The abatement of indigo carmine using active chlorine electrogenerated on ternary Sb_2O_5-doped Ti/RuO_2-ZrO_2 anodes in a filter-press FM01-LC reactor

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ABSTRACT

Dimensionally Stable Anodes (DSA) of Sb_2O_5-doped Ti/RuO_2-ZrO_2 are prepared by the Pechini method to perform the degradation of indigo carmine (IC) under conditions similar to textile wastewater effluents. XRD results along with Rietveld refinement reveal that the co-deposited phases on the DSA exhibit a tetragonal crystal structure ($P4/mmm$) for RuO_2 and monoclinic structure ($P2/m$) for ZrO_2. Degradation tests conducted in solutions containing 0.64 mM IC and 0.05 M NaCl using a filter-press reactor (FM01-LC) show that the degradation rate is faster and more efficient at $200\,A\,m^{-2}$ with a flow rate of $5\,L\,min^{-1}$, although the energy consumption is moderately higher. Under this condition, the pollutant is efficiently removed, and converted to aliphatic acid compounds of low molecular weight, as indicated by 90 % Chemical Oxygen Demand (COD), 22 % Total Organic Carbon (TOC) elimination, along with an Average Oxidation State (AOS) value equal to 3.0. The energy consumptions revealed that it is feasible to carry out the IC degradation under reasonable operating costs. Topological and Natural Bond Orbital (NBO) analyses are computed using density functional theory (DFT), and combined with experimental results to propose a reaction pathway for IC abatement.

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1. Introduction

Textile wastewaters containing a high concentration of recalcitrant dye residues are a challenge for chemical and biological degradation methods [1], because of their enhanced resistance to light and chemical oxidation as a result of their molecular stability [2] that turns them toxic to any aquatic ecosystem. Indigo carmine (Fig. 1a) or acid blue 74 (3, 3- dioxo-2, 2-bis-indolyden-5, 5-disulfonic acid disodium salt) is a typical recalcitrant dye used for staining in the textile industry due to its high solubility ($10\,g\,L^{-1}$ at 25 °C) [3], and as additive for pharmaceutical manufacturing and medical diagnosis [4]. IC is considerably toxic, whence it is necessary to remove it from wastewater [5].

The choice of a treatment method entails multiple factors involving the physical chemistry, composition and concentration of the wastewater, as well as its efficiency and cost. Indirect electrochemical oxidation seems more suitable for treating textile effluents in comparison with other methods, because of their high conductivity, low chemical reactivity, avoid surface polymerization (i.e. poisoning effect) and electrode fouling hindering anode-catalytic activity in direct oxidation [6–8]. This method involves the electro-generation of a strong oxidizing agent (redox reagents) on the anode surface, which degrades the pollutant in the bulk solution according to eqs. (1)-(2) [9,10]:

$$A^z \rightarrow A^{z+1} + e^- \tag{1}$$

$$A^{z+1} + R \rightarrow A^z + RO + H_2O \tag{2}$$

where A^z/A^{z+1} is the redox couple of the oxidizing agent, while R and RO are the reduced and oxidized forms of the organic pollutants, respectively. Electro-catalytic materials such as boron doped diamond (BDD) and Dimensionally Stable Anodes (DSA) are

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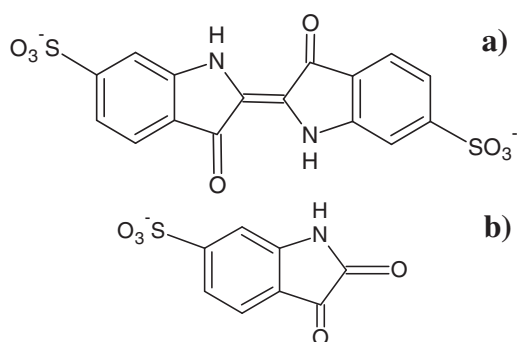
Fig. 1. Chemical structures of a) indigo carmine dye and b) isatin 5-sulfonic acid.

required to successfully carry out the above mechanism. These anodes are very stable upon the passage of electric current, and exhibit good activity towards the oxidation of organic compounds [8].

Textile wastewaters typically contain chlorides resulting from the pigment fixation on fibers. Although BDD anodes could form hydroxyl radicals (i.e. strong oxidants) on their surface ($^{\bullet}OH$, E = 2.8 V vs SHE), their performance are remarkably affected in chloride media [11]. Additionally, the high cost of these materials limits their commercial applications at industrial scale. Accordingly, DSA anodes are better choice for chloride media because of their corrosion-resistant and good electrocatalytic properties to form chlorine and lower fabrication costs. Active chlorine species (Cl_2/Cl^-, E = 1.36 V vs. SHE; $HClO/Cl^-$, E = 1.49 V vs SHE; ClO^-/Cl^-, E = 0.89 V vs. SHE) are known to be strong oxidants for organic compounds [12]. For these purposes, RuO_2 is the most commercialized DSA [13,14]. In order to improve the properties and durability of this electro-catalyst, valve metal oxides (i.e. TiO_2, ZrO_2, SnO_2, Ta_2O_5, Nb_2O_5) stabilize the Ru^{IV} cations within the crystal lattice of the oxide [15]. This condition improves the specific capacitance [16], increases the electro-catalytic activity [17], and decreases the dosage of catalyst in the anode [18].

