)$_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.

$$2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (25)

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

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

Nidheesh and Gandhimathi (2014c) compared the decolorization and degradation efficiencies of EF, peroxi-coagulation (PC) and pH-regulated peroxi-coagulation (PC-pH) processes from real textile wastewater. Based on the experimental results, the authors concluded that the color and COD removal efficiency of EF process is mainly by the oxidation of pollutants and the efficiency of peroxi-coagulation is mainly by the combination of oxidation and separation processes. The authors observed a higher sludge production for
PC and PC-pH processes at higher pH values and concluded that the higher removal efficiencies at higher pH values is mainly by electrocoagulation process. The sludge produced from PC process was reused as a heterogeneous EF catalyst for the abatement of same real textile wastewater and observed 97% of color, 47% of COD and 33.2% TOC reductions.

4.3 Fered-Fenton and Anodic Fenton processes

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

Anodic Fenton process is a Fenton related electrochemical peroxidation process. It can be considered as a modified form of peroxy-coagulation process. One of the major disadvantages of peroxy-coagulation process is the sludge production due to the formation of Fe(OH)$_3$ in excess of iron(III) in the solution. The main problem for this is the lack of sufficient quantity of hydrogen peroxide production at the cathode surface (As per conventional Fenton's reaction, the theoretical ratio of ferrous to hydrogen peroxide is 1. But
in peroxi-coagulation process, the concentration of ferrous ion increases and that of hydrogen peroxide comes to saturation or decreases with electrolysis time). This results in higher sludge formation and may cause scavenging reactions as given below \textit{(Brillas et al., 2009)}.

\begin{align}
\text{Fe}^{2+} + \text{HO}^* & \rightarrow \text{Fe}^{3+} + \text{HO}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{FeO}_2\text{H}^{2+} + \text{H}^+ \leftrightarrow \text{HO}_2^- + \text{Fe}^{2+} + \text{H}^+ 
\end{align}

This can be reduced by the external addition of hydrogen peroxide, known as anodic Fenton process. \textit{Ghosh et al. (2012)} studied the degradation of methylene blue and titan yellow dye solutions using this method (but authors mentioned it wrongly as EF process) and observed 98\% and 96\% respective dyes removal after 60 min of electrolysis at pH 3, 1 mM of H$_2$O$_2$ and current density of 4.31 mA cm$^{-2}$. \textit{Eslami et al. (2013)} compared the efficiencies of anodic Fenton process (but authors mentioned it wrongly as EF process) with conventional Fenton process for the removal of color and COD from real textile wastewater and higher removal efficiency for anodic Fenton process was observed. The decolorization and COD removal efficiencies of anodic Fenton process after 60 min of electrolysis were found as 72.9\% and 70.6\%, respectively, within 350 mA current and externally added 1978 mg L$^{-1}$ H$_2$O$_2$ concentration. At the same time, 52.3\% of color and 51.2\% of COD were removed via Fenton process after 120 min of treatment at 1978 mg L$^{-1}$ H$_2$O$_2$ concentration and 250 mg L$^{-1}$ of ferrous ion concentration.

In order to improve the efficiency of anodic Fenton process and to reduce the negative effect of hydroxyl ions produced by the water reduction at cathode, \textit{Saltmiras and Lemley (2000)} used divided electrolytic cell. Anode cell and cathode cell are connected with a salt bridge. Then the anode cell is enriched with the electrolytically generated ferrous ions and Fenton reactions occur with the external addition of hydrogen peroxide. Thus, anodic Fenton process reduces the external addition of large quantity of iron salts as in conventional Fenton
process and the effluent pH can be partially neutralized by combining the treated solutions from each cells (Wang and Lemley, 2002). But the scale up of anodic Fenton with a salt bridge is a little difficult task because the salt bridge requires frequent replacement of the saturated NaCl solution (Wang and Lemley, 2003). To overcome this, Lemley group developed membrane anodic Fenton process, in which an ion exchange membrane used between anode cell and cathode cell, instead of salt bridge.

