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Ravindra Kumar Gautam, Mahesh Chandra Chattopadhyaya

Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment

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3 Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment

Farshid Ghanbari and Mahsa Moradi

ABSTRACT
Dye-consuming industries, especially textile industries, are among the prime consumers of water, by which a huge proportion of the aquatic environment has been compromised due to the discharge of dyes, which are, most often, persistent and toxic. Conventional physicochemical processes cannot completely remove dyes from water and wastewater due to their complex structures. Nowadays, electrooxidation (EO) processes are proposed for the degradation of synthetic dyes. Employing electrons as the major reagent, EO processes are well known for being among clean processes. The advantages of electrochemical processes (ECPs) include environmental compatibility, versatility, amenability of automation, and high energy efficiency. These processes are classified into two main categories. First, direct EO, in which hydroxyl radicals are produced on the anode surface. The hydroxyl radical generated is a powerful oxidant that degrades dye structure. Second, indirect EO, where either oxygen- or chlorine-based oxidizing agents are electrochemically produced in the solution. Indirect EO is also divided into two processes, involving the production of an oxidizing agent (H₂O₂) at the cathode and the generation of active chlorine species at the anode. The electrogenerated H₂O₂ in the presence of a transitional metal (Fe²⁺) can produce the hydroxyl radicals in a process called electro-Fenton. This chapter presents (1) direct EO theory, principles, and various studies of dye degradation by direct EO; (2) applications of indirect EO in different conditions; and (3) advances and challenges of electrochemical oxidation in colored wastewater treatment.

Keywords: Electrochemical oxidation, Dye, Textile wastewater, Electro-Fenton, Chlorine-mediated electrooxidation

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3.1 INTRODUCTION

An urban population demands high quantities of raw materials, water, and energy, some of which turns into environmental pollution. Water is a vital substance for all creatures and its quality is crucial for the future of humankind. One of the main problems confronted by the human race is to provide clean water to the vast majority of the population around the world (Mollah et al. 2001). When consumers make use of water, it is disposed of as wastewater, most often containing a variety of substances and pollutants. Indeed, the “tragedy of the commons” arises when significant amounts of pollutants are constantly and sometimes ignorantly released into the environment, which should be a safe and sound place for all creatures, imposing extremely devastating effects and problems (Feeny et al. 1990). The use of water by humans in several industrial activities increases the amount of dissolved chemicals in water, consequently reducing water quality. Water polluted with chemicals threatens public health and the environment and increases the costs of water remediation. Among chemicals, dyes have long been utilized in dyeing, paper and pulp, textiles, plastics, leather, cosmetics, and food industries. Dyes are compounds that absorb light within the visible range, between 380 and 700 nm. They are very detectable contaminants, because of their intense color in water bodies (dos Santos et al. 2007). Dyes have complex aromatic molecular structures, making them more stable and resistant to microbial degradation (Yavuz et al. 2012). Dyes are composed of a group of atoms responsible for their color, which is called the chromophore, as well as an electron-withdrawing or donating substituent that influences the color of the chromophore, called the auxochrome (dos Santos et al. 2007). Dyes are classified based on their chemical structures, physical properties, and applications in various processes. The most important chromophores are azo (–N=N–), carbonyl (–C=O), nitro (–NO₂), and quinoid groups. Moreover, the major classification of synthetic dyes normally used includes anthraquinone, indigoide, triphenylmethyl, xanthene, azo derivatives, and so on (Panakoulias et al. 2010; Yavuz et al. 2012). Table 3.1 shows the structures of various dyes with some of their properties. Dyes can also be classified according to their usage, such as reactive, disperse, direct, vat, sulfur, cationic, acid, mordant, ingrain, and solvent dyes that are listed in the color index (C.I.) by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. The C.I. name of a dye indicates how it is used with materials and its hue, and its number specifies the chronological order of its commercial introduction (Salleh et al. 2011; Hao et al. 2000; O’Neill et al. 1999).

Since the amount of dye production in the world is not determined, the amount of discharge of residual dyes is also unknown. However, it is reported that over 700,000 t of dyes are produced per year (Hai et al. 2007). In the dyeing process, the degree of fixation of dyes in matter (especially fibers) is never complete; therefore, about 10%–15% of the dyes are lost during the dyeing process, and enter wastewater streams (Moradi et al. 2016). Hence, a large volume of wastewater containing dye is discharged into the waters that receive it. Most dyes are visible in water at even 1 mg/L concentration. Besides the aesthetic aspect and consumers’ concern, dyes reduce sunlight emission into the aquatic environment, disturbing aquatic plant life (Ghanbari et al. 2014b; Rodríguez et al. 2009). The color appearing in water bodies stemming from the arrival of dyes can also interfere with the ultraviolet (UV) disinfection processes in wastewater treatment. Moreover, they consume dissolved oxygen in water bodies, leading to the domination of anaerobic conditions, resulting in the death of fish and producing toxic smells (Sun et al. 2011; Petrucci et al. 2015). Dye precursors, including halogenated, methylated, or nitrated anilines and phenols, are listed as priority toxic pollutants. As dyes are synthesized to be stable in the cases of their chemical and photochemical properties, they are highly persistent in the environment, remaining unchanged for long periods of time (Hamza et al. 2009).

Among different groups of dyes, azo dyes are the most common synthetic dyes that are widely used in the textile industry. In fact, azo dyes make up 60%–70% of all dyes. Azo dyes contain xenobiotic substitutions, including azo, sulfonic acid, nitro, chloro, and bromo functional groups (Petrucci et al. 2015; Ramírez et al. 2013). The main concern related to azo dyes stems from the
### Table 3.1
Introduction to Some Synthetic Dyes along with Their Properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>CAS No.</th>
<th>Type of Dye</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Black 5; Remazol Black B</td>
<td>C_{36}H_{21}N_{5}Na_{4}O_{19}S_{6}</td>
<td>991.81</td>
<td>17095-24-8</td>
<td>Azo</td>
<td><img src="image1" alt="Structure 1" /></td>
</tr>
<tr>
<td>Acid Yellow 36; metanil yellow; Acid Gold Yellow G</td>
<td>C_{18}H_{14}N_{3}Na_3O_3S</td>
<td>375.38</td>
<td>587-98-4</td>
<td>Azo</td>
<td><img src="image2" alt="Structure 2" /></td>
</tr>
<tr>
<td>Acid red 1; Amido Naphthol Red G; azophloxine</td>
<td>C_{38}H_{13}N_{3}Na_{2}O_{8}S_{2}</td>
<td>509.42</td>
<td>3734-67-6</td>
<td>Azo</td>
<td><img src="image3" alt="Structure 3" /></td>
</tr>
</tbody>
</table>

(Continued)
### TABLE 3.1 (CONTINUED)

**Introduction to Some Synthetic Dyes along with Their Properties**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>CAS No.</th>
<th>Type of Dye</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange G; Acid Orange 10; Wool Orange 2G</td>
<td>( \text{C}<em>{16}\text{H}</em>{10}\text{N}<em>{2}\text{Na}</em>{2}\text{O}<em>{7}\text{S}</em>{2} )</td>
<td>452.37</td>
<td>1936-15-8</td>
<td>Azo</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>MO; Acid Orange 52; helianthin</td>
<td>( \text{C}<em>{14}\text{H}</em>{14}\text{N}<em>{3}\text{NaO}</em>{3}\text{S} )</td>
<td>327.33</td>
<td>547-58-0</td>
<td>Azo</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Rhodamine B; Basic Violet 10; Brilliant Pink B</td>
<td>( \text{C}<em>{28}\text{H}</em>{31}\text{ClN}<em>{2}\text{O}</em>{3} )</td>
<td>479.01</td>
<td>81-88-9</td>
<td>Xanthene</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>Malachite green; Basic Green 4</td>
<td>( \text{C}<em>{23}\text{H}</em>{25}\text{ClN}_{2} )</td>
<td>364.91</td>
<td>569-64-2</td>
<td>Triphenylmethane</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
</tbody>
</table>
Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment

Crystal violet; Methyl Violet

10B; Basic Violet 3

C₆H₃N₃Cl

407.98

548-62-9

Triphenylmethane

Indigo carmine; Acid Blue 74;
amacid brilliant blue

C₈H₆N₃Na₂O₆S₂

466.35

860-22-0

Indigoid

Remazol Brilliant Blue R;
Reactive Blue 19

C₂₂H₁₃N₂Na₂O₁₁S₃

626.54

2580-78-1

Anthraquinone

Alizarin Red S; acid mordant red;
Mordant Red 3

C₁₄H₇NaO₇S

342.26

130-22-3

Anthraquinone
types of precursors used in their synthesis, which appear only after the reduction and cleavage of the azo bond to aromatic amines, which are toxic and carcinogenic to humans (Jaafarzadeh et al. 2015; Pinheiro et al. 2004). With this background, it is clear why scientists and researchers have been extensively studying dyes and colored effluents. It should also be noted that the most common pollutants used in most studies are dyes, as simple models of organic pollutants.

Synthetic dyes are widely used in the textile industry, and unused dye remains in water after processing. Textile industries consume large amounts of water, organic chemicals, and salts for wet processing activities, such as dyeing and finishing of products. The average water consumption in the textile industry for the production of 1 kg final product is 60–400 L (Ali et al. 2009). Moreover, depending on the fabric’s weight, the chemicals used are from 10% to over 100% (Asghar et al. 2015). Hence, billions of liters of wastewater from the world’s textile plants are released every day. These wastewaters can contain up to 20 g of dyes, their intermediates, and salts per liter, which can cause health and environmental impacts (Singh et al. 1998). Due to the variation of products and various stages and processes undergone in a textile plant, textile wastewater is a multicomponent wastewater containing various types of pollutants. Therefore, such wastewater is characterized by strong color, high amounts of total dissolved solids (TDS), high chemical oxygen demand (COD), highly fluctuating pH (2–12), and low biodegradability, with a 5-day biochemical oxygen demand/COD of less than 0.25 (Eslami et al. 2013; Ramírez et al. 2013). The presence of synthetic dyes leads to the recalcitrance of textile effluents (Aquino et al. 2014). Within the textile industry, frequent changes of dyes used in the dyeing process induce remarkable variation in wastewater characteristics, especially in parameters such as pH, color, and COD. With this background, there are three points of importance in the case of textiles, including textile production, application, and disposal. There have been remarkable improvements within the first two sectors, while the latter is probably the least improved. In fact, the need for color-free effluent due to public concern, along with strict regulatory requirements, render dye wastewater treatment labored, considerable, and costly. Different qualities of textile wastewaters are documented in the literature. Table 3.2 illustrates some important characteristics of real textile wastewater studied in various countries being treated by the electrochemical processes.

There are various methods for treating textile wastewater and water polluted with dyes. These methods are divided into three main categories, involving biological, chemical, and physical processes (Forgacs et al. 2004; Hao et al. 2000). Biological processes include aerobic and anaerobic treatments that are economical and environmentally friendly. All researchers attempt to take advantage of biological methods. Biological treatments/processes need high reaction times, requiring huge reactors and large areas. These processes are ineffective in the treatment of dyes, which have complicated structures and low biodegradability. Moreover, biological processes cannot completely treat colored effluent due to the toxicity of dyes to the microorganisms employed in these processes. Hence, effluent treated by biological processes cannot meet discharge standards in terms of color and COD (Rocha et al. 2014). Chemical processes include various processes such as adsorption, coagulation, and advanced oxidation processes (AOPs). Typically, AOPs can be widely defined as aqueous phase oxidation techniques intermediated with highly reactive species, such as hydroxyl radicals, in the processes that result in destruction of the dyes. AOPs include the Fenton process, ozonation, photocatalysis, and wet air oxidation, which have been studied to degrade colored wastewater. With hydroxyl radicals as the main oxidative agents, complete mineralization of pollutants to carbon dioxide, water, and inorganic compounds, or at least a conversion of the organics into highly oxidized, more innocuous products, can be obtained (Asghar et al. 2015; Wang et al. 2011). Physical processes (membrane technologies) have rarely been considered for the removal of dyes and the treatment of textile wastewater, due to the high cost and potential of membrane clogging. The latter issue necessitates the cleaning and substitution of membrane modules, imposing high costs. The advantages and limitations of some processes are presented in Table 3.3. Nowadays, electrochemical oxidation opens a new perspective on the field of wastewater treatment, especially the treatment of refractory organic compounds such as dyes.
TABLE 3.2
Some Characteristics of Real Textile Wastewater in Various Countries

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>650</td>
<td>470</td>
<td>1310</td>
<td>870</td>
<td>460–1500</td>
<td>1018</td>
<td>530.7</td>
<td>1224</td>
<td>1787</td>
<td>1354</td>
<td>347</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>N/A</td>
<td>N/A</td>
<td>180</td>
<td>N/A</td>
<td>100–500</td>
<td>N/A</td>
<td>175</td>
<td>323.8</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>pH</td>
<td>10.2</td>
<td>8.8</td>
<td>6.5</td>
<td>11.0</td>
<td>9–10</td>
<td>12.4</td>
<td>8.04</td>
<td>4.8</td>
<td>7.06</td>
<td>8.84</td>
<td>8.7</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>2.70</td>
<td>7.2</td>
<td>1.26</td>
<td>2.63</td>
<td>2.1–2.9</td>
<td>5.9</td>
<td>16.3</td>
<td>2.91</td>
<td>2.8</td>
<td>1.93</td>
<td>12</td>
</tr>
<tr>
<td>Color</td>
<td>1204 (Hazen unit)</td>
<td>N/A</td>
<td>2024 ADMI</td>
<td>1340 (Pt. Co)</td>
<td>N/A</td>
<td>7504 (Hazen unit)</td>
<td>Dirty green</td>
<td>N/A</td>
<td>N/A</td>
<td>2175 ADMI</td>
<td>1100 (Pt. Co)</td>
</tr>
<tr>
<td>Total organic carbon (TOC) (mg/L)</td>
<td>N/A</td>
<td>120</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>394</td>
<td>N/A</td>
<td>N/A</td>
<td>109</td>
</tr>
</tbody>
</table>
Electrochemistry is a branch of physicochemistry whose importance is well recognized within all sciences and technologies. It deals with the charge transfer at the interface of an electrode (a semiconductor or conductor) and the electrolyte (ionic conductor). In fact, electrochemistry either uses electrical energy to bring about a chemical reaction or generates electrical energy by means of chemical action. Electrochemical processes (ECPs) include two components: reduction, which occurs at the cathode (negative electrode), and oxidation, which takes place at the anode (positive electrode) (Grimm et al. 1998).

