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Review

Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review

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ABSTRACT

As the environment preservation gradually becomes a matter of major social concern and more strict legislation is being imposed on effluent discharge, more effective processes are required to deal with non-readily biodegradable and toxic pollutants. Synthetic organic dyes in industrial effluents cannot be destroyed in conventional wastewater treatment and consequently, an urgent challenge is the development of new environmentally benign technologies able to mineralize completely these non-biodegradable compounds. This review aims to increase the knowledge on the electrochemical methods used at lab and pilot plant scale to decontaminate synthetic and real effluents containing dyes, considering the period from 2009 to 2013, as an update of our previous review up to 2008. Fundamentals and main applications of electrochemical advanced oxidation processes and the other electrochemical approaches are described. Typical methods such as electrocoagulation, electrochemical reduction, electrochemical oxidation and indirect electro-oxidation with active chlorine species are discussed. Recent advances on electrocatalysis related to the nature of anode material to generate strong heterogeneous •OH as mediated oxidant of dyes in electrochemical oxidation are extensively examined. The fast destruction of dyestuffs mediated with electrogenerated active chlorine is analyzed. Electro-Fenton and photo-assisted electrochemical methods like photoelectrocatalysis and photoelectro-Fenton, which destroy dyes by heterogeneous •OH and/or homogeneous •OH produced in the solution bulk, are described. Current advantages of the exposition of effluents to sunlight in the emerging photo-assisted procedures of solar photoelectrocatalysis and solar photoelectro-Fenton are detailed. The characteristics of novel combined methods involving photocatalysis, adsorption, nanofiltration, microwaves and ultrasounds among others and the use of microbial fuel cells are finally discussed.

Contents

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1. Introduction

The contamination of water bodies by man-made organic chemicals is definitely a critical issue that the recent water framework directives are trying to address in order to ensure good water quality status and healthy ecosystems [1,2]. Although major attention is currently paid to persistent and emerging pollutants, especially if they are likely to endocrine disrupting activity, water pollution by synthetic dyes is also of great concern due to the large worldwide production of dyestuffs. Several studies have reported that there are more than 100,000 commercially available dyes with an estimated annual production of over 7×10^5 tons of dye-stuff [3]. Industries such as textile, cosmetic, paper, leather, light-harvesting arrays, agricultural research, photoelectrochemical cells, pharmaceutical and food produce large volumes of wastewater polluted with high concentration of dyes and other components [4]. The pollutants in these effluents include organic and inorganic products like finishing agents, surfactants, inhibitor compounds, active substances, chlorine compounds, salts, dyeing substances, total phosphate, dissolved solids and total suspended solids (TSS) [5]. However, coloring matter is the major problem because it creates an esthetic problem and its color discourages the downstream use of wastewater [6]. Esthetic merit, gas solubility and water transparency are affected by the presence of dyes even in small amount or concentrations [7].

Dyes can be classified as Acid, Basic, Direct, Vat, Sulfur, Reactive, Disperse, metal complexes, etc., including antraquinone, indigoide, triphenylmethyl, xanthene and phthalocyanine derivatives. This classification expresses a general characteristic property of the dye (see more information in Ref. [8]). For example, Acid means that it is negatively charged, Basic when it is positively charged, Reactive if it is an anionic dye used in the textile industry, Mordant if it contains a metallic ion, Vat when it derives of natural indigo, Disperse when it is a non-ionic dye used in aqueous dispersion and so on. This nomenclature, followed by the name of its color and an order number, gives the color index (C.I.) name of the dye [8].

According to Jin et al. [9] and Solís et al. [10], about 280,000 tons of textile dyes are currently discharged in effluents every year because large volumes of wastewaters are generated in various processes of this industry such as sizing, scouring, bleaching, mercerizing, dyeing, printing and finishing [11,12]. For example, Reactive dyes with good water solubility and easily hydrolyzed into insoluble forms are lost in about 4% during dyeing [4]. As a result, dye effluents contain chemicals that are toxic, carcinogenic, mutagenic or teratogenic to various fish species [7]. Azo dyes are the most widely used dyes and represent over 70% of their total production [2,4,10,13]. They are complex aromatic compounds with large structural diversity that always provide a high degree of chemical, biological and photocatalytic stability and breakdown resistance with time, exposure to sunlight, microorganisms, water and soap; in other words, they are resistant to degradation [14]. For this reason, many studies have been focused mainly on the removal of azo dyes from waters. Nevertheless, the introduction of synthetic fibers has led to the appearance of some niche markets that require the use of other classes of dyes, becoming a new great environmental problem.

An extensive literature has reported the characteristics and applications of most important methods for removing dyes from water [3,4,8,10,13,15–20]. Fig. 1 summarizes their main technologies classified as physicochemical, chemical, advanced oxidation processes (AOPs), biological and electrochemical. The mechanisms for color removal involve physical dye separation, breakdown of the dyes or decolorization by adsorption/biodegradation [3,5,8].

The physicochemical techniques include coagulation/flocculation, adsorption and membrane separation. In coagulation, Sulfur and Disperse dyes are removed from the electrostatic attraction between oppositely charged soluble dye and polymer molecule. Acid, Direct, Vat and Reactive dyes also coagulate but do