4.4 Photoelectro-Fenton process

A combination of UV radiation along with EF process, known as photoelectro-Fenton (PEF) process, produces more hydroxyl radicals than that in conventional EF process. This enhances the rate of dye degradation by the Fenton's reaction. The additional hydroxyl radicals are produced by the photochemical reduction of Fe$^{3+}$ ions from UV light irradiation as in Eq. 28 (Brillas et al., 1998 a, b; Muruganandham and Swaminathan, 2004). On the other hand the regeneration of Fe$^{2+}$ ions by this reaction (Eq. (28)) catalyzes also the Fenton's reaction (Eq. 15) to produce more $^\cdot$OH. The photolysis of in situ produced H$_2$O$_2$ in the presence of UV light also produces additional $^\cdot$OH according to Eq. (29) (Brillas, 2014), but the amount of $^\cdot$OH produced by this reaction is not significant because of very low absorption coefficient of H$_2$O$_2$.

$$\text{Fe}^{3+} + \text{H}_2\text{O} + \nu \rightarrow \text{HO}^\cdot + \text{Fe}^{2+} + \text{H}^+ \quad (28)$$

$$\text{H}_2\text{O}_2 + \nu \rightarrow 2\text{HO}^\cdot \quad (29)$$

Production of hydroxyl radicals and regeneration of ferrous ions from the photodegradation of iron complexes and ferric carboxylates is another advantage of PEF over conventional EF process. The photo-reduction of ferric hydroxyl complexes especially Fe(OH)$^{2+}$ produces additional $^\cdot$OH as in Eq. 30 (Gogate and Pandit, 2004; Kavitha and Palanivelu, 2004; Brillas
Similarly, photo-reactive ferric carboxylates also undergoes degradation process and produces additional ferrous ions and •OH according to Eq. (31) (Brillas, 2014).

Many researchers put an interest on dye removal using PEF process. Khataee et al. (2014) compared the efficiency of EF and PEF processes for the abatement of C.I. Acid Blue 5 under recirculation mode with a cathode containing multi walled carbon nanotubes. The authors observed dye removals of 98% after 60 min of electrolysis for PEF processes. Similarly, Bedolla-Guzman et al. (2016) compared the efficiencies of anodic oxidation, EF and PEF processes for the degradation of Reactive Yellow 160 dye, using BDD anode. The authors observed dye removal efficiency order as: PEF>EF>anodic oxidation. Similar results are reported by Solano et al. (2015) for the degradation of Congo red dye and El-Ghenemy et al. (2015) for the abatement of malachite green oxalate dye. Khataee et al. (2010a) used carbon nanotube-polytetrafluoroethylene cathode for the removal of C.I. basic red 46 by the oxalate catalyzed PEF process and compared its efficiency with the efficiencies of EF and PEF processes. The authors reported that oxalate catalyzed PEF process has higher dye removal efficiency than that of PEF and EF process. Abatement of 244 mg L\(^{-1}\) Acid Red 29 by PEF process using BDD anode and carbon–PTFE cathode in an undivided cell was studied by Almeida et al. (2012) and observed an almost complete dye mineralization. Garcia-Segura et al. (2012) compared the Direct Yellow 4 degradation efficiencies of EF, PEF and photo-assisted EF process. Photo-assisted EF was performed by applying EF treatment for a particular time, followed by the photolysis of treated dye solution. They reported higher dye removal efficiency for PEF process (almost total mineralization). The authors also observed an equivalent dye removal capacity of PEF process for photo-assisted EF process after giving sufficient time for the EF process to produce intermediates that can be mineralized by the photolysis. Peralta-Hernández et al. (2008) compared the Orange II removal efficiencies of direct photolysis, EF and PEF processes and observed 31%, 63% and 83% of TOC removals,
respectively. Mineralization of Acid Red 14 by PEF process using an activated carbon fiber cathode was examined by Wang et al. (2008b) and compared its efficiency with EF process. The authors observed 60–70% mineralization efficiency for EF process and more than 94% mineralization efficiency for PEF process. Mineralization and decolorization of aqueous solution containing Acid Violet 7 and Reactive Black 5 by EF and PEF processes using a vitreous carbon electrode cathode was studied by Salazar and Ureta-Zañartu (2012) and observed more than 90% mineralization efficiency for PEF process.

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

$$k_{app} = 1310.4 \frac{[CA]^{0.48}[pH]^{0.55}}{[Dye]^{1.07}Q^{0.84}}$$

(32)

where, $k_{app}$ is the apparent rate constant following first order kinetic, CA is the catalyst concentration in mM, $I$ is the applied current in A, $Q$ is the flow rate in L h$^{-1}$.

