Photoelectrochemical Advanced Oxidation Processes on Nanostructured TiO$_2$ Catalysts: Decolorization of a Textile Azo-Dye

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Abstract—This work describes a novel approach for water treatment by photoelectrocatalysis, based on nanostructured TiO$_2$. The decolorization of aqueous solutions containing the azo-dye RR243 is carried out in a tubular photocatalytic reactor working in semi-batch mode under electrical polarization of the catalyst. Two different nanostructured catalysts were tested: nanotubular TiO$_2$ obtained by conventional anodization (CA), and a novel photoactive nanoporous TiO$_2$ obtained by plasma electrolytic oxidation (PEO). Neither UV irradiation of the TiO$_2$ catalysts nor the electrical bias individually considered lead to a significant reduction of the dye concentration. By irradiating the catalysts with UVC light while applying an electrical bias to the same, the concentration of the dye decreased from 25 L to 2.5 mg/L using the nanotubular CA TiO$_2$ catalyst, and to less than 1.8 mg/L using the novel nanoporous PEO TiO$_2$ in 50 min. The main advantages of this method over current approaches for the degradation of pollutants are both the considerable processing time reduction and a suitable and easy-to-scale-up reactor design. A further advantage is the relatively easyness in the production of the TiO$_2$ catalysts by PEO.

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INTRODUCTION

In compliance with the strict regulations on water quality, in recent years the processes for water and wastewater treatments were mostly conceived to address the removal of refractory organic compounds, such as dyes, solvents or pesticides. Chemical oxidation treatments involving transient radical species, also referred to as Advanced Oxidation Processes (AOPs), are among the most investigated methods for the removal of recalcitrant organics [1]. An alternative approach to conventional chemical generation of radicals is the heterogeneous photochemical catalysis based on the use of titanium dioxide [2, 3]. Titanium dioxide is a wide band gap (rutile 3.0 eV, anatase 3.2 eV) semiconductor which in the presence of water or air produces highly reactive radicals when irradiated with UV light (λ < 380 nm). The photoactivity of the titanium dioxide is extremely dependent on the level of crystallinity and on the crystalline phase composition, where anatase is the required crystal phase. In photoelectrochemical AOPs two main issues should be addressed: the form (dispersed powder, supported powder, film etc.) and the efficiency of the catalyst and the engineering of the whole process.

Heterogeneous photochemical catalysis has recently found application in AOPs, where the titanium dioxide catalyst is used in the form of dispersed nanopowders in aqueous solutions [4, 5]. The main disadvantage of this approach is that a separation treatment is required after use. The immobilization of TiO$_2$ nanopowders deposited by sol-gel technique onto metallic wire meshes [6] and the development of nanotubular TiO$_2$ films obtained by electrochemical anodization [7] overcome this problem, and open new perspectives in the field. In fact, supported nanostructured titanium dioxide can be used as electrode, and studies available in literature explain the potentialities of this class of AOPs [8, 9].

Several studies reported in literature describe the preparation of nanotubular TiO$_2$ films by anodic oxidation of titanium substrates. Nanostructured titanium dioxide coatings can also be obtained by Plasma Electrolytic Oxidation (PEO), which involves anodization at potentials above the breakdown voltage of the coating. After the pioneering works done more than one century ago by Russian researchers and in 30’s by German researchers on high voltage electrolysis, it was only in the 70’s that Markov and Markova demonstrated the

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1 The text was submitted by the authors in English.
feasibility of using PEO process for the production of ceramic coatings on light metal alloys [10]. In principle, the PEO process could be an extremely effective route to obtain photoactive titanium dioxide coatings, with the additional possibility of modifying the photoactivity of the coating by doping [11]. However, as a matter of fact, the studies available in literature mainly report difficulties in controlling the crystalline phase composition, which strongly affects the photoactive properties [12, 13]. Indeed, to the authors knowledge there are very few investigations on TiO₂ obtained by PEO due to poor photocatalytic properties of the resulting coatings. Furthermore, there is an issue concerning the scalability of this process because of the extremely high currents flowing during the initial stages of the anodic oxidation process.

In the present study, the decolorization of an organic recalcitrant azo-dye of use in the textile industry was carried out in a laboratory reactor working in semi-batch model. The UV activation of the catalysts was coupled to the electrochemical activation of the same by supporting the TiO₂ catalysts on polarizable titanium meshes. Two different photoactive TiO₂ catalysts were employed, having a self-organized nanotubular morphology obtained by conventional anodization or a novel porous structure obtained by PEO. In the present investigation, it is demonstrated that nanoporous TiO₂ catalysts obtained by PEO shows faster degradation kinetics than self-organized nanotubular TiO₂. The photoelectrochemical reactor described in the present paper allowed 90% decolorization of the azo-dye RR243 in less than 50 min of processing time. Furthermore, the integration of an innovative photoactive electrode obtained by PEO lead to an easier industrialization of the whole process, contributing to make a significant step forward in the development of electrophotocatalytic processes for water decontamination.

EXPERIMENTAL

Preparation of the Nanostructured TiO₂ Catalysts

Nanoporous titanium dioxide samples were obtained by PEO of Grade 1 titanium tubular wire meshes (exposed area 540 cm², supplied by Tessitura Tele Metalliche Rossi Srl). The nanoporous TiO₂ coatings were obtained in a two electrodes cell where the couterelectrode was a titanium alloy mesh. The electrolyte consisted of 0.5 M H₂SO₄ maintained at –3.5°C for the whole duration of the oxidation treatment by means of a cryostat (HAAK D10). The PEO was carried out at the constant cell voltage of 160 V for 20 min. After oxidation, the titanium dioxide films were rinsed in distilled water and dried in nitrogen flow. No thermal pre- and post-treatments were carried out on PEO TiO₂. The average thickness of the resulting titanium dioxide films was 1 μm. The average porosity was 5% as evaluated by means of ImageJ software analysis of SEM surface micrographs.

The properties of the TiO₂ coatings obtained by low temperature PEO were compared with those of nanotubular titanium dioxide films obtained by conventional anodization (CA) of titanium sheets (2 cm²) and wire meshes (540 cm²) of Grade 1 commercial purity titanium. In both cases, the nanotubular titanium dioxide coatings were obtained by anodization in 1 M H₂SO₄ and 78.5 mM HF at 20 V and room temperature for 24 h. A two electrode cell was used, where the counterelectrode consisted of graphite bars. Annealing pre- and post-treatments at 400°C for 2 h in air were required to obtain the nanotubular morphology and a photoactive crystalline phase composition. The nanotubular titanium dioxide coating had an approximate thickness of about 500 nm, pore size of 150 nm and pore spacing of 150 nm.

Morphological, Structural and Photoelectrochemical Characterization of the TiO₂ Catalysts

The surface morphology was investigated by means of Scanning Electron Microscopy (SEM—Zeiss® EVO 50) equipped with LaB₆ source, operated at 20 kV accelerating voltage. The crystallographic structure of the titanium dioxide coatings was assessed by X-ray diffraction (XRD) using a Philips PW1830 instrument, with CuKₐ₁ radiation and Bragg-Brentano geometry. XRD was performed in the 2θ angular range of 30–90°.

An estimation of the grain size can be calculated according to Scherrer equation. The weight fraction of anatase \(f_A\) (%) was calculated according to [14], where \(I_{R110}\) and \(I_{R101}\) are the intensity of the XRD reflection peaks of (110) rutile at 2θ = 27.45° and of the (101) anatase at 2θ = 25.30°:

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f_A = \frac{1}{1 + 1.26 \times \frac{I_{R110}}{I_{A101}}} \times 100
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