In the last two decades, electrochemistry science has been utilized for the remediation of polluted water and wastewater. In environmental remediation, ECPs employ electrical energy to remove pollutants through chemical reactions. In fact, electron transfer is mainly responsible for removing pollutants in electrochemical reactors. Therefore, in most cases, no addition of chemicals is required for the remediation of pollutants, thus introducing the electrochemical process as a green technology. ECPs for water and wastewater treatments have many innate advantages that include:

1. Low or moderate capital cost due to operation in ambient temperature and atmospheric pressure
2. Ease of automation
3. Simple control of the reaction rate by adjusting the electrical current
4. Environmental compatibility
5. Process safety regarding operation in mild conditions (Chen 2004; Rajeshwar et al. 1994; Ghanbari et al. 2014a; Walsh 2001)

Conventional ECPs in environmental remediation are: electrocoagulation, electroreduction, electroflotation, and electrooxidation (EO). The electrocoagulation and electroflotation processes are based on the separation mechanism. In other words, dyes are concentrated in the solid phase as sludge. The electroreduction process has rarely been considered for degradation of dyes and colored effluents, because of its low efficiency and persistence of dyes in electrochemical reduction (Chen 2004; Brillas et al. 2015). EO or electrochemical oxidation processes involve methods in which one or more oxidizing agents are produced, either at the surface area of the electrode or within the bulk solution, decomposing dyes and organic pollutants to more oxidizing organics or even mineral compounds. EO processes are able to oxidize or decompose organic compounds, including dyes, through capture of one or more electrons from an organic pollutant (Anglada et al. 2009; Martínez-Huitle et al. 2006).

In this chapter, EO processes, along with configurations and mechanisms, are comprehensively discussed.

### 3.2 ELECTROCHEMICAL OXIDATION OR ELECTROOXIDATION

Regarding high efficiency and variety in procedures, electrochemical oxidation is presumably the most applicable electrochemical method for the degradation of dyes and the treatment of textile wastewater. In this method, an oxidizing agent is produced on the anode surface or bulk solution that is responsible for the degradation of dyes (Sirés et al. 2014; Ghanbari et al. 2016; Rodriguez et al. 2009).

Two main approaches of EO that have been widely applied for degrading dyes involve:

1. Anodic oxidation
2. Electrogeneration of oxidizing agents in solution

Figure 3.1 illustrates the classification of the EO processes based on this chapter’s perspective.

![Classification of EO processes](See color insert)
3.2.1 **Anodic Oxidation**

Anodic oxidation is the oxidation of organic compounds through direct electrolysis (via electron transfer) or electrogenerated hydroxyl radicals on the anode surface. These methods are comprehensively discussed within the following sections.

### 3.2.1.1 Direct Electrolysis

In this method, electron transfer is responsible for the degradation of organic compounds. In this way, organic compounds are firstly adsorbed on the anode surface, then they are oxidized to other products via electron transfer. Reaction 3.1 indicates the interaction between the anode’s surface and the organic compounds. In this reaction, S and C are representatives of the anode’s surface and the organic compound, respectively.

\[
S + C \rightarrow S - C + ne^- \rightarrow \text{Product} \quad (3.1)
\]

This reaction occurs only at potentials lower than that of oxygen evolution, which is highly dependent on the anode material. This process has rarely been applied to degrade dyes, since its removal efficiency is low. Also, a polymer layer is formed on the anode surface, decreasing catalytic activity. This action depends on the type and nature of the electrode and the organic pollutants (Panizza et al. 2009a). Moreover, due to the probable presence of chloride and sulfate ions in the electrolyte, the mechanism identification of direct electron transfer is difficult.

### 3.2.1.2 Electrogenerated Hydroxyl Radicals: Mediated Anodic Oxidation

Based on the literature, organic pollutants can be mineralized through electrolysis at potentials higher than the thermodynamic potential of oxygen evolution (1.23 V/SHE) by means of some electrodes. Various potentials for the reaction of oxygen evolution on different anodes are summarized in Table 3.4.

In this way, the oxidation of organic compounds at the anode occurs through the transfer of oxygen (originating from water) to the products. This transfer is known as the *electrochemical oxygen transfer reaction* (Reaction 3.2).

\[
\text{Organic compounds} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + n\text{H}^+ + ne^- \quad (3.2)
\]

### TABLE 3.4

<table>
<thead>
<tr>
<th>Electrode</th>
<th>V/SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$</td>
<td>1.47</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>1.52</td>
</tr>
<tr>
<td>Pt$^a$</td>
<td>1.6</td>
</tr>
<tr>
<td>Graphite$^a$</td>
<td>1.7</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>1.9</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>1.9</td>
</tr>
<tr>
<td>Boron-doped diamond (BDD)$^a$</td>
<td>2.3</td>
</tr>
</tbody>
</table>

$^a$ Conditions: 0.5 M sulfuric acid

$^b$ Conditions: 1 M sulfuric acid
To activate water for the electrochemical oxygen transfer reaction, two mechanisms have been hypothesized: (1) dissociative adsorption of water; (2) electrolytic discharge of water (Panizza 2010; Panizza et al. 2009a; Fóti et al. 1999). These mechanisms are indicated in the next subsection.

3.2.1.2.1 Dissociative Adsorption of Water
In this mechanism, water is adsorbed on the anode’s surface and a hydroxyl radical is formed on the surface of the anode.

\[
\text{MO}_x + \text{H}_2\text{O} \rightarrow \text{MO}_x(\text{HO}^+) + \text{H}^+ + e^- \tag{3.3}
\]

In the following reaction, the adsorbed hydroxyl radical interacts with the anode in such a way that a higher oxide is formed.

\[
\text{MO}_x(\text{HO}^+) \rightarrow \text{MO}_{x+1} + \text{H}^+ + e^- \tag{3.4}
\]

The redox couple of \(\text{MO}_{x+1}/\text{MO}_x\) in the electrochemical cell acts as a mediator for the oxidation of organic compounds (Reaction 3.5). This oxidation is selective, through which partial oxidation of pollutants occurs in solution. It should be noted that acidic media are necessary for degradation via mediated anodic oxidation.

\[
\text{MO}_{x+1} + \text{R} \rightarrow \text{MO}_x + \text{RO} \tag{3.5}
\]

This species is called chemisorbed active oxygen, which is formed using Pt–Ru-based electrodes with catalytic activity. The “active electrode” is defined for this mechanism. In fact, the anode material is of paramount importance in determining the mechanism of the oxidation of organics. This method has limitations in the degradation of organic pollutants, including poor degradation of simple organic pollutants or intermediates, electrode deactivation by chemosorption of carbon monoxide, and the probable occurrence of side reactions (Reaction 3.6) instead of the main reaction (Anglada et al. 2009; Kapal’ka et al. 2010; Panizza et al. 2009a; Comninellis 1994).

\[
\text{MO}_{x+1} \rightarrow \text{MO}_x + \frac{1}{2}\text{O}_2 \tag{3.6}
\]

3.2.1.2.2 Electrolytic Discharge of Water
In contrast with the first mechanism, in this mechanism, the hydroxyl radical produced has a weak interaction with the anode surface, so that it can directly react with the organic compounds. In fact, physisorbed “active oxygen” is the main agent for the degradation of organic pollutants. A physisorbed hydroxyl radical on the anode surface mineralizes the organic compounds to \(\text{CO}_2\) and water. In this mechanism, “nonactive” electrodes are considered, by which no catalytic active site is provided to directly react with the organic compounds. In other words, the anode electrode provides an inert site to remove the electrons and only oxidation of water occurs on the anode surface. Hence, nonselective oxidation of organics takes place and complete mineralization may be carried out based on Reaction 3.7.

\[
\text{MO}_x(\text{HO}^+) + \text{R} \rightarrow \text{MO}_x + \text{CO}_2 + \text{H}_2\text{O} + \text{H}^+ + e^- \tag{3.7}
\]

This reaction should compete with preventive side reactions of \(\text{O}_2\) evolution or hydrogen peroxide generation, based on Reactions 3.8 and 3.9, respectively:

\[
\text{MO}_x(\text{HO}^+) \rightarrow \text{MO}_x + \frac{1}{2}\text{O}_2 + \text{H}^+ + e^- \tag{3.8}
\]
The nonactive electrodes, thanks to their high efficiency, have been considered for water and wastewater treatment. Among the nonactive electrodes, PbO$_2$, SnO$_2$, and boron-doped diamond (BDD) are the most applicable electrodes for the degradation of organics. Looking at Table 3.4, BDD is a promising electrode with high oxidation power; its bond with the hydroxyl radical is weak. Moreover, its high stability and resistance against deactivation have persuaded scientists and researchers to pay attention to the synthesis and application of BDD in different technologies (Panizza et al. 2009a; Simond et al. 1997; Sirés et al. 2014; Comninellis 1994).

In EO processes, two mechanisms may occur simultaneously. Therefore, continued reactions occur on the anode’s surface and electrolytes in the degradation of pollutants such as dyes. The mechanism of the electrochemical oxidation of organic compounds on “active” and “nonactive” anodes is schematically presented in Figure 3.2.

It is worthwhile emphasizing that the efficiency of EO in both mechanisms depends on three factors: (1) the electrode material and its properties; (2) the amount of active oxygen produced on the anode’s surface (chemically or physically adsorbed); (3) the occurrence of the oxygen evolution reaction instead of the main reaction (hydroxyl radical production reaction) (Martínez-Huitle et al. 2006).

To assess the efficiency of ECPs, two indicators have been frequently considered for a comparison of processes: current efficiency (CE) and electrical energy consumption (EEC).

$$\text{CE} = \left(\frac{\text{COD}_0 - \text{COD}_t}{\text{FV}_e} \times 100\right)$$

where:
- COD$_0$ and COD$_t$ are chemical oxygen demands (g/L) at time $= 0$ and time $= t$, respectively
- $I$ is the applied current (A)
- $F$ is Faraday’s constant (96,485 C/mol)
- $V_e$ is the volume of electrolyte (L)
- $z = 8$ is the oxygen equivalent mass (g/eq)

![Figure 3.2](image-url)
\[
\text{EEC} = \frac{I \cdot V}{1000}
\]

(3.11)

where:
- \( I \) is the applied current (A)
- \( V \) is the applied voltage (V)

EEC can be calculated based on the COD removed (kWh/COD removed) (Brillas et al. 2015), volume of electrolyte (kWh/m\(^3\)) (Ghanbari et al. 2014c), and dye removed (kWh/dye removed) (Martínez-Huitle et al. 2009).

### 3.2.1.2.3 Dye Degradation by Pt Anode

A platinum anode is a conventional electrode for electrochemical degradation with high catalytic activity. Sanromán et al. (2004) studied the decolorization of structurally varied dyes by platinum anode. Azo dye (methyl orange [MO]), indigoide dye (indigo), polymeric (Poly R-478), and triphenylmethane (phenol red, fuchsin, crystal violet, bromophenol blue, and methyl green) were selected for the evaluation of electrochemical oxidation. The decolorization rate principally depended on the chemical structure of the dyes. Complete decolorization was first attained for bromophenol blue, followed by MO and methyl green, while the efficiency of decolorizing phenol red was 30% after 60 min of electrolysis. Accordingly, the rate constant of bromophenol blue decolorization was 30-fold more than that of phenol red.

Jović et al. (2013) used the platinum anode for degradations of Reactive Blue 52, Reactive Black 5, Reactive Green 15, and Reactive Yellow 125. Complete decolorization occurred for all dyes in less than 60 min of electrolysis. EEC for 60 min of electrolysis for all the studied dyes was 0.048–0.090 kWh/m\(^3\). The highest COD removal efficiency was obtained for Reactive Blue 52, in such a way that COD reduced from 138.5 to <30 mg/L in 20 min and at 12 V applied voltage.

Hattori et al. (2003) studied the performances of platinum and diamond electrodes in different configurations for the degradation of amaranth dyestuff. The results showed that platinum, in the role of anode, was not able to mineralize amaranth dye, while a diamond anode could significantly mineralize it. In another study, decolorization of amaranth dye was investigated using platinum wire as the anode and 1000 mV potential, by which the removal efficiencies of color, total organic carbon (TOC), and COD were 95.4%, 30%, and 35%, respectively (Fan et al. 2008). Socha et al. (2005) investigated the effect of temperature on anodic oxidation with a platinum anode in the range of 30°C–80°C. Regarding their results, it can be stated that temperature did not markedly influence dye degradation. With an increase in temperature from 30°C to 80°C, decolorization, COD, and TOC removal increased from 76.7% to 78.9%, 35.1% to 36.4%, and 13.8% to 18.7%, respectively. Decolorization of Reactive Orange 4 was also investigated, using a Ti/PtO\(_x\) anode. The results of this study indicated that decolorization was dependent on the electrolyte. In this way, chloride salt was more efficient in comparison with sulfate salt, particularly at low current densities. Solar irradiation and UV light significantly improved decolorization compared with dark conditions. The rate constants (\(k_d\)) of sunlight, UV light, and dark conditions were 0.084, 0.607, and 0.024 h\(^{-1}\) respectively (López-Grimau et al. 2006).