Coupling of conventional photocatalysis with PEF process received great attention in recent years. The principles of photocatalysis were explained well by various researchers (Bahnemann, 2004; Girish Kumar and Gomathi Devi, 2011; Rauf et al., 2011; Lam et al., 2012). Iranifam et al. (2011) used ZnO nanoparticles as the photo catalyst for the removal of C.I. Basic Yellow 28 from aqueous solution and compared the dye removal efficiencies of ultraviolet-C (UV-C), EF, UV/ZnO, PEF and PEF/ZnO processes. The authors found the decreasing color removal efficiency order as: PEF/ZnO > PEF > UV/ZnO > EF > UV-C. Similarly, Khataee and Zarei (2011) reported the C.I. Direct Yellow 12 removal efficiency order as: PEF/ZnO>PEF>EF>UV/ZnO. Photocatalytic treatment of C.I. Acid Red 17 using immobilized TiO$_2$ nanoparticles combined with PEF process was investigated by Khataee et al. (2010b) and it was observed the color removal decreasing order as: PEF/UV/TiO$_2$> PEF >
The authors observed 93.7%, 85.9%, 66.8% and 20% decolorization efficiencies for PEF/UV/TiO$_2$, PEF, EF and UV/TiO$_2$ processes respectively. Similar order was reported by Zarei et al. (2010b) for the removal of C.I. Basic Red 46. The authors observed 98.8% mineralization of 20 mg L$^{-1}$ C.I. Basic Red 46 dye at 6 h of electrolysis using PEF/TiO$_2$ process.

4.5 Solar Photoelectro-Fenton

PEF process has been found as an effective tool for the abatement of dyes from water medium. But the higher energy consumption of artificial UV light used in PEF process increases the operational cost of this process (Brillas, 2014). In order to solve this disadvantage of PEF process and to increase the chance of applying this process in the real field, Brillas’ group (Flox et al., 2007a, 2007b) proposed a modified form of PEF process, known as solar photoelectro-Fenton (SPEF) process for the degradation and removal of various organic persistent pollutants. In this process, the EF treated wastewater is irradiated with sunlight ($\lambda>$300 nm), instead of artificial UV light as in PEF process. Therefore, SPEF method is cheap, uses renewable energy source, high energy efficient, amenable to automation, versatile and safe (Martínez-Huitle and Brillas, 2009; Brillas, 2014). It is also found that the efficiency of SPEF is higher than that of PEF process due to the greater intensity of UVA and UVB lights of sunlight which can photolyze the ferric carboxylate complexes more rapidly (Garcia-Segura et al., 2013; Brillas, 2014). Also, compared to EF process, SPEF process is more potent than EF, with higher mineralization efficiency, higher current efficiency and lower energy consumption (Salazar et al., 2011). Garcia-Segura and Brillas (2016) compared the performance of SPEF for the degradation of monoazo, diazo and triazo dyes in water medium. Acid Orange 7, Acid Red 151 and Disperse Blue 71 were considered as the model monoazo, diazo and triazo dyes, respectively. SPEF process is very
much efficient for the degradation of monoazo dye with almost complete mineralization after 3 h of electrolysis. At the same time, the dye degradation efficiency of SPEF is high for triazo dye than diazo dye.

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

4.6 Sonoelectro-Fenton:

Application of ultrasound for the treatment of water and wastewater received a great attention during the recent years (Gogate et al., 2002; Sivasankar and Moholkar, 2010; Bagal and Gogate, 2014). Acoustic cavitation is the forcing phenomenal for the degradation of organic pollutants in the presence of ultrasound in water medium. It is the process of formation, growth, and succeeding collapse of microbubbles or cavities due to ultrasound in a water medium (Gogate and Pandit, 2004). The collapse of bubbles occurs within 50 ns, and the process is almost adiabatic (Chakma and Moholkar, 2013), results in the generation of higher pressure (in the range of 500–5,000 bar) and temperature (in the range of 1,000–
15,000 K) in the reactor (Suslick, 1989). Due to this cavitation phenomenon, hydroxyl radicals are formed as given below (Li et al., 2010).

$$\text{H}_2\text{O} + \text{)))) \rightarrow \text{OH}^* + \text{H}^* \quad (33)$$

where )))) refers to the application of ultrasound.

