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Photocatalytic degradation of salicylic acid and caffeine emerging contaminants using titania nanotubes

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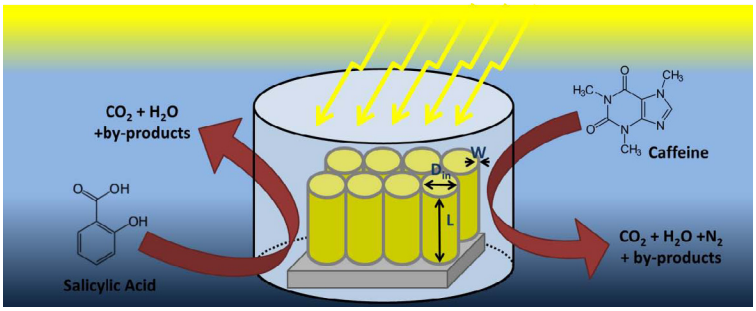
HIGHLIGHTS

- Titania nanotubes with 5–20 μm length synthesized under galvanostatic anodization.
- Close to 50% photocatalytic degradation of caffeine and salicylic acid was attained.
- 10 μm nanotubes length was optimum for photocatalysis.
- Small dependence of photocatalytic efficiency on solutions pH attained.
- TNT films give reproducible activity after 10 photocatalytic cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous photocatalysis can be a suitable add-on process to conventional wastewater treatment methods aiming to the full degradation of emerging contaminants contributing to water pollution. This work examines the photo-degradation of two frequently detected emerging contaminants (caffeine and salicylic acid) using titanium dioxide nanotubular films (TNTs) so as commercial TiO_2 nanoparticulate films (Evonik P25) for comparison. The TNT films were prepared by electrochemical anodization of titanium metal and reached lengths of 20 μm, with a high growth rate (10 μm/h). They present an open porous structure with large specific surface area suitable for efficient adsorption of the contaminants and formation of a large number of photocatalytic active sites. After calcination at 450 °C, TNT films obtain the anatase crystal structure, absorb well in the UV range and present significant photocatalytic activity with high degradation rates for both examined emerging pollutants. Furthermore, they present small variability of their photocatalytic efficiency in a big range of the solutions pH values and under consecutive photocatalytic cycles, rendering them suitable at various wastewater treatment conditions.

1. Introduction

The quality of surface waters in Europe has significantly improved, ultimately, due to the strict application of municipal wastewater treatment plants (MWWTPs) in all members of the European Union. Although, conventional treatment technologies produce water that meets the current legislation [1] (removal of carbon, nitrogen, phosphorus and pathogens), it has been demonstrated that the removal of a variety of micro-pollutants such as pharmaceuticals (PhCs), hormones, personal care products (PCPs), endocrine disrupting compounds (EDCs), etc. is inadequate. Several investigations have demonstrated the existence of recalcitrant pollutants in rivers, lakes, seas, groundwater and drinking water at

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concentrations ranging from dozens of ng L^{-1} to thousands of μg L^{-1} [2–5]. Such contaminants are biologically active compounds, not easily biodegradable, normally water soluble and therefore can be found in wastewater effluents and can easily end up in natural waters.

Caffeine (CAF) and salicylic acid (SA) are two contaminants frequently detected on MWWTPs. Caffeine is a common component of different widely used products such as coffee, tea, drugs etc. [11]. Although it presents high temporal variability [6], it is the most frequently observed compound in effluents with significantly high concentrations [3,7–10]. As a consequence, caffeine seems to be present in all waters influenced by human domestic emissions [8,9], even detected at remote locations hardly affected by human settlements [6]. Salicylic acid is a transformation product of acetylsalicylic acid used on the production of analgesics like aspirin, as well as an additive in cosmetics and foodstuff [9]. Many studies have shown that SA is consistently detected in WWTP effluents and in surface water samples collected near WWTPs [8,9,12].

As conventional secondary treatment methods applied at MWWTPs do not break down organic pollutants of special concern, effective advanced treatment technologies are needed to ensure the aquatic's "good status" reclaimed also by European Union legislation [13]. The advanced oxidation process (AOPs) have been studied intensively in the laboratory and pilot-scales and have proved to degrade organic pollutants based on the formation of hydroxyl radicals which are highly reactive and non-selective [14–17]. AOPs are a quite ecological and less complex route – compared to other remediation options such as activated carbon, clays, chlorine dioxide and ferrate (VI) [18,4] – and can deal with contaminants of emerging concern without the necessity of adding harmful or toxic chemical reagents. Amongst the AOPs, heterogeneous photocatalytic processes use semi-conducting metal oxides that can absorb light of appropriate wavelength dictated by the semiconductor's band gap (E_g), creating pairs of electron (e^-)/hole (h^+) charge carriers that can efficiently generate hydroxyl and superoxide anion radicals on their surface [19]. Various metal oxides have been tested so far, with titanium dioxide (TiO_2) having the most attractive attributes, such as low cost, earth abundance, chemical stability, good photocatalytic efficiency and low-toxicity [20]. Among the different crystal structures of TiO_2, the anatase, with an energy gap of 3.2 eV, is usually assigned as the most efficient for photocatalytic applications [19].