### 3.2.1.2.4 Dye Degradation by PbO\(_2\) Anode

Lead dioxide (PbO\(_2\)), thanks to its high oxygen evolution overpotential, can generate hydroxyl radicals as a nonactive electrode. Several studies have been conducted on the decolorization of synthetic dyes and colored wastewater using a PbO\(_2\) anode. Awad et al. (2005) investigated decolorization and degradation of two azo dyes (Acid Blue 120 and Basic Brown 4). Based on the results, the electrolyte type was remarkable in influencing the degradation and decolorization of the dyes. An NaOH electrolyte performed better compared with an H\(_2\)SO\(_4\) electrolyte. Using an H\(_2\)SO\(_4\) electrolyte, electrode
poisoning occurred as a consequence of the formation of an adherent film on the anode surface. The COD removals from Acid Blue 120 using NaOH and H₂SO₄ electrolytes were 76% and 37.5%, respectively, while the values for Basic Brown 4 were 77.5% and 45%.

Zhou and He studied the efficiency of EO on Basic Red 46 via a β-PbO₂ electrode modified with fluorine resin. The color and COD removals obtained by EO were 20.1% and 15.8%, respectively, under these conditions: 0.5 A applied current, pH 5.0, temperature 25°C, and 3 g/L Na₂SO₄. Combining wet oxidation (high temperature [160°C] and pressure [0.5 MPa]) and EO, removal efficiency increased considerably to 98.5% and 43.2% for color and COD, respectively. This combination depicted that no decay took place when the initial concentration rose from 500 to 2000 mg/L. The authors expressed that the combination of wet oxidation and EO is a suitable configuration for a wider concentration range (Zhou et al., 2007).

Ghalwa et al. (2012) studied decolorization of Reactive Orange 7 (RO7) by three lead oxide–based anodes. A carbon rod/PbO₂ anode could decolorize 97.6% of RO7 after 15 min electrolysis, while complete COD removal was achieved within 300 and 350 min of electrolysis for RO7 and real textile wastewater, respectively. Within 15 min reaction time, the decolorization efficiency of RO7 using Pb + Sn/PbO₂ + SnO₂ and Pb/PbO₂ anodes was 95.3% and 94.6%, respectively. Using Pb + Sn/PbO₂ + SnO₂ and Pb/PbO₂ anodes, further reaction time was required to achieve complete COD removal of both RO7 and real textile wastewater in comparison with the carbon rod/PbO₂ anode. Hence, the carbon rod-modified PbO₂ anode was more efficient than the other modifications.

In another study, Yahiaoui et al. (2014) used central composite design (CCD) for the optimization of Basic Yellow 28 (BY28) removal by Pb/PbO₂ anodes at pH 2. The effects of temperature, current density, initial BY28 concentration, and agitation speed on BY28 removal were examined. The optimum conditions obtained were a temperature of 60°C, current density of 8.125 mA/cm², agitation speed of 720 rpm, and initial BY28 concentration of 134 mg/L; under these conditions, 93% decolorization was attained. They also showed that after 3 h of electrolysis, biodegradability in terms of the BOD₅/COD index increased from 0.076 to 0.3, revealing that anodic oxidation with a PbO₂ anode can be used as a pretreatment before the biological processes.

Panizza and Cerisola studied methyl red degradation by anodic oxidation using a PbO₂ anode. The results indicated that to achieve 90% COD removal at 0.5, 1, 1.5, and 2 A applied current, the required reaction times were 7.6, 6.4, 5.6, and 4.3 h, respectively. The authors stated that a pH value in the range of 3.0–7.0 did not significantly affect the degradation rate. Methyl red degradation followed first-order kinetics, and the rate constant increased with an increase in applied current (Panizza et al. 2007).

### 3.3.1.2.5 Dye Degradation by DSA Anode

In 1966, Beer discovered metal oxides of titanium that were coated by the thermochemical coprecipitation method. These metal oxides include platinum-group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum). These anodes were registered under the trademark DSA®. Since that time, many applications of DSA have been observed in different industries, as some industries, such as the chlor-alkali industry, need a nonconsumable anode in the electrolyte. In the EO process, this property is an important factor, because release of metal ions into water resources can be an issue of concern from the public health point of view (Panizza 2010). Nowadays, various metal oxides and combinations of them are coated on titanium and have been used for the degradation of textile dyes. Several studies have been carried out on the decolorization of dyes by Ti/MOₙ anodes. DSA electrode applications are more related to chlorine evolution for indirect EO. For instance, many studies have explored the performance of DSA electrodes on the decolorization of Reactive Blue 4 (Carneiro et al. 2002), Reactive Red 120 (Panakoulis et al. 2010), Reactive Red 198 (Catanho et al. 2006), Reactive Blue 81 (Kusmierek et al. 2011), Orange II (Li et al. 2011), and methyl red (Morais et al. 2013).
Ciríaco et al. (2011) studied the degradation of Acid Orange 7 (AO7) by Ti/SnO$_2$-Sb$_2$O$_4$ anode. They used the following equation to determine the degree of combustion of organic pollutants in terms of combustion efficiency:

$$\eta_c = \frac{32}{12} \left( \frac{n}{4x} \right) \frac{d\text{TOC}}{d\text{COD}}$$

(3.12)

where:

- TOC and COD are given in mg/L
- $n$ is the number of electrons transferred to the electrode in the process for complete combustion of the AO7 molecule
- $x$ is the number of carbon atoms of the organic compound

The electrochemical combustion reaction of AO7 is

$$C_{16}H_{11}N_2SO_4Na + 32H_2O \rightarrow 16CO_2 + 2NH_3^+ + SO_4^{2-} + Na^+ + 67H^+ + 68e^-$$

(3.13)

Based on these equations, the value of $\eta_c$ for AO7 was 0.39 at 10 mA/cm$^2$. The combustion efficiency of AO7 was low, because the azo bond was oxidized more easily, which resulted in the reduction of COD without any reduction of TOC. The reductions of the studied parameters were as follows: TOC < COD < absorbance (230 nm) < absorbance (486 nm).

Chaiyont et al. (2013) synthesized a mixed metal oxide film coating of IrO$_2$–SnO$_2$–Sb$_2$O$_5$ supported on a titanium substrate. The performance of Ti/IrO$_2$–SnO$_2$–Sb$_2$O$_5$ was evaluated by decolorization of MO. Applying electrode potentials of 1.5 and 1.75 V, MO decolorization efficiencies were similar, achieving over 98% decolorization after 50 min of electrolysis. At a higher potential (2.0 V), decolorization decreased to 89% after 300 min of electrolysis. This reduction in decolorization can be attributed to the fact that the oxidation of water to evolve oxygen competes with hydroxyl radical generation, which is the main agent that oxidizes organic matter.

An undivided mode of the filter press reactor for electrochemical oxidation was applied by del Río et al. (2011). They used stainless steel and Ti/SnO$_2$–Sb–Pt electrodes as the cathode and anodes respectively. Reactive Orange 4 was selected to be degraded in this system under conditions of 0.8 g/L Reactive Orange 4, 0.1 M Na$_2$SO$_4$, and 125 mA/cm$^2$. The results demonstrated that TOC removal was higher than COD removal. This higher mineralization rate could be attributed to the previous oxidation of the intermediates, making them more easily mineralized. This reveals that, although more TOC removal efficiency was obtained, the remaining TOC was more difficult to oxidize because a greater number of moles of O$_2$ were required.

Shestakova et al. (2015) combined anodic oxidation (Ti/Ta$_2$O$_5$–SnO$_2$) with the sonochemical process for the decolorization of methylene blue. Using electrolysis alone, complete decolorization occurred, applying 20 mA and 3 h of electrolysis with an energy consumption of 8.46 kWh/m$^3$; while, using the sonochemical process, complete decolorization was obtained, requiring 162 kWh/m$^3$ energy in similar conditions. Combining the sonochemical and electrolysis processes, the reaction time and energy consumption were reduced to 1 h and 56.43 kWh/m$^3$, respectively. TOC removal efficiency of 38.4% was achieved after 2 h of applying a combination of sonochemical and electrolysis processes, which was 1.5 times higher compared with EO only and 10.5 times higher than the sonochemical process alone.

Duan et al. (2015) fabricated Ti/Ru–Sb–SnO$_2$ successfully by the selective potential pulse electrodeposition method in a single electrolytic solution. Dye decolorization was evaluated for various deposition cycles of Ti/Ru–Sb–SnO$_2$. Ti/Ru–Sb–SnO$_2$ with 200 deposition cycles showed the best performance in the decolorization of methylene blue, Orange II, and MO, as the rate constants of first-order kinetics were $23.0 \times 10^{-3}$, $25.1 \times 10^{-3}$, and $25.2 \times 10^{-3}$ min$^{-1}$ respectively. Moreover, the
service life of Ti/Ru–Sb–SnO$_2$ with 200 deposition cycles was 18.3 h, which was 1.54 times more than that of the control electrode.

Chen et al. (2005) compared the performances of Ti/BDD with Ti/SnO$_2$–Sb$_2$O$_5$ for COD removal of various reactive dyes. Table 3.5 shows the corresponding results. As can be seen, not only are the COD removal efficiencies of the Ti/BDD anode higher than those of Ti/SnO$_2$–Sb$_2$O$_5$, but a Ti/BDD anode also provides higher CE compared with Ti/SnO$_2$–Sb$_2$O$_5$.

In general, DSA, as the active electrode, exhibited poor efficiency in the production of hydroxyl radicals for oxidation of dyes in a nonchlorine electrolyte.

### 3.2.1.2.6 Dye Degradation by BDD Anode

BDD makes an excellent electrode with a very wide potential window in aqueous solution, low capacitance, and low background current. Recently, BDD electrodes have been attracting much attention in many sciences and technologies such as electrochemistry, analytical chemistry, environmental engineering, medical sciences, and so on. Nowadays, BDD has been stabilized as the best anode for EO of organic compounds (Brillas et al. 2015; Panizza et al. 2009a, Alfaro et al. 2006). The application of anodic oxidation with BDD for oxidation of various compounds is ever increasing. Several research groups have focused on BDD application in pollutant remediation.

The effect of current densities (30, 60, and 90 mA/cm$^2$) on Alphazurine A (AZA) removal has been studied by Bensalah and coworkers (Bensalah et al. 2009). The results indicated that complete COD removal was achieved after 10 h of electrolysis, which was independent of the current density. In contrast, CE was highly dependent on current density. Obviously, an increase in current density reduces CE. Bensalah et al. (2009) declared that the oxidation of AZA could be carried out both by direct EO and mediated oxidation. Due to the presence of sodium sulfate as the supporting electrolyte, it was also possible for persulfate to be formed during the electrolysis with the BDD anode. Persulfate is a strong oxidant that can efficiently oxidize organic compounds.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Charge (Ah/L)</th>
<th>Initial COD (mg/L)</th>
<th>Residual COD (mg/L)</th>
<th>Current Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ti/BDD</td>
<td>Ti/SnO$_2$–Sb$_2$O$_5$</td>
</tr>
<tr>
<td>Cibacron Yellow HW200</td>
<td>3.52</td>
<td>737</td>
<td>28</td>
<td>526</td>
</tr>
<tr>
<td>Cycafix Yellow FLN250</td>
<td>3.02</td>
<td>610</td>
<td>31</td>
<td>386</td>
</tr>
<tr>
<td>Cycafix Navy-Blue F2B</td>
<td>2.77</td>
<td>659</td>
<td>64</td>
<td>453</td>
</tr>
<tr>
<td>Monozol Black SGRN</td>
<td>2.52</td>
<td>710</td>
<td>78</td>
<td>451</td>
</tr>
<tr>
<td>Monozol Blue BRF-150</td>
<td>2.52</td>
<td>634</td>
<td>71</td>
<td>466</td>
</tr>
<tr>
<td>Monozol Red F3B150</td>
<td>2.39</td>
<td>654</td>
<td>72</td>
<td>425</td>
</tr>
<tr>
<td>Monozol T-blue HFG</td>
<td>4.03</td>
<td>980</td>
<td>93</td>
<td>712</td>
</tr>
<tr>
<td>Monozol Yellow F3R150</td>
<td>2.52</td>
<td>667</td>
<td>74</td>
<td>423</td>
</tr>
<tr>
<td>Procion Blue HE-RD</td>
<td>3.02</td>
<td>902</td>
<td>89</td>
<td>551</td>
</tr>
<tr>
<td>Reactive Blue R</td>
<td>2.90</td>
<td>803</td>
<td>61</td>
<td>390</td>
</tr>
<tr>
<td>Reactive Red HE-7B</td>
<td>2.52</td>
<td>402</td>
<td>19</td>
<td>216</td>
</tr>
<tr>
<td>Samafix Red S-3B</td>
<td>2.52</td>
<td>607</td>
<td>38</td>
<td>370</td>
</tr>
<tr>
<td>Samafix Yellow S-3R</td>
<td>2.52</td>
<td>440</td>
<td>50</td>
<td>277</td>
</tr>
<tr>
<td>Unicion Green S6B</td>
<td>4.03</td>
<td>711</td>
<td>8</td>
<td>484</td>
</tr>
<tr>
<td>Unicion Red S-3BF80</td>
<td>2.27</td>
<td>589</td>
<td>66</td>
<td>381</td>
</tr>
</tbody>
</table>


Note: Current density: 100 A/M$^2$; temperature: 30°C; volume 25 mL; initial dyes concentration: 1000 mg/L; initial pH: 4.70–6.73.
The authors also indicated that EEC decreased with increases in temperature and agitation speed. The EEC (kW/kg COD) values for 95% COD removal were 102.3, 92.4, and 89.6 for temperatures of 25°C, 40°C, and 60°C, respectively, under conditions of 60 mA/cm$^2$ current density, initial COD of 500 mg/L, and 0.5 M Na$_2$SO$_4$ as the supporting electrolyte.

Abdessamad et al. (2013) studied the effect of electrode arrangement on Alizarin Blue Black B (ABB) removal by anodic oxidation with BDD. The results demonstrated that the removal efficiency of a bipolar arrangement was 1.2 times higher than that of a monopolar arrangement. In addition, the electrochemical oxidation of ABB in the bipolar arrangement resulted in almost direct oxidation of ABB, while large amounts of intermediates were not accumulated. In the monopolar arrangement, the electrolysis led to the formation of different intermediates. The phytotoxicity test, in terms of the germination index, indicated that anodic oxidation can significantly detoxify ABB.

