
Removal Of Some Azo Dyes from Industrial Waste Water By Electrochemical Methods

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The reuse of wastewater has become an absolute necessity. Demands to the cleaning industrial and domestic wastewater to avoid environmental pollution and especially contamination of pure water resources are becoming national and international issues. Innovative, cheap and effective methods of purifying and cleaning wastewater before discharging into any other water systems are needed. Effluents from dyeing industry are not only colored but also contain high amounts of COD and dissolved solids. Textile industry is considered as one of the most polluting sectors in terms of effluent composition and volume of discharge. Dyes are gradually emerging as a class of anthropogenic organic substances that pose serious threat to environment. Dye bath effluents are not only aesthetic pollutants by their color but also interfere with light penetration that disturbs biological processes. Furthermore, dye effluent may contain chemicals that are toxic, carcinogenic, mutagenic or teratogenic for microbes and fish species. Dyes are commonly classified from their chromophore group. The majority of these compounds consumed at industrial scale are azo ($-N=N-$) derivatives, although anthraquinone, indigoide, triphenylmethyl, xanthene, sulphur and phthalocyanine derivatives are frequently utilized [1]. Dyes could also be classified into: Acid (it is negatively charged), Basic (it is positively charged), Reactive (an anionic dye used in the textile industry), Mordant (a metallic ion is required for showing their color or staining selectivity), Vat (it derives of natural indigo), Disperse (a non-ionic dye used in aqueous dispersion). The azo dyes form the largest group 60 –70% among the synthetic colorants [2]. They are among the major pollutants of wastewaters from textile industries; in many areas, these industries discharge wastewaters having strong color, variable pH and temperature, high COD and low biodegradability and therefore are difficult to treat satisfactorily [3]. Their chromophoric system consists of azo groups ($-N=N-$) in association with aromatic systems and auxochromes ($-OH$, $-SO_3$, etc.). The azo class of compounds accounts for 60 –70% of all dyes. Azo dyes give bright, high-intensity colors, much more so than the next most common dye class, anthraquinones [4]. The toxicity and carcinogenic nature of these dyes and their predecessors pose a threat to the environment [5]. Lethal levels may be reached, affecting aquatic systems and associated flora and fauna. Many treatments have been investigated for their effectiveness in either removing dyes from dye-containing effluents or decolorizing dyes through liquid fermentations [6]. The proper treatment of aqueous wastes is

fundamental to the preservation of environmental equilibria and the quality of aquatic systems. The presence of these pollutants in waters can change their appearance and cause visible colorization of the water or alter the clarity. Due to their large-scale production and extensive application, synthetic dyes can cause considerable non aesthetic pollution and are serious health-risk factors. Although the growing impact of environmental protection on industrial development promotes eco-friendly technologies [7], reduced consumption of water and lower output of wastewater [8], there release of important amounts of synthetic dyes to the environment causes public concern and legislation problems are a serious challenge to environmental scientists [9]. The impact and toxicity of these pollutants in the environment have been extensively studied [10-15]. However, the knowledge concerning their carcinogenic, mutagenic and bactericide properties is still incomplete owing to the large variety of dyes produced. Since dyes usually present high stability under sunlight and resistance to microbial attack and temperature, the large majority of these compounds are not degradable in conventional wastewater treatment plants. The research of powerful and practical treatments to decolorize and degrade dyeing wastewaters to decrease their environmental impact has then attracted increasing interest over the past two decades. An extensive literature reporting the characteristics and applications of most important conventional technologies developed for this purpose including physico-chemical and chemical methods, advanced oxidation processes (AOPs), microbiological treatments and enzymatic decomposition, has been collected in several critical reviews [16-18]. The main electrochemical procedures utilized for the remediation of dyestuffs wastewaters are given in (Scheme 1) Electrocoagulation (EC), direct electrochemical oxidation (EO) with different anodes and indirect electro-oxidation with active chlorine are typical methods for the removal of these pollutants. The treatment by emerging technologies such as electro-Fenton (EF) and photoassisted systems like photoelectro-Fenton (PEF) and photoelectrocatalysis has recently received great attention, but the possible role of electrochemical reduction has -been clarified in much lesser extent. Note that electrochemical oxidation, electro Fenton and photoassisted electrochemical systems have been classified as electrochemical advanced oxidation processes (EAOPs).