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

$$\text{H}_2\text{O}_2 + \text{)))) \rightarrow 2\text{OH}^* \quad (34)$$

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

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

In the presence of ultrasound, the regeneration of ferrous ions from intermediate complex produced via conventional Fenton process also occurs as in Eq. (35) (Pradhan and Gogate, 2010; Bagal and Gogate, 2014). This results in an enhancement of Fenton reactions in the electrolytic cell.
The arrangement of sono probe (one type of ultrasound source) and electrode also affects the efficiency of SEF process. There are three types of probe-electrode arrangement (Compton et al., 1997) in a sono-electrochemical reactor, namely face-on, side-on and sonotrode. Among this arrangement, face-on orientation has higher mass transfer capability and is depends on ultrasound power, electrode-horn distance and electrode area (Ramachandran and Saraswathi, 2011). These authors also tested the efficiency of angular geometry and compared with that of face-on orientation. But the mass flux values of face-on orientation are two to three times higher than that of angular geometry. Thus, face-on geometry is the better probe-electrode arrangement in a SEF reactor. This arrangement reduces the layer formation on the cathode surface and enhances the efficiency of SEF process. Thus the enhancement in the efficiency of SEF process is mainly due to physical and chemical mechanisms (Babuponnusami and Muthukumar, 2012). Physical mechanism related to the high mixing and electrode surface cleaning by the addition of ultrasound in the EF reactor. This enhances the mass transfer between electrode and solution in addition to higher hydrogen peroxide production. The chemical mechanism is due to the additional radical formation in the cell as explained above.

SEF process has been found as an efficient tool for the abatement of dyes from aqueous solution. An enhancement in hydrogen peroxide production and dye removal rate with the addition of ultrasound in EF process was observed by Li et al. (2010b). Authors concluded that in SEF process, low frequency ultrasound has a positive effect on dye mineralization. The rate of dye removal by SEF process is 10 fold higher than that of sonolysis and 2 fold higher than that of conventional Fenton process (Martínez and Uribe, 2012). Abatement of reactive blue 19 dye using SEF process was investigated by Siddique et al. (2011). The authors observed an almost complete removal of dye and 56.47% of TOC from unhydrolyzed reactive blue 19 dye solution at a frequency of 80 kHz. At the same time, 81% of
TOC removal was observed for hydrolyzed reactive blue 19 solution. Similar way, 85% of TOC and more than 90% of color introduced by azure B were removed efficiently by SEF process in the presence of reticulated vitreous carbon cathode and platinum gauze counter electrode (Martínez and Uribe, 2012). Oturan et al. (2008b) observed a synergistic effect in SEF process (compared to EF process) in degradation of azobenzene at low frequencies (i.e. 20 and 60 80 kHz) and an improvement in degradation kinetics for early treatment times.

Similarly, Şahinkaya (2013) observed a negligible increase in treatment efficiency of SEF process, when compared with the capital and operating costs of sonication. Lounis et al. (2016) examined the performance of SEF for the degradation of Orange G in various water mediums like pure water, natural water and seawater. The dye removal rate was very high in sea water medium followed by pure water and natural mineral water. Complete dye removal was observed for sea water and pure water medium, while 94% of dye removal was observed for natural mineral water medium.

4.7 Bioelectro Fenton

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

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

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

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(36)}
\]

Besides the electricity generation, MFC have several other advantages. Self-regeneration capacity of microorganism reduces the catalyst cost in MFC compared to conventional chemical fuel cells (Fernándezde Dios et al., 2013). Absence of pollutant generation
(including all toxic substances) during any operations in MFC makes this cell as an environmentally friendly energy system (Gong et al., 2011).

Rabaey and Rozendal, (2010) showed that a MFC can generate a voltage of 0.8 V to an open circuit and this low-voltage electricity can be used for other electrolytic process like hydrogen peroxide production in EF process. By this reaction, 78.85 mg L$^{-1}$ of H$_2$O$_2$ production in the cell after 12 h of electrolysis was observed by Fu et al. (2010b). This hydrogen peroxide undergoes conventional Fenton’s reaction and produces •OH. But in BEF, the production of hydrogen peroxide requires only two-electron transfer. Thus a BEF system generates electricity, produces •OH in cathodic compartment and causes degradation of organic pollutants. The working principles of a BEF system are shown in Fig. 5.

**Fig. 5** Energy generation and subsequent pollutant removal reactions in MFC assisted-AFT system. Reprinted with permission from Liu et al., (2012). Copyright 2012, Elsevier.
Effect of MFC combined with *in situ* and *ex situ* EF processes on the abatement of dye was examined by Fernández de Dios et al. (2013). The authors carried out the experiments both in batch and continuous flow mode for the removal of lissamine green B and crystal violet from aqueous solution. 94% of lissamine green B and 83% of crystal violet removals were observed by the researchers after 9 h of electrolysis in MFC combined with *in situ* EF process. For this condition, respective TOC amounts of 82% and 70% were removed from the same BEF reactor respectively for lissamine green and crystal violet. At the same time more than 95% of dye removal and 85% of TOC removal were observed in a bubble column reactor used in MFC combined with *ex situ* EF process.