The effect of the reactor type (divided and undivided) on Orange G azo dye was studied by El-Ghenemy and coworkers (El-Ghenemy et al. 2014). They concluded that the divided reactor had a superior oxidation ability in comparison with the undivided one at constant current density. Complete color removal was observed in both systems. However, the color removal process was always more rapid in the divided reactor. At similar current densities, complete color removal was achieved in a shorter time in the divided reactor. TOC decay was also faster using the divided reactor, in such a way that total mineralization was obtained in an electrolysis time of less than 330 min at 66.7 mA/cm$^2$, while total mineralization in the undivided reactor was achieved after 420 min of electrolysis at 150 mA/cm$^2$. The dye degradation consistently followed a pseudo-first-order kinetic, and its apparent rate constant rose with an increase in the current density.

Chen and coworkers (Chen et al. 2006) investigated Orange II degradation by anodic oxidation with a Ti/BDD electrode. The results demonstrated that alkaline conditions, a high temperature, and low current density were suitable for Orange II degradation. Nevertheless, the pH value did not significantly influence system efficacy. The concentration of Na$_2$SO$_4$, as the supporting electrolyte, in the range of 1500–3000 mg/L did not influence oxidation efficiency.

Araújo et al. (2015) indicated that the type of electrolyte (Na$_2$SO$_4$, HClO$_4$, H$_3$PO$_4$, or NaCl) did not significantly affect Rhodamine B degradation by anodic oxidation using conductive-diamond electrodes (p-Si–BDD). However, applying these electrolytes, the rate constants obtained differed in such a way that NaCl had the lowest rate constant value. This result was in contrast to the results gained in other studies. This phenomenon can be attributed to Cl$_2$ generation at the BDD surface, which decreased the generation of active chlorine species. Thus, the oxidation efficiency of the dye was decreased. In the case of chloride media, chlorinated organics were formed as intermediates by the attack of ClO$^-$ on organic compounds.

Tsantaki and colleagues (Tsantaki et al. 2012) selected an actual textile wastewater sample to evaluate anodic oxidation by BDD. At optimum conditions (current density 8 mA/cm$^2$, inherent temperature, and acidic conditions), TOC removal was about 70% after 180 min of electrolysis. Compared with synthetic dyes (a sample of 17 commercial dyes), COD removal was higher in the case of the actual textile wastewater. This behavior was associated with the presence of other organic compounds in the textile wastewater that may have been oxidized more easily than the synthetic dyes. Moreover, the energy consumed was lower for the textile wastewater in comparison with the synthetic effluent (75 vs. 135 kWh/kg COD).

Another study on real textile wastewater was conducted by Martínez-Huitite et al. (2012). It was observed that an increase in temperature had a strong influence on COD removal at all current densities. Complete COD removal was achieved after 9 or 10 h of electrolysis. It was reported that adding only 5 g/L of sodium sulfate to the textile wastewater increased removal efficiency remarkably. In addition, in the presence of sodium sulfate, less time was needed to remove COD and, also, the cell potential required was lower. Hence, EEC was notably reduced. Table 3.6 presents the studies of dye removal using a BDD anode.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Dye</th>
<th>Conditions</th>
<th>Color Removal (%)</th>
<th>COD or TOC Removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Si/BDD</td>
<td>Alizarin Red S</td>
<td>Dye = 5 mM, T = 25°C, time = 300 min, j = 30 mA/cm²</td>
<td>100</td>
<td>Complete TOC removal at 28 Ah/L</td>
<td>Faouzi et al. 2007</td>
</tr>
<tr>
<td>BDD</td>
<td>Orange G</td>
<td>Dye = 0.52 mmol, pH = 3.0, T = 35°C, j = 100 mA/cm², time = 60 min</td>
<td>100</td>
<td>99 (TOC), time = 270 min</td>
<td>El-Ghenemy et al. 2014</td>
</tr>
<tr>
<td>BDD</td>
<td>Novacron Yellow C-RG</td>
<td>Dye = 200 mg/L, 0.25 M Na₂SO₄, T = 25°C, agitation speed: 400 rpm, time = 480 min, j = 30 mA/cm²</td>
<td>&gt;95</td>
<td>86 (TOC)</td>
<td>Rocha et al. 2014</td>
</tr>
<tr>
<td>BDD</td>
<td>Methyl violet</td>
<td>TOC = 100 mg/L, pH = 3, 0.05 M Na₂SO₄, T = 35°C, time = 60 min, j = 100 mA/cm²</td>
<td>100</td>
<td>100 (TOC), time = 360 min</td>
<td>Hamza et al. 2009</td>
</tr>
<tr>
<td>BDD</td>
<td>MO</td>
<td>Dye = 100 mg/L, pH = 3, 0.05 M Na₂SO₄, T = ambient, time = 138 min, j = 31 mA/cm²</td>
<td>94</td>
<td>60.3 (TOC)</td>
<td>Ramírez et al. 2013</td>
</tr>
<tr>
<td>BDD</td>
<td>Reactive Green 19</td>
<td>Dye = 100 mg/L, pH = 7, 0.05 M Na₂SO₄, T = 25°C, time = 30 min, j = 300 mA/cm²</td>
<td>20</td>
<td>50 (TOC), time = 3 h</td>
<td>Petrucci et al. 2015</td>
</tr>
<tr>
<td>BDD</td>
<td>MO</td>
<td>Dye = 50 mg/L, 0.1 M Na₂SO₄, time = 120 min, j = 50 mA/cm²</td>
<td>&gt;90</td>
<td>35.5 (COD), 25.1 (TOC)</td>
<td>Zhou et al. 2011</td>
</tr>
<tr>
<td>BDD</td>
<td>Reactive Black 5</td>
<td>Dye = 100 mg/L, pH = neutral, 0.02 M Na₂SO₄, Q = 100 mL/min, time = 50 min, j = 1 mA/cm²</td>
<td>97</td>
<td>51 (COD), 29.3 (TOC), time = 25 min</td>
<td>Yavuz et al. 2012</td>
</tr>
<tr>
<td>BDD</td>
<td>Erichrome Black T</td>
<td>Dye = 100 mg/L, pH = 4.6, 5000 mg/L Na₂SO₄, time = 120 min, j = 30 mA/cm²</td>
<td>100</td>
<td>77 (TOC) at 17 Ah/L</td>
<td>Bedoui et al. 2009</td>
</tr>
<tr>
<td>Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment</td>
<td></td>
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</tr>
<tr>
<td><strong>BDD</strong> Basic Blue 3</td>
<td>Dye = 40 mg/L, pH = 4.6, 0.02 M Na$_2$SO$_4$, T = 30°C, Q = 109.5 mL/min, time = 60 min, j = 0.875 mA/cm$^2$</td>
<td>99</td>
<td>86.7 (COD)</td>
<td>Yavuz et al. 2011</td>
<td></td>
</tr>
<tr>
<td><strong>BDD</strong> Bromoamine acid</td>
<td>Dye = 125 mg/L, pH = natural, 0.001 M Na$_2$SO$_4$, T = 30°C, Q = 550 mL/min, time = 120 min, j = 15.5 mA/cm$^2$</td>
<td>100</td>
<td>85.29 (TOC)</td>
<td>Liu et al. 2015</td>
<td></td>
</tr>
<tr>
<td>p-Si/BDD Methylene blue</td>
<td>Dye = 58 mg/L, pH = 3, time = 240 min, j = 40 mA/cm$^2$</td>
<td>100</td>
<td>100 (COD) at time = 6 h</td>
<td>Akrout et al. 2015</td>
<td></td>
</tr>
<tr>
<td><strong>BDD</strong> Malachite green</td>
<td>Dye = 20 mg/L, pH = 3, 0.1 M Na$_2$SO$_4$, time = 60 min, j = 32 mA/cm$^2$</td>
<td>100</td>
<td>91 (COD) at time = 3 h</td>
<td>Guenfoud et al. 2014</td>
<td></td>
</tr>
<tr>
<td><strong>BDD</strong> Auramine-O</td>
<td>COD = 150 mg/L, pH = 6, 0.05 M Na$_2$SO$_4$, T = 30°C, time = 90 min, j = 50 mA/cm$^2$</td>
<td>N/A</td>
<td>95 (COD)</td>
<td>Hmani et al. 2012</td>
<td></td>
</tr>
<tr>
<td><strong>Si/BDD</strong> Acid Black 210</td>
<td>Dye = 500 mg/L, pH = 6.8, 0.2 M buffer phosphate, time = 120 min, j = 25 mA/cm$^2$</td>
<td>100</td>
<td>64.6 (TOC) at time = 5 h</td>
<td>Costa et al. 2009</td>
<td></td>
</tr>
<tr>
<td><strong>BDD</strong> Amido black</td>
<td>Dye = 0.05 mM, pH = 7, 0.01 M Na$_2$SO$_4$, time = 90 min, j = 40 mA/cm$^2$</td>
<td>77.7</td>
<td>40 (COD)</td>
<td>Akrout et al. 2013</td>
<td></td>
</tr>
<tr>
<td><strong>Nb/BDD</strong> Vat Blue 1</td>
<td>Dye = 0.1 mM, pH = 11.3, 1.0 mM sodium thionite, time = 90 min, I = 500 mA</td>
<td>100</td>
<td>90 (TOC) at time = 6 h</td>
<td>Diagne et al. 2014</td>
<td></td>
</tr>
<tr>
<td><strong>BDD</strong> Acid Yellow 1</td>
<td>Dye = 1 g/L, pH = 11.3, T = 30°C, 0.5 M HClO$_4$, time = 120 min, I = 1500 mA</td>
<td>100</td>
<td>Nearly 85 (COD)</td>
<td>Rodriguez et al. 2009</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** j = current density; T = temperature; I = applied current.
3.2.1.2.7 Degradation of Dye by Carbon-Based Electrodes

Carbon-based electrodes have scarcely been utilized for dye degradation through anodic oxidation. They include graphite, activated carbon fiber (ACF), graphite felt, carbon pellet, and carbon fiber. However, thanks to large surface areas and the low price of carbon electrodes, both EO and adsorption mechanisms for dye removal from aqueous solutions may be fulfilled (Panizza et al. 2009a).

Yi and Chen (Yi et al. 2008) investigated Alizarin Red S (ARS) dye wastewater using ACF as anode material. They used ACF (with a specific surface area of about 1000 m²/g) as both adsorbent and anode. The experimental results showed that the amount of decolorization was greater than 98% after 60 min of electrolysis, while it was 84.7% when ACF was used as an adsorbent. They compared the ACF and carbon fiber (with a specific surface area of about 4.4 m²/g) on decolorization. The decolorization of ARS was much higher with the ACF anode than with the carbon fiber anode. The reason for this was the high specific surface area of the ACF anode compared with the carbon fiber anode.

The effect of the specific surface area of ACF was also studied for AO7 degradation. Three ACFs were used: ACFₐ (823.4 m²/g), ACFₐₐ (1292.5 m²/g), and ACFₐₐₐ (1558.1 m²/g), and their performances were compared with the performances of Ti/Pt and graphite. The decolorization efficiency of AO7 followed this order: ACFₐₐₐ > ACFₐₐ > ACFₐ > Pt/Ti > graphite. These results proved the influence of the specific surface area on EO with ACF electrodes. It was reported that the sodium sulfate concentration did not influence the decolorization of AO7 (Zhao et al. 2010).

Kariyajjanavar et al. (2013) showed that an increase of sodium sulfate from 5 to 20 g/L did not affect the degradation of Vat Black 27, while with an increase to more than 20 g/L, decolorization was significantly enhanced, in a way that decolorization efficiencies were <5% and >90% for 20 and 35 g/L, respectively.

3.2.1.2.8 Comparison of Anode Materials

The performance of an anode depends on its material. Not only does the anode material determine the efficiency of the dye removal system, but it also identifies the degradation mechanism of organic compounds. Panizza and Cerisola (Panizza et al. 2007) compared the efficiencies of Ti–Ru–Sn ternary oxide, platinum, lead dioxide, and BDD anodes for the oxidation of methyl red. A decrease in absorbance at 520 nm is illustrated in Figure 3.3. As can be seen, as expected, BDD performed best...
in the decolorization of methyl red; it could completely decolorize after 3 h, while PbO$_2$ provided the same level of decolorization after 6 h. Pt and TiRuSnO$_2$ could decolorize only about 80% and 50%, respectively, after 6 h of electrolysis. The decolorization and COD removal efficiencies for methyl red performed in the following order: BDD > PbO$_2$ > Pt > TiRuSnO$_2$.

Panakoulas et al. (2010) noted that decolorization and mineralization rates of Reactive Red 120 were very fast using BDD in comparison with Ti/IrO$_2$–RuO$_2$, which is a DSA electrode. Moreover, intermediates produced utilizing a BDD anode were aliphatic organics, while aromatic organics were formed during electrolysis with Ti/IrO$_2$–RuO$_2$. The BDD anode demonstrated high efficiency in degrading dyes through anodic oxidation. This point was also observed in Table 3.5, where a Ti/BDD anode was compared with Ti/SnO$_2$–Sb$_2$O$_5$ (DSA anode). In all cases, the BDD anode was more successful than the DSA anode in removing COD. In addition, BDD had a higher CE.

Ammar et al. (2012) degraded alizarin red using three anodes (BDD, PbO$_2$, and Pt). Anodic oxidation was comparatively examined under these conditions: 100 mg/L dye solution (containing 70 mg/LTOC), 0.05 M Na$_2$SO$_4$, 100 mA/cm$^2$, pH 7.0. The results demonstrated that Pt reduced only 28% of TOC at the end of electrolysis, while TOC was reduced by 98% and 90% using BDD and PbO$_2$ anodes, respectively, at 18 Ah/L. The apparent rate constant for decolorization followed this sequence: Pt ($2.5 \times 10^{-3}$ s$^{-1}$) < PbO$_2$ ($4.5 \times 10^{-3}$ s$^{-1}$) < BDD ($8.66 \times 10^{-3}$ s$^{-1}$), which indicates the order of oxidation power of these three anode materials in anodic oxidation of the dye.