1. Electrocoagulation

A traditional physico-chemical treatment of phase separation for the decontamination of dyes wastewaters before discharge to the environment is coagulation. It consists in the addition of coagulating agents such as Fe^{3+} or Al^{3+} ions, usually in the form of chlorides, for dyes precipitation. The electrochemical technology can produce similar effects by means of the EC method [19-21]. This technique uses a current to dissolve Fe (or steel) or Al anodes immersed in the polluted water, giving rise to the corresponding metal ions that yield different Fe^{2+} (and/or Fe^{3+}) or Al^{3+} species with hydroxide ion depending on the medium pH. These species act as coagulants or destabilization agents that bring about charge neutralization for dyes separation from the wastewater. The coagulated particles can also be separated by electroflotation when they are attached to the bubbles of H_2 gas evolved at the cathode and transported to the top of the solution where they can be separated. In general, the following main processes take place during an EC treatment [22, 23]: (i) Electrode reactions to produce metal ions from Fe or Al anodes and H_2 gas at the

cathode.(ii) Formation of coagulants in the wastewater.(iii) Removal of dyes with coagulants by sedimentation or by electro-flotation with evolved H₂.(iv) Other electrochemical and chemical reactions involving reduction of organic impurities and metal ions at the cathode and coagulation of colloidal particles.Many advantages for EC have been reported [24]:(i) More effective and rapid organic matter separation than in coagulation.(ii) pH control is not necessary, except for extreme values.(iii) The amount of chemicals required is small.(iv) The amount of sludge produced is smaller when compared with coagulation. For example, the sludge formed in the EC method with Fe contains higher content of dry and hydrophobic solids than that produced in coagulation by the action of FeCl₃ followed by the addition of NaOH or lime.(v) The operating costs are much lower than in most conventional technologies.However, this method presents as major disadvantages:(i) Anode passivation and sludge deposition on the electrodes that can inhibit the electrolytic process in continuous operation mode.(ii) High concentrations of iron and aluminum ions in the effluent that have to be removed.

2. Electrochemical reduction

A limited number of papers have been published dealing with the direct electroreduction of dyes in aqueous solution on suitable cathodes. The reason of the low interest for this conventional electrochemical technique is that it offers poor decontamination of wastewaters in comparison to more potent direct and indirect electro-oxidation methods, as will be detailed below.

3. Electrochemical oxidation

Electrochemical oxidation or electro-oxidation (EO) is the most popular electrochemical procedure for removing organic pollutants from wastewaters. This technique has been recently used for decolorizing and degrading dyes from aqueous solutions. It consists in the oxidation of pollutants in an electrolytic cell by:(i) Direct anodic oxidation (or direct electron transfer to the anode), which yields very poor decontamination.(ii) Chemical reaction with electrogenerated species from water discharge at the anode such as physically adsorbed “active oxygen” (physisorbed hydroxyl radical (-OH)) or chemisorbed “active oxygen” (oxygen in the lattice of a metal oxide (MO) anode).The action of these oxidizing species leads to total or partial decontamination.The existence of indirect or mediated oxidation with different heterogeneous species formed from water discharge has allowed the proposal of two main approaches for the pollution abatement in wastewaters by EO [25]:(i) The electrochemical conversion method, in which refractory organics are selectively transformed into biodegradable compounds, usually carboxylic acids, with chemisorbed “active oxygen”.(ii) The electrochemical combustion (or electrochemical incineration) oxidized to CO₂ and inorganic ions, with physisorbed (-OH). This radical is the second strongest oxidant known after fluorine, with a high standard potential ($E^0 = 2.80 \text{ V vs. SHE}$) that ensures its fast reaction with most organics giving dehydrogenated or hydroxylated derivatives up to conversion into CO₂.In both cases high cell voltages are applied to the electrochemical cell for the simultaneous oxidation of pollutants and water, thus maintaining the anode activity. The use of low cell voltages avoiding O₂ evolution frequently causes the loss of anode activity because some by-products formed from direct anodic oxidation can be adsorbed on its surface and hence, this procedure is not utilized for wastewater treatment in practice. It has been found that the nature of the anode material influences strongly both the selectivity and efficiency of the

EO process. To interpret this behaviour, a comprehensive model for organics destruction in acidic medium including the competition with the oxygen evolution reaction has been proposed [25]. The predictions of this model fit quite well with recent results obtained with conductive diamond electrodes such as BDD, which present the highest O₂ over voltage known [26].