In most cases photocatalytic treatment is performed with TiO_2 nanoparticulate powders [14,21] suspended in effluents. But there is a major drawback since after the completion of the photocatalytic purification process, separation of the TiO_2 powder from the solution is essential. The necessary separation-filtration steps can be outstripped by using immobilized photocatalysts in the form of thin films on appropriate substrates [22]. One versatile technique to prepare TiO_2 films is the electrochemical anodization of a Ti foil using organic electrolytes, containing water and F^- ions [23,24]. One-dimensional nanostructures of anodized and well aligned TiO_2 nanotubes (TNTs) vertically oriented onto titanium metal substrate are developed with electrochemical anodization, presenting high active surface area, extended light harvesting, vectorial electron transport [25] and improved lifetime of charge carries [26]. During the past years many studies were performed by controlling the electrochemical conditions of anodization in order to tune the TNTs morphology, their dimensions (length, diameter, tube wall) and shape (circular or hexagonal, regular or irregular, smooth or with ripples, in close packing or well separated configurations) [27]. The photocatalytic activity of potentiostatic grown nanotubes has been well studied in the past against diverse organic pollutants [23,28], indicating an optimum performance for those having lengths of 5–10 μm [26,29]. Relevant works with TNTs prepared under galvanostatic anodization are in general missing despite this technique presenting several beneficial characteristics relative to the potentiostatic, such as the faster NTs growth rate and the preference for close packing arrangement. Besides, the main morphological characteristics including TNTs diameter and length are very similar to those attained using potentiostatic polarization, rendering galvanostastic grown TNTs suitable for practical photocatalytic applications [30].

Herein we present the synthesis of well aligned and vertically oriented TiO_2 nanotube arrays on titanium metal substrate (foil) using primary the one-step electrochemical anodization. By adjusting the anodic oxidation conditions appropriately, different TNTs samples, with tunable geometry, were obtained with tube lengths from 1.5 till 20 μm. The photocatalytic properties of TNTs were examined by degrading two contaminants of emerging concern frequently detected in wastewaters, namely caffeine (psychostimulant [3]) and salicylic acid (anti-inflammatory and analgesic drug [8]) at various pH values. Up to our knowledge, their photocatalytic degradation under both acidic and alkaline environment is investigated for the first time (at least for the caffeine), so the obtained results could boost further the research of emerging pollutants' photocatalytic elimination toward a future practical application in the treatment of real water effluents.

2. Materials and methods

2.1. Reagents and materials

Acetone (99.5%), 2-propanol (99.8%), methanol (99.9%) and Triton-X surfactant were purchased from Sigma–Aldrich. Perchloric acid (70%) and salicylic acid (99%) were supplied by Riedel de Haen. Caffeine (98%) was obtained from Alfa Aesar, sodium hydroxide (98%) by Merck, ammonium fluoride (98 + %) by Chem Lab, ethylene glycol (99%) by Penta and acetylacetone (99.5%) by Fluka. Commercial titanium dioxide P25 powder was supplied by Evonik used as standard material for comparison purposes. Titanium foil (thickness 0.125 mm, 99.6 + %) was purchased from Goodfellow.

2.2. Synthesis of materials

Well aligned and vertically oriented TiO_2 nanotube arrays were synthesized by a one-step electrochemical anodization technique, using the same instrumentation described in detail in [24]. Briefly free surfaces of 1.32 cm^2 from 20 × 20 × 0.125 mm titanium foils were used as anodic electrodes and a Pt mesh as the counter electrode, both immersed into an organic electrolyte consisting of 98% vol. ethylene glycol, 2% vol distilled water and 0.3% wt NH_4F. The anodization procedure was carried out in a lab-made Teflon cell under galvanostatic conditions by applying 3.15 mA cm^{-2} with an Autolab PGSTAT-30 potentiostat (Ecochemie). Anodization time was varied, from 30 min to 2 h among the different samples, in order to obtain the desired length for the TNTs. In addition, a potentiostatic anodization process was held using an electrolyte with 3% vol H_2O under 30 V for 30 min in order to obtain nanotube structures shorter than the galvanostaticaly formed ones. Last, the synthesized samples were annealed at 450 °C for 1 h at a rate of 5 °C min^{-1}. As a reference material, thin films of commercially available TiO_2 (Evonik P25) powders were deposited onto precleaned optically transparent microscopy glass substrates using the doctor blade technique [22]. In summary, 0.5 g P25 powder was dissolved in 2.7 mL distilled water, 0.1 mL acetylacetone and a drop of Triton-X surfactant to improve the adhesion of the TiO_2 onto the glass surface. Afterwards, the P25 paste suspension was spread onto the glass substrates using a glass rod. Subsequently, the films, after a drying step, were annealed using the same condi-