Regarding the literature and experts’ points of view, Table 3.7 summarizes the advantages and limitations of the anode materials.

### 3.2.2 ELECTROGENERATION OF OXIDIZING AGENTS IN SOLUTION

Electrogeneration of oxidizing agents is usually divided into two categories; (1) electrogeneration of active chlorine species and (2) electrogeneration of hydrogen peroxide. In the electrogeneration of active chlorine species, these are generated at anodes such as DSA, BDD, PbO$_2$, and Pt, while the electrogeneration of hydrogen peroxide occurs at carbon-based cathodes. The electrogeneration of

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>Low oxygen evolution overpotential, stable and fairly available, genuine, without requiring further processing</td>
<td>Low efficiency in anodic oxidation, expensive</td>
</tr>
<tr>
<td>Boron-doped diamond (BDD)</td>
<td>High oxygen evolution overpotential, high stability, very effective in production of oxidants, high corrosion steadfastness, inert surface with low adsorption properties and strong tendency to resist deactivation</td>
<td>Extremely expensive</td>
</tr>
<tr>
<td>Dimensionally stable anode (DSA)</td>
<td>High oxygen evolution overpotential, fairly inexpensive</td>
<td>Fast fading of efficiency, short life service</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>Easy preparation, high oxygen evolution overpotential, cheap and available</td>
<td>Lead ions may be released into the solution</td>
</tr>
<tr>
<td>Graphite</td>
<td>Inert, very cheap and abundant, low oxygen evolution overpotential,</td>
<td>Low efficiency in anodic oxidation, surface corrosion occurs at high potentials</td>
</tr>
</tbody>
</table>

active chlorine species is performed using an electrolyte containing chloride ion, while a chloride-
free electrolyte is usually used for the electrogeneration of hydrogen peroxide.

### 3.2.2.1 Chlorine-Mediated Electrooxidation

Chloride is one of the most abundant ions in polluted waters and wastewaters. Chlorine-mediated oxidation is claimed to be the most commonplace *in situ* oxidant generation process. In fact, electrochlorination is counted among promising treatment processes for wastewaters containing high amounts of chloride. In wastewaters containing chloride ions, active chlorine species such as Cl₂, HClO and/or ClO⁻, ClO₂⁻, ClO₃⁻, and ClO₄⁻ are formed via EO. In electrochlorination, regarding the oxidation power of the active chlorine species, either partial oxidation or complete mineralization may occur. Applying chloride-mediated EO favors textile wastewater treatment, due to the presence of chloride in such wastewater resulting from dye fixation on fibers (Palma-Goyes et al. 2015). The active chlorine species generated during electrochlorination have a great affinity to chromophoric groups, in such a way that a high rate and efficient decolorization of dyes are fulfilled. Based on a study conducted by Petrucci et al. (2015), in which BDD was used as the anode material and the target dye to be degraded was Reactive Green 19 (RG19), the reaction time needed to achieve more than 90% dye removal was significantly reduced merely in the presence of chloride. Accordingly, electrochlorination is undoubtedly a viable option for the treatment of textile wastewaters, unless the formation of chloroderivatives is ignored. In other words, the main drawback of chlorine-based treatment processes is the formation of toxic organic chloroderivatives. Numerous studies have been conducted to trace and monitor these compounds. However, it has been claimed that the concentrations of these derivatives are negligible or zero if the process is comprehensively optimized, taking these derivatives into consideration. In fact, it has been stated that even in the case of the formation of such derivatives, further electrolysis of wastewater most often fulfills degradation and destruction of these intermediates. For instance, based on the results achieved in the above mentioned study, optimum values of chloride lead to further degradation of RG19 without the formation of persistent intermediates.

Referring back to the introduction of the process, ambiguities and complexities are still there in the exact nature of the chemical and electrochemical reactions occurring during electrochlorination. An indirect transfer of oxygen occurs both on the anode’s surface and in the bulk solution via chlorine, hypochlorous acid, or hypochlorite, which is strongly dependent on the pH value. Initially, chlorine is electrogenerated as a result of chloride oxidation at the anode, based on the following reactions:

\[
\text{Cl}^- \leftrightarrow \text{Cl}^\text{ads} + e^- \quad (3.15)
\]

\[
\text{Cl}^- + \text{Cl}^\text{ads} \leftrightarrow \text{Cl}_2 + e^- \quad (3.16)
\]

With pH values less than 3.3, the primary active chloro-species is Cl₂ (Anglada et al. 2009). When the point concentration of Cl₂ exceeds its solubility, the electrogenerated Cl₂ forms bubbles. Likewise, it may be partially diffused away from the anode to react with chloride, forming trichloride as a consequence (Reaction 3.17), or else it quickly becomes hydrolyzed to hypochlorous acid as well as chloride ions (Reaction 3.18). Depending on the pH value, the hypochlorous acid can be further dissociated toward the production of hypochlorite ions (Reaction 3.19). Further on, ClO⁻ may take part in an oxidation process based on Reaction 3.20.

\[
\text{Cl}_2 \text{(aq)} + \text{Cl}^- \leftrightarrow \text{Cl}_3^- \quad (3.17)
\]

\[
\text{Cl}_2 \text{(aq)} + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (3.18)
\]

\[
\text{HClO} \leftrightarrow \text{ClO}^- + \text{H}^+ \quad (3.19)
\]
ClO\(^-\) + H\(_2\)O + 2e\(^-\) ⇔ Cl\(^-\) + 2OH\(^-\)  \hspace{1cm} (3.20)

In an alkaline medium, the hypochlorite ions can oxidize the organics in the vicinity of the anode and/or in the bulk of the solution (Scialdone et al. 2014).

Organics + OCl\(^-\) → Intermediates → CO\(_2\) + Cl\(^-\) + H\(_2\)O  \hspace{1cm} (3.21)

HClO and ClO\(^-\) are strong oxidants; nevertheless, their actions to degrade organics in volume reactions are highly dependent on the pH value and chlorine concentration in the solution. The domination of chlorine species is strongly dependent on the pH value (Table 3.8).

Anodically generated chlorine and hypochlorite are the major agents responsible for oxidation of organic pollutants. Regarding Table 3.8, the active chlorine species–mediated oxidation is supposed to occur at higher rates in acidic conditions, due to the higher E\(^0\) values allocated to HOCl and Cl\(_2\). Nevertheless, the EO of the wastewater causes desorption of the chlorine, inhibiting it from acting as an oxidizer. In this way, higher pH levels may theoretically promote electrochemical oxidation, since HOCl and OCl\(^-\) are not highly affected by the desorption of gases and are efficient oxidizers acting throughout the reactor (Anglada et al. 2009). Likewise, hypochlorite ion concentration can be diminished through its anodic oxidation to chlorite, chlorate, and perchlorate:

ClO\(^-\) + H\(_2\)O → ClO\(_2\) + 2H\(^+\) + 2e\(^-\)  \hspace{1cm} (3.22)

ClO\(_2\) + H\(_2\)O → ClO\(_3\) + 2H\(^+\) + 2e\(^-\)  \hspace{1cm} (3.23)

ClO\(_3\) + H\(_2\)O → ClO\(_4\) + 2H\(^+\) + 2e\(^-\)  \hspace{1cm} (3.24)

Within active chlorine species–mediated systems, oxychloro species take the responsibility for the transfer of oxygen, based on Figure 3.4. Bonfattiet et al. (2000) have described the mediating role of chloride, illustrating the electrochemical oxygen transfer reaction (EOTR) via the adsorbed oxychloro species that are intermediates of the chlorine evolution reaction. In fact, chloro and oxychloro radicals coadsorbed at the electrode surface are of quite high importance in determining the mechanism of electrochemical incineration. Likewise, coelectroadsorption of hydroxyl radicals should also be noted. Within EOTR, *OH\(_{ads}\) plays a critical role which its reactivity as a function of metal oxide electrode nature has been declared by Comninellis while in chlorine mediated EO systems, oxychloro species are also in charge of oxygen transfer.

Based on Figure 3.4, chloride ions inhibit the oxygen evolution reaction, causing a rise in anode potential and higher reactivity of adsorbed oxidized chloride species.

Based on the results reported within the literature, chloride concentration, as an influential parameter in electrochlorination, has a bilateral effect on the process’s efficiency that should be optimized carefully. In a study carried out by Bonfatti et al. (2000), it was found that increasing the chloride concentration up to 5 g/dm\(^3\) brought about more efficient electrochemical mineralization with a higher rate, while a further increase of chloride to 10 g/dm\(^3\) revealed adverse effects.
on the efficiency of the process. But, generally, it has been well established that dye degradation is strongly enhanced in the presence of inorganic mediators such as active chlorine species. It has been reported that chloride affects the behavior of the anodes in an efficient manner (Sala et al. 2012). In the presence of chloride, EO can be conducted within lower potentials in comparison with the potentials needed in direct anodic oxidation. Sala et al. stated that the amount of chlorine species generated electrochemically is highly influenced by the amounts of hydroxyl radicals. Based on a comprehensive review conducted by Trasatti and coworkers (Trasatti 1987), adsorption of oxychloro radicals has been reported to be the most probable mechanism. Accordingly, the reaction mechanism of chlorine electrogeneration is supposed to be related to the acid base equilibrium at the anode surface, which is actually the source and start point of chlorine electrogeneration. The corresponding reactions are as follows:

\[
\begin{align*}
\text{AS} - \text{OH}^+ & \leftrightarrow \text{AS} - (\text{OH})_{\text{ads}} + \text{H}^+ & (3.25) \\
\text{AS} - (\text{OH})_{\text{ads}} & \leftrightarrow \text{AS} - \text{O}_{\text{ads}} + \text{H}^+ + e^- & (3.26) \\
\text{AS} - \text{O}_{\text{ads}} + \text{Cl}^- & \rightarrow \text{AS} - (\text{OCl})_{\text{ads}} + e^- & (3.27) \\
\text{AS} - (\text{OCl})_{\text{ads}} + \text{Cl}^- + \text{H}^+ & \leftrightarrow \text{AS} - (\text{OH})_{\text{ads}} + \text{Cl}_2 & (3.28) \\
\text{AS} - (\text{OCl})_{\text{ads}} + \text{Cl}^- & \leftrightarrow \text{AS} - (\text{O})_{\text{ads}} + \text{Cl}_2 + e^- & (3.29)
\end{align*}
\]

where AS represents active sites on the electrode surface.

Sales Solano et al. (2013) investigated the decontamination of real textile wastewater using a BDD anode. They found that NaCl, in comparison with Na\textsubscript{2}SO\textsubscript{4}, provided higher degradation efficiency regarding the electrogeneration of strong chlorine active species on the BDD anode surface, attacking the chromophore group of dyes, thereby eliminating the wastewater color. Based on their work, by increasing NaCl concentration, it was observed that degradation efficiency in terms of COD removal was enhanced up to 100% temperature is also of importance, although less so in comparison with the pH level and chloride concentration. With temperatures lower than 100°C, there is a clear evolution of hydrogen, oxygen, and chlorine, while as the temperature increases, their
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generation is strongly suppressed. Nevertheless, marginal amounts of hydrogen can be found even at higher temperatures, although these amounts are much lower than those expected to be generated based on Faraday’s law.

Although electrochlorination is reported to be highly dependent on chloride concentration and pH, various results have been gained in electrochlorination studies applying active and nonactive anodes, indicating that in such processes, the anode material is also of importance, since the EO of chloride to chlorine should occur at high rates. It should also be noted that it is essential for the anode material to be inactive, due to the need to hinder active sites being blocked through adsorption (physio-sorption). Based on the literature, platinum or mixtures of metal oxides have been employed in the electrochlorination process, as they have suitable electrocatalytic features along with good stability.

DSA electrodes are mainly of interest because of their high CE of chlorine gas evolution, due to suitable catalytic features for this kind of reaction. In fact, electrochemical corrosion of DSA anodes is limited to the electroactive surface layer. Likewise, due to the suitable shape and integrity of a DSA structure, the coating can be regenerated over and over again. Based on a study carried out by Scialdone et al. (2009), using DSA as an anode, the presence of chloride led to a significant increase in CE. DSA electrodes present quite a low oxygen overpotential, while they display high electrocatalytic activity for chlorine generation (Zhang et al. 2014a).

Apart from the anode materials mentioned, graphite and nonactive anodes such as BDD and PbO$_2$ are among favorable anode selections that provide significantly high efficiencies for the degradation of dyes in chloride-mediated systems. In EO systems applied to the treatment of chloride-containing wastewaters such as textile wastewater, potentials higher than that needed for oxygen evolution lead to the cooperation of electrochlorination and hydroxyl radical-based EOTR. In this condition, optimization of the process and prediction of how the parameters’ roles will affect process efficiency and operation become complex.

In some cases, such as when the inactive BDD electrode is exerted, physisorbed hydroxyl radical species cooperate with the chlorine active species. In this way, the following reactions are expected to occur (Petrucci et al. 2015):

\[
\text{HO}^- + \text{Cl}^- \rightarrow \text{ClOH}^- \quad (3.30)
\]

\[
\text{ClOH}^- \leftrightarrow \text{Cl}^- + \text{OH}^- \quad (3.31)
\]

\[
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^- \quad (3.32)
\]

\[
\text{Cl}_2^- + \text{HO}^- \rightarrow \text{HOCl} + \text{Cl}^- \quad (3.33)
\]

Figure 3.5 comprehensively illustrates the reactions that are hypothesized to occur during EO in the presence of chloride using BDD.

Based on Figure 3.5, it should be noted that in chloride-mediated EO, incineration reactions are considered to occur more in the volume instead of the surface of the anode (Sales Solano et al. 2013).

Based on what is stated, BDD anodes are an attractive choice, since hydroxyl radicals are formed on the surface of such anodes; nevertheless, the performance of such radicals are dramatically affected in chloride media (Palma-Goyes et al. 2015). Besides, the high cost of BDD anodes should also be considered, especially in the case of their application at the industrial scale.