Gaudet et al. found an improvement in the stability of the RuO_2-SnO_2 catalyst ([RuO_2] = 0 to 80 wt %) due to the formation of a solid solution [19]. Zeng et al. reported that there is a critical concentration at which the increase of Sn content within the structure of the Ti/RuO_2-SnO_2-TiO_2 catalyst enhances its activity to form active chlorine, as well as its stability and corrosion resistance [20]. The incorporation of traces of antimony (Sb_2O_5) as ternary oxide (Ti/RuO_2-Sb_2O_5-SnO_2) was found to improve the activity to form active chlorine, which increased the degradation efficiencies

for environmental remediation [21]. The use of ternary oxides as anodes to degrade organic compounds has been hardly investigated, particularly the mixture RuO_2-ZrO_2. To our current state of knowledge, only one study has been dedicated to the fabrication of Sb_2O_5-doped Ti/RuO_2-ZrO_2 for dye decolorization using active chlorine [22]. However, this analysis was focused on characterizing the textural properties and composition of Ti/RuO_2 and Sb_2O_5-doped Ti/RuO_2-ZrO materials, and dye degradation tests were restricted to micro-electrolysis experiments. Accordingly, there is a lack of information concerning the degradation mechanism of dyes on Sb_2O_5-doped Ti/RuO_2-ZrO_2 electro-catalysts, as well as the analysis of active chlorine performance for IC abatement in macro-electrolysis, and their decomposition pathway. In order to draw on the practical advantages offered for this method, and reveal limitations under pilot plant conditions (e.g. scaling-up) in terms of current efficiency and energy consumption of the process, the present study aims to analyze the degradation of Indigo Carmine on Sb_2O_5-doped Ti/RuO_2-ZrO_2 electrocatalysts in a bench-scale FM01-LC reactor (Fig. 2), which has been extensively used for other electrochemical processes. Indeed, this evaluation cannot be inferred from micro-electrolysis conditions. The synthesis of the electrocatalysts, their microstructure (XRD, SEM-EDS), chemical (TGA-DSC), and electrochemical characterization are analyzed to get the first insights of the system. Dye removal efficiencies and energy consumptions are discussed as a function of different hydrodynamic conditions and applied currents imposed in the reactor. To better understand the degradation mechanism, active sites in IC undergoing advanced oxidation are verified via quantum chemistry calculations. None of these analyses have been undertaken yet, and it is expected that they can contribute to the solution of major problems generated in the textile wastewater industry.

2. Experimental

2.1. Preparation of electrodes

DSAs were synthetized using the Pechini method on titanium plates, where a Sb_2O_5-doped Ti/RuO_x-ZrO_x film was impregnated on this material, according to Pérez et al., 2008 [23]. Analytic grade reagents of $RuCl_3 \cdot H_2O$ (Sigma-Aldrich), $ZrO(NO_3)_2 \cdot H_2O$ (Sigma-Aldrich) and $SbCl_3$ (sigma-Aldrich) were utilized as metallic precursors in a polymeric mixture prepared with 1:0.3:0.004 molar ratio of Ru:Zr:Sb; 0.12 mol Citric Acid as chelating agent and 16 mol Ethyleneglycol as reaction solvent. The polymeric mixture was kept stirred for 30 minutes at 80 °C. A thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses were carried
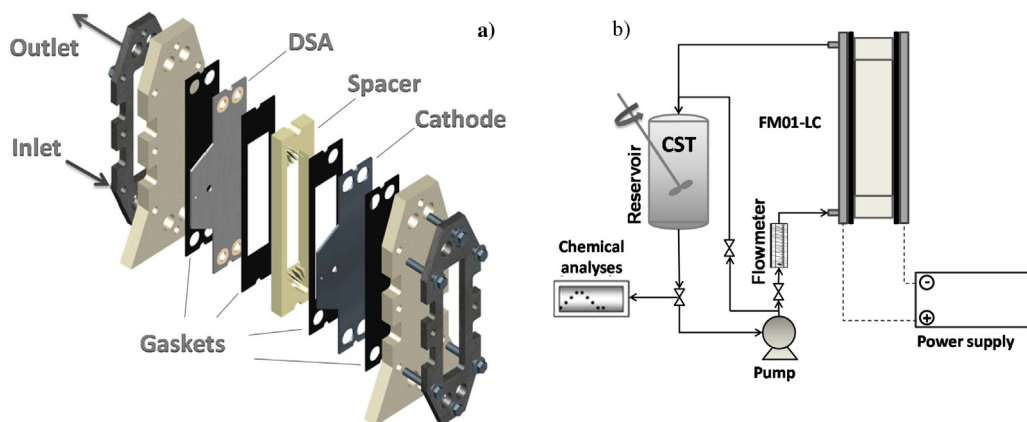

Fig. 2. a) Sketch of the components of the filter-press FM01-LC reactor. b) Diagram of the experimental set-up utilized to perform the degradation of indigo carmine in the FM01-LC reactor.