Recently, Zhang et al. (2015) developed a new BEF reactor capable of supplying hydrogen peroxide and eliminating its residual concentration (Fig. 6). The investigators achieved this by alternating switching between microbial electrolysis cell (MEC) and microbial fuel cell (MFC). In MEC mode of operation, degradation of pollutants occurs by the electrolytic generation of $\text{H}_2\text{O}_2$ and subsequent generation of hydroxyl radicals by the reaction with ferrous ions. The residual hydrogen peroxide after the MEC mode of operation consumes during the MFC mode of operation, by using hydrogen peroxide as electron acceptor. The authors tested the efficiency of this BEF system for the abatement of 50 mg L$^{-1}$ methylene blue solution. Almost complete decolorization and mineralization of the dye solution were achieved after 8 h and 16 h in MEC mode of operation. The residual hydrogen peroxide concentration was observed as 180 mg L$^{-1}$ and this was consumed completely in MFC mode of operation within 39 h of operation.

Coupling EF and microbial oxidation process is effective for treating real textile wastewater (Roshini et al., 2017). Combined EF and aerobic-microaerophilic process is able to remove 86.4% COD, 85.8% color and 56.1% TOC of textile wastewater. Similarly, 82.5%
COD, 52.7% color and 41% TOC were removed by EF process followed by aerobic microbial process..

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

### 5. Scale up of EAOPs cells

Application of EAOPs for the abatement of dyes was largely investigated at lab scale. A few studies were investigated even in continuous flow mode of operation, which resembles the practical conditions for the dye wastewater treatment. The next step of investigation is pilot scale studies for dye removal by EAOPs. The scale up of an electrolytic reactor depends on its geometric, kinematic, current/potential and thermal similarity between the reactors (Gupta and Oloman, 2006). Geometric similarity can be achieved by keeping the dimensional ratios as constant. But it is not advisable to increase the inner electrode spacing. Because, with increase in electrode spacing, the ohmic drop between electrodes increases, which
results in reduction in the efficiency of EAOPs. The increased spacing requires higher voltages for the optimal operation and this increases the energy consumption of the cell, consequently increases the cost of operation. Therefore, during scale up process of electrolytic reactors, geometric similarity is usually sacrificed in favor of current/potential similarity (Gupta and Oloman, 2006). Current/potential similarity is also known as electrical similarity; which can be achievable by keeping constant differences in electrode potential and current density (Goodridge and Scott, 1994). This can be achieved by keeping a constant inner electrode gap during scale up process. The kinematic similarity depends on the inlet flow rate and this similarity can be achievable by keeping same residence time or flow rate during the scale up process. Thermal similarity is another important parameter to be considered during the scale up process. Most of the lab scale works were carried out at the room temperature. But the effluents from the textile industry have the temperature near to the 100 °C. Therefore, a mismatching between the lab scale efficiency and real field efficiency will occurs. Because in the case of Fenton based EAOPs, the elevated temperature decreases the stability of oxygen and hydrogen peroxide. This decreases the efficiency of EAOPs at elevated temperature.

6. Conclusions and perspectives

EAOPs have a great potential to remove dyes from water medium. Comparing to direct EAOPs, indirect EAOPs, especially that based on Fenton chemistry has received increased attention in the last decade. AO process, a well-known direct EAOPs, is also very efficient to remove dyes from aqueous solution. The higher cost of high oxygen over potential anode is one of the main drawbacks of this process. Various types of Fenton process based EAOPs, naming EF, PEF, SEF, peroxi-coagulation, fered Fenton, anodic Fenton etc. have been applied effectively for the removal of dyes. Total decolorization of dyes has been achieved in
most of the cases. But the mineralization efficiency is, in general, less than that of
decolorization efficiency. This is mainly due to the less degradation rate of by-products in all
the EAOPs. Ferrous ion is found as an efficient catalyst among various forms of iron for the
removal of dyes in EF and related processes. EF like reactions, heterogeneous EF and 3D EF
processes are the new trends in dye removal by EF based processes. The external addition of
iron salt has been replaced with sacrificial iron anode in peroxi-coagulation process. But the
sludge production and increased passivation rate of electrodes decreases the degradation
efficiency of this process. The efficiency of EF process has been increased significantly by
the addition of UV light (PEF) and ultrasound (SEF). The rate of removal of PEF and SEF
processes are generally higher than that of EF process, but these latest processes are more
costly because of coupling with highly energy consuming processes. The practical
implementation of PEF process has been simplified by the introduction of solar energy
(SPEF). Combined biological process and EAOPs is also a new trend in this field. In BEF,
electricity produced from MFC has been used for the production of hydroxyl radicals. But the
time taken for the removal of dyes by BEF is much higher than that of EF process.

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