Rajkumar et al. (2007) used titanium mesh coated with TiO$_2$–RuO$_2$–IrO$_2$ as an anode for the degradation of Reactive Blue 19 (RB19). Complete decolorization was achieved within a short electrolysis period. However, under conditions of 400 mg/L RB19 with 1.5 g/L NaCl concentration, the COD and TOC removal rates were 55.8% and 15.6%, respectively. Regarding these results, with
an increase in electrolysis time, the molecular weight of the intermediate compounds formed was lowered. Moreover, as an interesting result, electrochemical oxidation of RB19 in the presence of chloride did not generate any chlorinated organics as by-products.

Araújo et al. (2015) showed that oxidation of Rhodamine B (RhB) with a p-Si–BDD anode in NaCl electrolyte produced seven sub-product. No complete removal of all by-products formed was accomplished after 500 min of electrolysis. Figure 3.6 shows electrochemical degradation pathways for RhB in NaCl solution. Seven by-products were produced, including: (I₁) phthalic acid, (I₂) benzoic acid, (I₃) 3-dinitrobenzoic acid, (I₄) 2,5-hydroxybenzoic acid, (I₅) α-hydroxyglutaric acid, (I₆) Intermediate 7, and (I₇) chloroform. Although chloroform was formed during the electrolysis process, the authors claimed that the presence of chloroform might have been related to some gas-phase reactivity along the complex analytical path itself. Hence, the reactions that occurred at the anode surface had a partial influence on chloroform formation, since other chlorinated compounds were not formed.

Table 3.9 summarizes electrochemical oxidation with active chlorine species to decolorize or mineralize different dyes or colored wastewaters by various anodes.

### 3.2.2.2 Electrooxidation by Electrogenerated Hydrogen Peroxide

Hydrogen peroxide, with the chemical formula of H₂O₂, is widely used for oxidation of substances because it is a powerful oxidant, with $E^\circ = 1.8$ V. Hydrogen peroxide is one of the most applicable oxidants in environmental remediation in all media (air, water, and soil). Moreover, hydrogen peroxide is well known as a green chemical, since its residuals in the environment are only oxygen and water, which do not threaten the ecosystem or public health (Neyens et al. 2003; Yu et al. 2015a). Hydrogen peroxide can be catalytically decomposed to hydroxyl radicals by transitional metals and UV light. The hydroxyl radicals decompose organic compounds as a nonselective
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The mixture of $\text{H}_2\text{O}_2$ and ferrous ions is well known as the Fenton reagent, which has been broadly applied for water and wastewater treatment. Ferrous ions act as a catalyst in acid media, decomposing hydrogen peroxide to hydroxyl radicals (Reaction 3.34), consequently producing ferric ions. The Fenton process is an oxidation process that has been extensively used for the degradation of dyes (Brillas et al. 2009; Nidheesh et al. 2013a).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{HO}^* + \text{Fe}^{3+} + \text{H}_2\text{O} \tag{3.34}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{Fe}^{2+} + \text{H}^+ \tag{3.35}
\]
TABLE 3.9  
Decolorization and Mineralization of Different Dyes or Colored Wastewater by Electrochemical Oxidation with Active Chlorine Species

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Anode</th>
<th>Condition</th>
<th>Color Removal (%)</th>
<th>COD or TOC Removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Red 184</td>
<td>Pt/Ti</td>
<td>Dye = 10^{-2} mol/L, applied potential = 12.7 V, electrolyte: NaCl, time = 50 min</td>
<td>&gt;90</td>
<td>N/A</td>
<td>Sakalis et al. 2006</td>
</tr>
<tr>
<td>Real textile wastewater</td>
<td>BDD</td>
<td>j = 40 mA/cm², NaCl = 5 g/L, time = 300 min</td>
<td>100</td>
<td>Almost 100 (COD), time = 600 min</td>
<td>Sales Solano et al. 2013</td>
</tr>
<tr>
<td>Reactive Green 19</td>
<td>BDD</td>
<td>Dye = 100 mg/L, j = 300 A/m², Na₂SO₄ = 0.05 M, NaCl = 0.01 M, T = 25°C, agitation rate = 250 rpm</td>
<td>100%</td>
<td>&gt;80% (TOC)</td>
<td>Petrucci et al. 2015</td>
</tr>
<tr>
<td>Indigo carmine</td>
<td>DSA of Sb₂O₅-doped Ti/RuO₂-ZrO₂</td>
<td>Dye = 0.64 mM, j = 200 A/m², 0.05 M NaCl, flow rate: 5 L/min</td>
<td>N/A</td>
<td>90% (COD), 22% (TOC)</td>
<td>Palma-Goyes et al. 2015</td>
</tr>
<tr>
<td>Acid Orange 7</td>
<td>BDD</td>
<td>Dye = 209.3 mg/L, 0.30 M NaCl, pH = 3, 100 mA/cm² T = 35°C, time = 15 min</td>
<td>100%</td>
<td>N/A</td>
<td>Scialdone et al. 2014</td>
</tr>
<tr>
<td>Acid Orange 7</td>
<td>Ti/RuO₂-Pt</td>
<td>Dye = 50 mg/L, NaCl = 0.001 M, j = 10 mA/cm², pH = 6.8, Na₂SO₄ = 0.005 M, time = 4 h</td>
<td>100</td>
<td>79.48 (TOC)</td>
<td>Zhang et al. 2014b</td>
</tr>
<tr>
<td>Acid Orange II</td>
<td>BDD</td>
<td>Dye = 50 mg/L, NaCl = 5 mM, j = 2.58 mA/cm², flow rate = 600 mL/L, time = 40 min</td>
<td>87</td>
<td>N/A</td>
<td>Zhang et al. 2014a</td>
</tr>
<tr>
<td>C.I. Reactive Orange 7</td>
<td>Ti/Sb–SnO₂</td>
<td>Dye = 60 mg/L, NaCl = 3.5 g/L, pH = 4, j = 19 mA/cm²</td>
<td>99.70</td>
<td>70.3 (COD)</td>
<td>Basiri Parsa et al. 2013</td>
</tr>
<tr>
<td>C.I. Reactive Yellow 186</td>
<td>Graphite</td>
<td>pH = 3.9; j = 34.96 mA/cm², dye = 500 µM, NaCl = 0.11 M, time = 15 min</td>
<td>99</td>
<td>73 (COD)</td>
<td>Rajkumar et al. 2015</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>Sb₂O₅-doped Ti/RuO₂-ZrO₂</td>
<td>Dye = 0.5 mM, NaCl = 1 M, j = 0.5 A/cm², T = 25°C</td>
<td>100</td>
<td>N/A</td>
<td>Rodríguez et al. 2014</td>
</tr>
</tbody>
</table>

*Note: j = current density, T = temperature, I = applied current.*
The high efficiency and simple operation of the Fenton process allow it to be considered as a popular process for dye removal from colored effluent. However, the process has some limitations that include the production of ferric sludge, the need for storage and shipment of concentrated \( \text{H}_2\text{O}_2 \), and the low regeneration of ferrous ions (Wang et al. 2010).

Hydrogen peroxide can be electrochemically generated in acidic media through the reduction of oxygen molecules at a carbon-based cathode (Reaction 3.36) (Nidheesh et al. 2012).

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2
\]  

Reaction 3.36

Hydrogen peroxide is continually electrogenerated in the electrochemical cell while air or oxygen is directly injected into the solution. The applied anode can be “active” or “nonactive” to generate hydroxyl radicals on its surface. Platinum and BDD are among the conventional anodes for this purpose. Indeed, the anode also participates in the degradation of pollutants through anodic oxidation. The electrogeneration of hydrogen peroxide, along with anodic oxidation, occurs in one electrochemical cell, increasing the removal efficiency of EO. Nonetheless, hydrogen peroxide alone does not fulfill the oxidation of macromolecules such as dyes, since a catalyst is required for the activation of hydrogen peroxide and, consequently, the production of hydroxyl radicals (Jiang et al. 2007; Sirés et al. 2014).

The addition of ferrous-ion salts (usually ferrous sulfate) to the electrochemical cell leads to the decomposition of electrogenerated hydrogen peroxide to hydroxyl radicals, which are responsible for the degradation of the organic compounds. The ferric ions can be reduced to ferrous ions at the cathode, based on Reaction 3.37. This reaction provides more availability of ferrous ions to react with the electrogenerated hydrogen peroxide, increasing the propagation of the reaction chain of the Fenton process (Sirés et al. 2007; Flox et al. 2006).

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad E^0 = 0.77 \text{ V/NHE}
\]  

Reaction 3.37

In fact, in this process, the Fenton reagent is electrochemically produced in the electrochemical cell, called the electro-Fenton (EF). In the EF, \( \text{H}_2\text{O}_2 \) is electrochemically produced while ferrous ions are chemically added from outside the reactor (Rosales et al. 2012). Enric Brillas and Mehmet Oturan have been the architects of the EF process for the degradation of environmental pollutants from the 1990s to date. The mechanism of an EF is schematically presented in Figure 3.7.

During these years, several studies have been conducted based on dye degradation by the EF process. In these processes, operating parameters include applied current (current density), pH, anode and cathode materials, initial concentration of dye, air or oxygen sparging, type and dosage of catalyst, and configuration of electrochemical cell (Nidheesh et al. 2012). Recent advances in EF processes have been more focused on the synthesis of the cathode electrode and the catalysts. Graphite felt, ACF, gas diffusion cathodes, carbon cloth, polytetrafluoroethylene (PTFE), reticulated vitreous carbon (RVC), and carbon sponge have been used for hydrogen peroxide generation in the EF process, while Pt, BDD, and DSA electrodes have been applied as the anode.

Panizza and Cerisola utilized a Pt anode and gas diffusion cathodes for alizarin red degradation. They found that faster degradation occurred at pH 3.0 with COD removal efficiency of 93% in 4 h of electrolysis. This was in agreement with other studies of Fenton-based processes. An evaluation of the effect of ferrous-ion dosage indicated that an increase of \( \text{Fe}^{2+} \) from 0.25 to 1 mM developed COD removal efficiency, while a further increase of the dosage of \( \text{Fe}^{2+} \) (2 Mm) did not do so. This phenomenon is related to the scavenging effect of ferrous ions in excess amounts consuming hydroxyl radicals, based on the following reaction (Panizza et al. 2009b):

\[
\text{Fe}^{2+} + \text{HO}^- \rightarrow \text{Fe}^{3+} + \text{HO}^-
\]  

Reaction 3.38
El-Desoky et al. (2010) studied EF for the degradation of Ponceau S azo dye with an RVC cathode and a platinum gauze anode. Under conditions of pH 2.5, cathode potential of $-1.0$ V (vs. SCE), 0.05 M Na$_2$SO$_4$, and 0.05 mM FeSO$_4$, complete decolorization was obtained within 30, 60, and 90 min for initial dye concentrations of 0.05, 0.1, and 0.3 mM, respectively. In this study, sodium sulfate was chosen as the best supporting electrolyte, while KCl and NaCl lowered the efficiency of the EF process due to the presence of Cl$^-$ ions. It was advised to avoid using chloride-containing media, as they produce chlorinated organics, which are carcinogenic by-products.

Lei et al. (2010) used Cu$^{2+}$ and Mn$^{2+}$ as catalysts for the decolorization of cationic red X-GRL with an ACF cathode and an RuO$_2$/Ti anode. Cu$^{2+}$ and Mn$^{2+}$ were more effective in degrading the dye in comparison with ferrous ions. The removal efficiencies of the three catalysts followed this order: Fe$^{2+} <$ Cu$^{2+} <$ Mn$^{2+}$. The higher standard reduction potential of Mn$^{3+}$ (Reaction 3.39) leads to an increase of the acceptance rate of electrons compared with Fe$^{3+}$. Hence, the regeneration of Mn$^{2+}$ is faster compared with the other transitional metals.

$$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+} \quad E^0 = 1.51 \text{ V/NHE} \quad (3.39)$$

Carbon black–modified graphite felt and PTFE were used in the EF process to decolorize MO. The modified graphite felt generated 472.9 mg/L H$_2$O$_2$ at pH 7.0 and current density of 50 A/m$^2$, while unmodified graphite generated only 40.3 mg/L H$_2$O$_2$. An interesting result was obtained from this study: H$_2$O$_2$ was effectively generated even without external aeration. This result indicated that the generation of enough oxygen at the anode can fulfill the generation of H$_2$O$_2$ without any external aeration. Complete decolorization of MO was achieved after 15 min by modified cathode, while mineralization reached 95.7% after 2 h of electrolysis, which was much more in comparison with the unmodified cathode (23%) (Yu et al. 2015a).

Ren et al. (2015) investigated the effect of the pore structure of mesoporous carbon–grafted activated carbon fibers (ACF@OMC) on the degradation of Rhodamine B and Orange II by the EF process. The ACF@OMC, with an average pore size of 5.4 nm, had the highest efficiency in comparison...
with the average pore sizes of 2.6 and 3.7 nm. The large pore size and ordered mesoporous structures improved the transformation and diffusion of O$_2$ on the surface of the cathode. A total of 99.7% of Rhodamine B was decolorized by ACF@OMC with an average pore size of 5.4 nm within 45 min, and 47.7% mineralization occurred in 360 min. The stability results showed that 94.2% of the dye could still be decolorized after using the cathode 10 times.

In another study (Le et al. 2015), a new cathode was introduced for the EF process, in which reduced graphene oxide (rGO) was electrochemically deposited on carbon felt. The use of a graphene-modified cathode completely decolorized AO7 after only 5 min of electrolysis. Almost 95% TOC removal was achieved in 8 h of reaction time. The stability of the cathode was examined after using 10 cycles. A fresh cathode could remove 73.9% of TOC in 2 h, while after 10 applications of the cathode, TOC removal reached 64.3%, which was a preventive for an otherwise excellent cathode.

