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Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters

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ABSTRACT

A large variety of electrochemical advanced oxidation processes (EAOPs) have been recently developed to remove organic pollutants from wastewaters to avoid their serious health-risk factors from their environmental accumulation and to reuse the treated water for human activities. The effectiveness of EAOPs is based on the in situ production of strong reactive oxygen species (ROS) like hydroxyl radical (•OH). Photoelectrocatalysis (PEC) has emerged as a promising powerful EAOP by combining photocatalytic and electrolytic processes. It consists in the promotion of electrons from the valence band to the conduction band of a semiconductor photocatalyst upon light irradiation, with production of positive holes. The fast recombination of the electron/hole pairs formed is avoided in PEC by applying an external bias potential to the photocatalyst that extracts the photogenerated electrons up to the cathode of the electrolytic cell. Organics can be oxidized directly by the holes, •OH formed from water oxidation with holes and other ROS produced between the electrons and dissolved O_2. This paper presents a general and critical review on the application of PEC to the remediation of wastewaters with organic pollutants. Special attention is made over the different kinds of photocatalysts utilized and preparation methods of the most ubiquitous TiO_2 materials. Typical PEC systems and main operation variables that affect the effectiveness of the degradation process are also examined. An exhaustive analysis of the advances obtained on the treatment of dyes, chemicals and pharmaceuticals from synthetic solutions, as well as of real wastewaters, is performed. Finally, research prospects are proposed for the future development of PEC with perspectives to industrial application.

Abbreviations: A, absorbance of the most intense UV/Vis peak; A_0, initial absorbance of the most intense UV/Vis peak; ACF, activated carbon fiber; Ag/AgCl, reference electrode of Ag/AgCl (KCl saturated); ALD, atomic layer deposition; AOP, advanced oxidation process; APS, atmospheric plasma spray; BDD, boron-doped diamond; BOD_5, biochemical oxygen demand at 5 days; c, organic concentration (mM or mg L^{-1}); c_0, initial organic concentration (mM or mg L^{-1}); CB, conductive band; CVD, chemical vapor deposition; COD, chemical oxygen demand (mg O_2 L^{-1}); COD_0, initial chemical oxygen demand (mg O_2 L^{-1}); DO, direct ozonation; DP, direct photolysis; DRS, diffuse reflectance spectroscopy; DSA®, dimensionally stable anode; EAOP, electrochemical advanced oxidation process; e^-_{CB}, electron in the conduction band; EDS, energy dispersive spectrometry; EF, electro-Fenton; EIS, electrochemical impedance spectroscopy; EO, electrochemical oxidation; E_{anod}, anodic potential (V); E_{bg}, band gap energy (eV); E_{cat}, cathodic potential (V); E_{cell}, potential difference of the cell (V); E_{fb}, flat band energy (V); FESEM, field-emission SEM; FTO, fluor-doped tin dioxide; h^+_{VB}, hole in the valence band; HPLC, high-performance liquid chromatography; I, current (A or mA); ITO, indium-tin oxide; j_{anod}, anodic current density (mA cm^{-2}); λ, wavelength of UV/Vis spectrum; λ_{max}, maximum wavelength of UV/Vis spectrum; LC–MS, liquid chromatography–mass spectrometry; NB, nanobelt; NT, nanotube; NTA, nanotube array; PANI, polyaniline; PC, photocatalysis; PEC, photoelectrocatalysis; PEF, photoelectro-Fenton; PTFE, polytetrafluoroethylene; PZC, point of zero charge; ROS, reactive oxygen species; SCE, saturated calomel electrode; SCL, space charge layer; SEM, scanning electron microscopy; SPEC, solar photoelectrocatalysis; t, electrolysis time; TEM, transmission electron microscopy; TOC, total organic carbon (mg C L^{-1}); TOC_0, initial total organic carbon (mg C L^{-1}); VB, valence band; UV, ultraviolet; UVA, ultraviolet A; UVB, ultraviolet B; UVC, ultraviolet C; Vis, visible; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy.

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Contents

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1. Introduction

One of the main current worldwide concerns is the growth of water pollution by organic compounds arising from many industrial, agricultural and urban human activities. The vast majority of these compounds are persistent organic pollutants, owing to their resistance to conventional chemical, biological and photolytic processes. As a result, they have been detected in rivers, lakes, oceans and even drinking water all over the world. This constitutes a serious environmental health problem mainly due to their toxicity and potential hazardous health effects (carcinogenicity, mutagenicity and bactericidality) on living organisms, including human beings [1–4].

Dyes, chemicals and pharmaceuticals are some of the most common recalcitrant organic pollutants. For instance, many industries including 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. As a result, about 280,000 tons of textile dyes are currently discharged in effluents every year and introduced in the aquatic environment [5]. This has induced many governments to apply legislation that prescribes and limits the emission of pollutants. To face this environmental problem, three different approaches have been considered: (i) the development of Green Chemical and Technological Processes, (ii) the use of the 3R (reduce, reuse and recycle) sustainability consciousness and (iii) the application of wastewater remediation technologies. The latter approach has received great attention because it is easily usable and can solve the contamination problems.

Current methods for wastewater treatment have been based on oxidation processes including physicochemical, biological, chemical and electrochemical treatments [5]. Note that no universal strategy on wastewater remediation is feasible because of the extremely diverse composition of industrial waste that usually contains a complex mixture of organic and inorganic compounds and mainly depends on the nature and concentration of pollutants.

Physicochemical techniques require high cost of equipment and usually present low effectiveness, particularly over dyes and pharmaceuticals. Biological treatments are environmentally friendly, produce less sludge than physicochemical systems and are relatively inexpensive. Nevertheless, their application is rather limited since treatment needs a large land area, has sensitivity toward toxicity of certain chemicals and operation time is very long. Over the past three decades, many advanced oxidation processes (AOPs) have been developed as more effective technologies to remove persistent organic pollutants from wastewaters [6]. AOPs are based on the *in situ* production of highly reactive hydroxyl radicals (•OH) that non-selectively react with most organics and are able to