Olvera-Vargas and coworkers (Olvera-Vargas et al. 2014) compared the efficiencies of Pt/carbon-felt and BDD/carbon-felt systems in the degradation of Azure B. Complete decolorization was achieved after 10, 15, and 45 min for BDD/carbon felt, Pt/carbon felt, and anodic oxidation (BDD) together with H$_2$O$_2$, respectively, in 0.05 M Na$_2$SO$_4$, 500 mA current, [Fe$^{2+}$] = 0.1 mM, pH 3.0, at room temperature. The apparent rate constants of BDD/carbon felt, Pt/carbon felt, and anodic oxidation (BDD) together with H$_2$O$_2$ were 0.37, 0.24, and 0.14 min$^{-1}$, respectively. Over 95% of TOC was removed in EF with BDD and anodic oxidation (BDD) together with H$_2$O$_2$, while EF with Pt could not provide the same efficiency. The formation and evolution of carboxylic acids in EF using BDD for Azure B degradation are presented in Figure 3.8. Oxamic and oxalic acids were accumulated at high concentrations, whereas formic, malic, pyruvic, and acetic acids were formed at low concentrations. Based on Figure 3.8, the carboxylic acids could be efficiently decayed in the EF process with the BDD system, which was also expected, considering the higher level of mineralization in terms of TOC removal.

Various studies applied a heterogeneous catalyst instead of ferrous ions for activation of H$_2$O$_2$. He et al. (2014) exerted Fe$_3$O$_4$ magnetic nanoparticles for the degradation of Reactive Blue 19. Optimal operating conditions were pH 3.0, current density of 3.0 mA/cm$^2$, 1.0 g/L Fe$_3$O$_4$, initial RB19 concentration of 100 mg/L, and reaction temperature of 35°C. Under these conditions, more than 89.7% of TOC was degraded after 180 min electrolysis. Their results demonstrated that Fe$_3$O$_4$ had a higher catalytic capacity than the ferrous ions.

![FIGURE 3.8](image-url) Time course of the concentration of the main short-chain carboxylic acids accumulated in solution during EF treatment of 200 mL 0.1 mM Azure B by BDD/carbon-felt cell using 300 mA and 0.05 M Na$_2$SO$_4$ at pH 3.0 and room temperature. (Reproduced from Olvera-Vargas, H. et al., Environmental Science and Pollution Research, 21, 8379–86, 2014).
Iglesias et al. (2013) used Fe alginate gel beads as a catalyst to remove Reactive Black 5 from aqueous solution. Optimum conditions were obtained by CCD, involving a voltage of 5.69 V, pH 2.24, and an iron concentration of 2.68 mM for 65% COD removal, 90% decolorization, and low energy costs of 35.61 kWh/kg COD and 24.41 kWh/kg dye.

Natural pyrite was used as a heterogeneous catalyst for the degradation of a new azo dye (4-aminophenoxy-2-p-tolylazo-naphthalene-1-sulfonic acid) (AHPS) by EF (BDD/graphite felt). In the presence of 2 g/L pyrite, complete decolorization of 175 mg/L AHPS occurred after 20 min reaction time at 300 mA applied current, while an 8 h reaction time was required for complete mineralization. This study showed that pyrite is a low-cost and reusable solid catalyst that can perform at a favorable pH without external acidification (Labiadh et al. 2015). Several studies with their efficiencies of EF systems for dye degradation are presented in Table 3.10.

3.2.2.2.1 Photoelectro-Fenton (PEF)

To enhance the efficiency of EF, a UV-assisted electrochemical process can be employed. In this scenario, not only can UV light directly decompose electrogenerated hydrogen peroxide to HO• (Reaction 3.40), but it can also regenerate ferrous ions by photolysis of ferric ions. In fact, the Fe(III) produced in Reaction 3.34 can be photo reduced by regenerating Fe2+ and producing more OH• radicals (Reaction 3.41) (Moreira et al. 2013; Moradi et al. 2015).

\[
\text{H}_2\text{O}_2 + \text{UV} \rightarrow \text{HO}^+ + \text{HO}^+ \quad (3.40)
\]

\[
\text{Fe(OH)}^{2+} + \text{UV} \rightarrow \text{Fe}^{2+} + \text{HO}^+ \quad (3.41)
\]

The combination of photolysis and EF is called the photoelectro-Fenton (PEF) process. It should be noted that, in many PEF studies, solar energy has been utilized instead of a UV lamp, reducing the electrical energy cost of UV lamps.

Thiam et al. (2016) studied PEF (BDD anode/air diffusion cathode) for the degradation of Ponceau 4R with UVA irradiation. Three mechanisms improved the oxidation of the dye: (1) anodic oxidation by (BDD(*OH)); (2) homogeneous hydroxyl radicals generated from the Fenton reagent; and (3) photodecomposition of the dye. Indeed, PEF has a synergistic effect on the degradation of organic pollutants. The total mineralization and color removal of 254 mg/L dye were achieved at 100 mA/cm² after 240 and 50 min, respectively. In this study, the oxidizing ability of PEF, EF, and EO with electrogenerated H₂O₂ (EO-H₂O₂) was assessed for decolorization of the dye in raw water. The dye solution became colorless after 180, 100, and 70 min for EO–H₂O₂, EF, and PEF, respectively.

Moreira et al. (2013) compared anodic oxidation with electrogenerated H₂O₂ (AO–H₂O₂), EF, PEF, and solar photoelectro-Fenton (SPEF) to degrade Sunset Yellow FCF (SY) azo dye. Figure 3.9 shows the removal of TOC for the ECPs. The AO–H₂O₂ could only remove 65% of TOC after 360 min, which is related to the generation of BDD(*OH) and (BDD(HO₂•)) at the anode’s surface. In EF, rapid mineralization was observed during the first 120 min; after that, the TOC removal rate decreased, which could be attributed to the forming of Fe(III)–carboxylate complexes that were hardly oxidized by •OH. In addition, 82% of TOC removal was attained after 360 min. In the cases of PEF and SPEF, the removal of TOC was 95% (240 min) and 93% (150 min), respectively. This increase in efficiency was due to the photodegradation of Fe(III)–carboxylate complexes. SPEF could degrade SY in a shorter time, which was ascribed to the more potent UV intensity provided by sunlight (Moreira et al. 2013).

The comparison of EF and SPEF has been studied in other research (Ruiz et al. 2011) for the decay of Acid Yellow 36 (AY36). In both processes, an increase in applied current improved TOC removal. However, EF degraded AY36 poorly; 71% of TOC was removed in 360 min using 3 A
### TABLE 3.10
Decolorization and Mineralization Degrees of Different Dyes and Colored Wastewater by Various EF Systems

<table>
<thead>
<tr>
<th>EF System (Anode/Cathode)</th>
<th>Dye</th>
<th>Condition</th>
<th>Color Removal (%)</th>
<th>TOC or COD Removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pt/carbon paper)</td>
<td>Reactive Red 195</td>
<td>Dye = 50 mg/L, pH = 3.0, I = 300 mA, Fe^{2+} = 0.2 mM, oxalate^{−} = 0.4 mM, time = 90 min</td>
<td>70</td>
<td>N/A</td>
<td>Djafarzadeh et al. 2013</td>
</tr>
<tr>
<td>(Pt/rotating graphite felt)</td>
<td>MO</td>
<td>Dye = 25 mg/L, pH = 3.0, j = 50 A/m², Fe^{2+} = 0.02 M, time = 15 min</td>
<td>100</td>
<td>58.7 (TOC) time = 2 h</td>
<td>Yu et al. 2014</td>
</tr>
<tr>
<td>(Graphite/graphite)</td>
<td>Rhodamine B</td>
<td>Dye = 10 mg/L, pH = 3.0, applied voltage = 8 V, Fe^{2+} = 10 mg/L, time = 180 min, 2.5 mg/L of NaHCO₃</td>
<td>99</td>
<td>N/A</td>
<td>Nidheesh et al. 2014</td>
</tr>
<tr>
<td>(Pt/Cu₂O/CNTs/PTFE)</td>
<td>Rhodamine B</td>
<td>Dye = 1.044 × 10⁻⁵ M, pH = 3.0, applied potential = 1.2 V, Na₂SO₄ = 0.05 M, time = 120 min</td>
<td>89</td>
<td>N/A</td>
<td>Ai et al. 2008</td>
</tr>
<tr>
<td>(Graphite/graphite)</td>
<td>Rhodamine B</td>
<td>Dye = 40 mg/L, pH = 3.0, I = 0.03 A, Fe^{2+} = 10 mg/L, time = 180 min, 2.5 mg/L of NaHCO₃</td>
<td>84.1</td>
<td>N/A</td>
<td>Nidheesh et al. 2013b</td>
</tr>
<tr>
<td>(RuO₂-IrO₂/graphite felt)</td>
<td>Orange II</td>
<td>Dye = 50 mg/L, pH = 3.0, j = 1.78 mA/cm², Fe^{2+} = 2 mM, time = 60 min</td>
<td>100</td>
<td>58 (TOC)</td>
<td>Lin et al. 2014</td>
</tr>
<tr>
<td>(Graphite/graphite)</td>
<td>MO</td>
<td>Dye = 150 mg/L, pH = 3.0, I = 2.1 A, Fe^{2+} = 2 mM, Cl^{−} = 12 mM, time = 30 min</td>
<td>98.34</td>
<td>50 (COD)</td>
<td>He et al. 2013</td>
</tr>
<tr>
<td>(Pt/carbon felt)</td>
<td>Naphtol blue black</td>
<td>Dye = 0.05 mM, pH = 2.0, I = 150 mA, Fe^{2+} = 0.05 mM, Na₂SO₄ = 0.05 M, time = 40 min</td>
<td>97.5</td>
<td>N/A</td>
<td>Bouasla et al. 2013</td>
</tr>
<tr>
<td>(Pt/carbon felt)</td>
<td>Malachite green</td>
<td>Dye = 0.5 mM, pH = 3.0, I = 200 mA, Fe^{2+} = 0.2 mM, Na₂SO₄ = 0.05 M, time = 22 min</td>
<td>100</td>
<td>100 (COD) time = 540 min</td>
<td>Oturan et al. 2008a</td>
</tr>
<tr>
<td>(Pt/modified gas diffusion electrode)</td>
<td>Amaranth</td>
<td>Dye = 100 mg/L, pH = 2.0, applied potential = -0.7 V, Fe^{2+} = 0.155 mM, H₂SO₄ and K₂SO₄ = 0.1 M, time = 90 min</td>
<td>79.3</td>
<td>67.3 (TOC)</td>
<td>Barros et al. 2014</td>
</tr>
<tr>
<td>(Pt/Co₃O₄/graphite)</td>
<td>Sulforhodamine B</td>
<td>Dye = 0.01 mM, pH = 2–3, applied voltage = 6 V, Na₂SO₄ = 10 g/L, time = 150 min</td>
<td>100</td>
<td>55 (TOC) time = 5 h</td>
<td>Liu et al. 2013</td>
</tr>
<tr>
<td>(BDD/stainless steel)</td>
<td>Reactive Red 180</td>
<td>Dye = 20 ppm, pH = 3, j = 20 mA/m², Fe^{2+} = 0.02 mM, Na₂SO₄ = 10 g/L, time = 60 min</td>
<td>Approximately 100%</td>
<td>N/A</td>
<td>(Almomani et al. 2012)</td>
</tr>
</tbody>
</table>

(Continued)
### TABLE 3.10 (CONTINUED)
Decolorization and Mineralization Degrees of Different Dyes and Colored Wastewater by Various EF Systems

<table>
<thead>
<tr>
<th>EF System (Anode/Cathode)</th>
<th>Dye</th>
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<th>Color Removal (%)</th>
<th>TOC or COD Removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BDD/stainless steel)</td>
<td>Reactive Blue 19</td>
<td>Dye = 20 ppm, pH = 3, j = 20 mA/m², Fe$^{2+}$ = 0.02 mM, Na$_2$SO$_4$ = 10 g/L, time = 120 min</td>
<td>Approximately 100%</td>
<td>N/A</td>
<td>Almomani and Baranova 2012</td>
</tr>
<tr>
<td>(Ti/PbO$_2$/C-PTFE-coated graphite chips)</td>
<td>Reactive Brilliant Red X-3B</td>
<td>Dye = 123 mg/L, pH = 3, I = 0.3 A, Fe$^{2+}$ = 0.1 mM, Na$_2$SO$_4$ = 0.05 M, time = 20 min</td>
<td>97</td>
<td>87 (TOC), time = 3 h.</td>
<td>Lei et al. 2013</td>
</tr>
<tr>
<td>(Pt/dual gas diffusion)</td>
<td>Tartrazine</td>
<td>Dye = 1000 mg/L, pH = 3, j = 35.7 mA/cm², Fe$^{2+}$ = 0.1 mM, Na$_2$SO$_4$ = 0.05 M, flow rate = 0.5 L/min, time = 60 min</td>
<td>100</td>
<td>66.1 (TOC), time = 2 h.</td>
<td>Yu et al. 2015b</td>
</tr>
<tr>
<td>(BDD/granular activated carbon (GAC) packed electrode)</td>
<td>MO</td>
<td>Dye = 97 mg/L, pH = 3, I = 300 mA, Fe$^{3+}$ = 0.5 mM, Na$_2$SO$_4$ = 0.05 M, time = 120 min</td>
<td>100</td>
<td>90 (TOC) time = 5 h</td>
<td>Bañuelos et al. 2014</td>
</tr>
<tr>
<td>(Pt/carbon sponge)</td>
<td>Basic Blue 3</td>
<td>Dye = 0.2 mM, pH = 3, I = 100 mA, Fe$^{3+}$ = 0.1 mM, NaNO$_3$ = 0.1 M, time = 120 min, flow rate = 150 mL/min</td>
<td>100</td>
<td>91.6 (TOC) time = 8 h</td>
<td>Özcan et al. 2008</td>
</tr>
<tr>
<td>(BDD/Pt)</td>
<td>Acid Yellow 36</td>
<td>Dye = 60 mg/L, pH = 3, I = 100 mA, Fe$^{3+}$ = 0.24 mM, SO$_4^{2-}$ = 0.05 M, time = 48 min</td>
<td>98</td>
<td>N/A</td>
<td>Cruz-González et al. 2010</td>
</tr>
<tr>
<td>(Pt/graphite felt)</td>
<td>Textile wastewater</td>
<td>Color = 2024 ADMI, pH = 3, I = 300 mA, Fe$^{3+}$ = 3 mM, time = 160 min</td>
<td>77.2</td>
<td>N/A</td>
<td>Ghanbari et al. 2015</td>
</tr>
<tr>
<td>(Pt/ACF)</td>
<td>Textile wastewater</td>
<td>COD = 1224 mg/L, pH = 3, j = 3.2 mA/cm², Fe$^{3+}$ = 2 mM, time = 240 min, oxygen sparging = 150 cm$^3$/min</td>
<td>N/A</td>
<td>75.2</td>
<td>Wang et al. 2010</td>
</tr>
</tbody>
</table>

Note:  j = current density, T = temperature, I = applied current.
applied current. SPEF, however, showed a high efficiency in TOC degradation compared with EF, since 95% of TOC decayed after only 180 min at 3 A applied current. When calculating EEC, it was revealed that SPEF was a viable method, having greater CE and lower energy cost.

Khataee and coworkers (Khataee et al. 2014) used a UVC lamp (15 W) for PEF (Pt anode/CNT-PTFE cathode) in the degradation of Acid Blue 5 (AB5). Figure 3.10 depicts the decolorization of 20 mg/L AB5 by PEF, EF, and photolysis. As can be seen, the combination of UVC with EF increased decolorization significantly with almost 100% efficiency after 20 min, while each process alone achieved less than 40% after 60 min reaction time.

PEF and SPEF processes have been considered for the degradation of Direct Yellow 4 (Garcia-Segura et al. 2014), Ponceau 4R (Thiam et al. 2015a), Reactive Red 195 (Djafarzadeh et al. 2013), Congo red (Solano et al. 2015), Allura Red AC (Thiam et al. 2015b), indigo carmine (Flox et al. 2006) and Direct Yellow 4 (Garcia-Segura et al. 2014). In all studies, it was shown that light irradiation could markedly improve the EF process.
3.2.2.2 Sonoelectro-Fenton (SEF) Process

Recently, ultrasound irradiation has been combined with the EF process to improve system performance. In the sonoelectro-Fenton (SEF) process, regeneration of Fe$^{2+}$ may occur through sonolysis of iron complexes, based on Reaction 3.42. Likewise, ultrasound cleans the surface of the electrode by means of dissolving the inhibiting layers, resulting in an improvement in mass transfer between solution and electrode. In sonolysis, sites of high temperature and pressure are generated with the collapse of the cavitation bubbles for short periods of time, decomposing the O–H bond, leading to the formation of •OH and H• (Reaction 3.43). Despite the destruction of pollutants via •OH, the sonolysis decomposes the pollutants through the pyrolysis process (Babuponnusami et al. 2012; Oturan et al. 2008b; Li et al. 2010).

$$\text{Fe} - \text{O}_2\text{H}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+} + \text{HO}_2^-(3.42)$$

$$\text{H}_2\text{O}^+(\text{aq}) \rightarrow \text{H}^+ + \text{HO}^-(3.43)$$

Furthermore, sonolysis in EF can accelerate the mass transfer rate of Fe$^{3+}$ toward the cathode for the electrogenerated Fenton reagent and consequently increase the generation of hydroxyl radicals. Abdelsalam et al. (2002) explored the SEF process with a Pt anode, RVC cathode, and a resonance frequency of 27 kHz for the degradation of meldola blue (MDB) dye. They stated that a small amount of ferrous ions could increase the rate constant of MDB degradation. However, with an increase of ferrous ions of up to more than 1 mM, the rate constant was considerably reduced. After 100 min of sonication, 67.7% of COD was eliminated with 0.1 mM MDB, constant potential of $-$0.7 V versus Ag, 0.5 mM Fe$^{2+}$, and 124 kHz.

In another study (Martínez et al. 2012), SEF was compared with Fenton oxidation and sonolysis for the degradation of Azure B dye. The rate constant of dye degradation by SEF was 10-fold more than that of the sonolysis, while this value was double that of Fenton oxidation. Figure 3.11 shows the differences in COD removal efficiencies of the three processes. It is clear that the highest COD removal efficiency was achieved by SEF (85%). SEF provided 98% decolorization at an applied potential of $-$0.7 V versus SCE after 60 min of reaction time, whereas 85% decolorization was attained without sonication.

Oturan et al. (2008b) also illustrated that ultrasound irradiation improved EF efficiency significantly for 2,4-dichlorophenoxyacetic acid and 4,6-dinitro-o-cresol degradation, albeit that no improvement was observed for the degradation of the dye (azobenzene) by SEF in comparison with EF. The authors concluded that the nature of the pollutant’s structure was an important factor. Moreover, the lowest ultrasound power was revealed to be more suitable for SEF.

3.2.2.2.3 Peroxi-Coagulation

In this process, both Fenton reagents can be electrochemically produced in such a way that the hydrogen peroxide and the ferrous ions are produced at the carbon-based cathode and iron anodes respectively. Indeed, an iron anode is used instead of a platinum or BDD electrode; so, this process is known as the peroxy-coagulation (PC) process. Despite the oxidation process by free radicals, the coagulation process also contributes to PC for dye removal via the production of Fe(OH)$_n$. The flocs produced effectively adsorb inorganic and organic pollutants such as dyes (Brillas et al. 2009; Ghanbari et al. 2015).

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (3.44)$$

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \quad (3.45)$$

$$\text{Fe}^{2+} \text{ or Fe}^{3+} + n\text{OH}^- \rightarrow \text{Fe(OH)}_{n(x)} \quad (3.46)$$
Zarei and coworkers (Zarei et al. 2009) studied PC for the removal of Basic Yellow 2 (BY2). Carbon nanotube (CNT)-PTFE and carbon-PTFE electrodes were evaluated as cathodes. The decolorization of BY2 during the first 10 min reached 62% and 96% by the carbon-PTFE and CNT-PTFE electrodes, respectively, at 100 mA applied current. Levels of TOC removal after 6 h of electrolysis were 81% and 92% for the carbon-PTFE and CNT-PTFE electrodes, respectively. Figure 3.12 displays a probable reaction sequence for the mineralization of BY2 by PC, based on the intermediates identified by Gas chromatography-mass spectrometry (GC–MS). The intermediates produced by PC for BY2 included: (I2) bis[4-(dimethylamino)phenyl]methanone, (I3) 4-dimethylaminobenzoic acid, (I4) p-hydroxybenzoic acid, (I5) hydroquinone, (I6) butenedioic acid, and (I7) ethanedioic acid.

Zarei and coworkers (Zarei et al. 2010) also studied PC on four dyes: Basic Blue 3 (BB3), malachite green (MG), Basic Red 46 (BR46), and Basic Yellow 2 (BY2). PC was conducted by a CNT-PTFE cathode and an iron anode at pH 3. Applying 100 mA electrical current, up to 90% decolorization was obtained after only 10 min for all the dyes. Mineralization was measured in terms of TOC for mixed dyes. The results showed that 93% mineralization occurred after 6 h of electrolysis. The performance of PC was also evaluated in real water samples and the results showed that 90% of the mixed dyes was removed within 40 min reaction time. The cost of the process was US$ 21.7/kg of removed dye.

Ghanbari and Moradi (Ghanbari et al. 2015) investigated four ECPs (electrocoagulation, electrochemical Fenton, EF, and PC) for the treatment of real textile wastewater. All the processes removed color sufficiently from the wastewater, inasmuch as between 77% and 94% decolorization efficiency was obtained. Figure 3.13 illustrates the COD removal efficiencies of the processes. As can be seen, EF and PC were able to provide 71.1% and 64.2% COD removal efficiency, respectively, at 300 mA applied current and pH 3. The BOD5/COD ratio of textile wastewater was increased from 0.137 to 0.362 and 0.317 after treatment by EF and PC. These results showed that EF and PC could
FIGURE 3.12 Proposed reaction sequence for the degradation of BY2 by PC. (Reproduced from Zarei, M. et al., Electrochimica Acta, 54, 6651–60, 2009.)

FIGURE 3.13 COD removal efficiency in four ECPs (EF and PC; pH 3 and 300 mA applied current). (Reproduced from Ghanbari, F. et al., Journal of Environmental Chemical Engineering, 3, 499–506, 2015.)
be used as pretreatment steps before the biological processes. However, the EECs were 63.64 and 23.19 kWh/kg COD removed for EF and PC, respectively, which were relatively high costs.

However, in the literature, other Fenton-based ECPs have also been reported that include electrochemical Fenton (ferrous ions are electrochemically produced by anode and H$_2$O$_2$ is chemically added), anodic Fenton, and Fered-Fenton (Fe$^{2+}$ and H$_2$O$_2$ are added to the electrochemical cell with DSA electrodes). Although these ECPs are based on Fenton oxidation, they do not electrochemically generate the oxidizing agent of H$_2$O$_2$. Schematic representations of the EF, PEF, SEF, and PC processes are presented in Figure 3.14.

### 3.3 CHALLENGES AND FUTURE OF EO

In the case of EO, there are several factors to be considered, including process optimization, EEC and other energy resources, the need for supporting electrolytes, electrode issues (material, synthesis, fabrication, design/geometry, and operational problems such as electrode passivation and
poisoning effect), the need for operators with high expertise, concerns related to intermediates, process scale-up, and so on.

As a general point of view, electrochemical advanced oxidation processes (EAOPs), including EO, are the so-called green processes that are attractive mainly due to the ability to mineralize organic compounds to harmless substances and minerals using electrons, which are clean reagents, leading to efficient detoxification without any reagent waste. Careful and precise optimization of EO and devoting full consideration to influential parameters, bring about an efficient and complete mineralization, alleviating solution toxicity. Ironically, where process optimization is ignored, such as operating in nonoptimized conditions—for example, in insufficient reaction time—this results in deficiencies in mineralization and a waste of energy. In such conditions, a dilemma arises, in the sense that the “mother” substances turn into “daughter” products, some of which have much higher toxicity. In addition, in wastewaters containing organics together with chloride and/or bromide ions, chlorinated and/or brominated organic compounds may appear within the effluent of an EO system, particularly in active chlorine-based EO systems. Indeed, halogenation of aromatic hydrocarbons during EO is of significant concern. The substitution of halides with hydrogen bonded with carbon results in the formation of more toxic and more persistent compounds that are more resistant to oxidation. Inorganic by-products also include chlorite, chlorate, perchlorate, and bromate, which are formed during the electrolysis of a solution containing chloride or bromide ions. Nonetheless, if an EO system is designed and operated properly with careful optimization and monitoring of the intermediates, concerns about the intermediates can be alleviated. One should also mention that although ease of operation is commonly indicated as one of the pros of electrochemical remediation processes, proper, safe, clean, and efficient operation of an EO system is not accomplished without the applicable contributions of scientists and experts.

Economic viability is a crucial parameter in the application of a process. In fact, when a process is optimized at laboratory scale, its feasibility and extension to the industrial scale is strongly dependent on economic issues. Within EO, the major influential economic factors involve costs related to EEC and the electrodes. As previously mentioned, EO is a green remediation process in which energy is consumed for the purpose of mineralizing organics. Although chemicals are not generally added during the operation, an electrical charge is applied, which is of paramount importance, so that researchers usually take it into account, calculating or estimating the amount of EEC and also the CE. Therefore, the need for electrical energy within EO is considered to be an important disadvantage of the process. Nevertheless, there are various strategies and solutions to decrease the amount of EEC in an EO system. For instance, attempts have been made in electrode fabrication to decrease EEC, such as the low-temperature diamond deposition method and the application of conductive diamonds. Likewise, the use of electrode materials with high oxygen overpotential prevents the drain of electricity, thereby lowering operational costs. Furthermore, the proper design of an EO cell through which mass transportation is enhanced leads to lower EEC. In addition, the application of an EO stage before biological treatment is favored, by which recalcitrant compounds are broken down into substances that are more easily biodegradable. In the case of costs related to the electrodes, numerous attempts have been made in the fabrication of electrodes and great achievements have been made in this way. BDD electrodes are supposed to be the most promising electrodes in EO, due to the features previously stated in this chapter. It is worthwhile to consider that, despite the significant cost of BDD electrodes, the advantages of applying them far outweigh the disadvantage of their high cost. Using BDD, highly efficient EO is obtained using less electrical energy, which is favored at EO scale within industries and other applications.

Electrodes and their related issues are the other challenging issues in the application of EO. Apart from their costs, as discussed, operational problems related to electrodes are also considerable. In fact, electrode passivation or fouling by oligomeric or polymeric materials is one of the most challenging issues in EO processes. Thanks to the electrogeneration of active, electrolytic hydroxyl radicals on BDD anodes, polymeric substances are oxidized on the anode surface, while
anodic corrosion may be the weak point of these electrodes. In this case, many studies have also investigated and focused on solutions to overcome electrode deactivation.

Another issue in EO processes is related to the supporting electrolyte, which is required for electrical charge transfer. In fact, the addition of the supporting electrolyte is not favored, mainly because it gives rise to solution TDS and, generally, induces impurities. On the other hand, textile wastewater usually contains enough electrolytes that have been added to it previously during the dyeing function in a textile mill to achieve better fixation. In this way, sodium chloride or sodium sulfate are the most commonly used electrolytes, particularly sodium chloride, which is cheaper. Consequently, sodium chloride in the dye wastewater may inevitably act as an electrolyte during EO treatment. Likewise, the initial presence of chloride in wastewater prompts the selection and application of active chlorine-based EO. Nevertheless, there may be cases in which the addition of an electrolyte is needed. However, most often, simple supporting electrolytes are added to the solution. Research has been conducted indicating that ion-exchange resins are promising substitutions that prevent workup challenges.

In general, EO as a green, promising process is attracting much attention and is continually undergoing numerous investigations. Research is shifting toward the use of new anode materials and applying nanomaterials as heterogeneous catalysts, especially within Fenton-based electrochemical systems. The application of EO in combination with other processes such as photolysis, sonolysis, and microwave technologies is also being explored.

REFERENCES


Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment


