



A new material consisting of TiO₂ supported on Nb₂O₅ as photocatalyst for the degradation of organic contaminants in aqueous medium

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ABSTRACT

The composite TiO₂/Nb₂O₅, prepared by the impregnation method, has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), electronic spectroscopy, and the surface area has been evaluated by Brunauer–Emmett–Teller (BET) technique. The photocatalytic activity was tested in photocatalytic degradation of three different classes of organic molecules in aqueous medium: atrazine (ATR), diclofenac (DFC) and indigo carmine (IC). Electro spray ionization mass spectrometry (ESI-MS) was used to identify the main by-products generated after the photocatalytic process and a mechanism for the degradation of each analyte was proposed. The degradation rate of each compound was determined by the data acquired from high performance liquid chromatography (HPLC) measurements. Finally ecotoxicological tests with *Artemia salina* showed little differences in the toxicity of diclofenac (DFC) and indigo carmine (IC), before and after the degradation process. However the toxic effects of ATR were reduced by half using the same oxidation approach.

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Introduction

In the last years, persistent water contaminants even in small amounts, such as pharmaceuticals, pesticides and dyes, are considered as an emerging environmental problem due to their continuous input. Among them stand atrazine (ATR), diclofenac (DFC) and indigo carmine (IC). Since they normally escape the conventional wastewater treatment, new processes have to be tested and/or developed for its removal. Atrazine (ATR), which has been banned from European Union [1], is one of the herbicide extensively applied in agriculture throughout the world. When consumed by humans at concentrations below government standards its serious side effects, such as the emergence of certain types of cancer [2], birth defects [3] and menstrual problems [4], are minimized. Atrazine has been the most widely used herbicide in the last 30 years for weed control in such crops as corn, sorgham, sugarcane, and pineapple [5]. After field application, ATR might partially or totally decompose into four major products [desethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DDA), or hydroxyatrazine (HYA)], nevertheless remaining in the

environment [6]. Different events can affect the concentration and its distribution in ecosystem areas, so this compound can remain retained in the soil column, infiltrated in ground or in surface waters and be transported with runoff [7].

Diclofenac (DFC) is a non-steroidal, anti-inflammatory drug commonly used as analgesic, antiarthritic and antirheumatic, and about 15% is excreted unchanged after human consumption [8]. In view of that, it is commonly detected in domestic wastewater treatment plants since its biodegradation and/or natural attenuation are limited [9].

Contamination resulting from dyes disposal is easily recognized in wastewaters even in very small amounts (<1 ppm for some of them) [10]. Even though, these compounds are extensively used in many industrial applications [11]. There are roughly 100,000 commercially available types of dyes and more than 7×10^5 tons are produced annually [12]. The correct disposal of industrial wastewaters containing dyes has received attention in the last few years, mainly because the eventual toxicity of some of the raw materials used in their synthesis (for instance, certain aromatic amines are used to produce azo dyes). Their wrong disposal has led to serious worldwide contamination [13]. Indigo Carmine is one of the most used dyes in a number of technological fields.

Advanced oxidation processes (AOPs) emerge as an alternative and effective technology to overcome the challenge to have safe

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water supplies. Due to its efficiency in the decomposition of organic materials the photocatalytic oxidation, one of the AOPs, has been the focus of many research groups. In an ideal situation, carbon dioxide, water, and other small inorganic molecules are the products of the process; however other organic products, which can be as hazardous as the starting material or even more lethal, are usually generated [14]. TiO_2 is regarded as the most efficient and environmental-friendly photocatalyst and has been widely used for the photodegradation of various pollutants [15]. Despite the wider band gap ranges (3.1–4.0 eV) in comparison to that of TiO_2 , Nb_2O_5 has been applied as photocatalyst in a number of processes [16], including oxidation of organic contaminants [17,18], photodegradation of organic dyes [19], and hydrogen production [18]. A porous titanium–niobium oxide semiconducting composite has also been employed in the photocatalytic degradation of bromocresol green dye [20].

The studies on the degradation of water organic contaminants have usually focused on the efficiency promoted by oxidation methodologies, whereas less attention has been given to the characterization of by-products probably formed after degradation conditions. For instance, GC–MS has been extensively used to identify by-products resulting from the degradation of a few azo dyes [21,22]. An alternative technique to be used for this purpose is electrospray ionization mass spectrometry (ESI-MS). This technique possesses the remarkable capability to gently transfer species from the condensed to the gas phase without inducing undesirable side reactions. Because of that, ESI-MS has been successfully applied in the monitoring of an increasing number of environmental methodologies [21].

Following our interest in the photocatalytic degradation of organic water contaminants [21,22] we herein describe the preparation of a TiO_2 – Nb_2O_5 composite and its use in the photocatalytic degradation of atrazine (ATR), diclofenac (DCF) and indigo carmine (IC). The eco-toxicity of the initial substrates and the by-products has been assessed in tests against *Artemia salina*.

Experimental

Materials and reagents

All chemicals were purchased from Sigma–Aldrich (Milwaukee, WI) and used without further purification. Doubly distilled water was used to prepare solutions. Commercial sea salt was purchased from material suppliers.

Composite preparation

The composite $\text{TiO}_2/\text{Nb}_2\text{O}_5$ was prepared by the method of impregnation, where the support Nb_2O_5 was added under vigorous stirring into a precursor solution (TiCl_4 /isopropanol) forming a suspension of TiO_2 and Nb_2O_5 . After 4 h of stirring, NH_4OH was added and the mixture was stirred for an additional time of 30 min. Then the mixture was kept in an oven for 24 h at 60 °C and at 550 °C for 2 h.

Characterization techniques

XRD patterns were collected with a Siemens D5000 instrument using a Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator in the diffracted beam. A scan rate of $1^\circ/\text{min}$ was applied to record a pattern in the 2θ range of 20–80°. Silicon was used as internal standard. UV–vis measurements were performed by using a Hitachi U-2010 spectrophotometer.

The surface area and porosimetry measurements were carried out on a ASAP2010 Micromeritics using N_2 as adsorbant at liquid nitrogen temperature. Before the N_2 adsorption, the material was

outgassed at 200 °C for 3 h in order to desorb the impurities or moisture from its surface. The total surface area was calculated from the N_2 adsorption isotherms using the BET method and the micropore surface area was derived from the t-plot curve.

The morphology of the composite sample was characterized using scanning electron microscopy (SEM) analysis using a JSM-6700 LV electron microscope operating at 5.0 kV.

Catalytic experiments

The prepared composite (30 mg) was added to an aqueous solution (50 mL) of ATR (5 mg L^{-1}), DFC (5 mg L^{-1}) or IC (30 mg L^{-1}). Then the system was exposed to ultraviolet radiation (UV lamp: Philips HPL-N, 36 W, wavelength ranging from 200 to 400 nm). For all assays, aliquots were taken at times of 0, 5, 15, 30, 60, 90 and 120 min, filtered using a 0.45 mm filter (Millipore, Jaffrey, NH) to eliminate solid particles and kept protected from light in a refrigerator prior to the HPLC-MS and TOC analyses. The total organic carbon (TOC) was measured in a TOC-V CPH instrument (Shimadzu, Tokyo, Japan). The aliquots were kept protected from light in a refrigerator at 4 °C prior to the ESI-MS and UV–vis analyses.

Analyses by direct infusion ESI were performed using a mass spectrometer (model IT-TOF, Shimadzu, Tokyo, Japan) with two analyzers in tandem: ion trap (IT) and time-of-flight (TOF). The mass spectrometer operating at high resolution and mass accuracy was optimized under the following conditions: (i) ESI voltage at -3.5 kV (negative ion mode); (ii) nebulizer gas (nitrogen) flow rate at 1.5 L min^{-1} ; (iii) curved desorption line (CDL) interface temperature at 200 °C; (iv) drying gas (nitrogen) pressure at 100 kPa; (v) octapole ion accumulation time of 100 ms. Mass spectra were obtained in the full scan mode within a m/z 100–500 range.

For the chromatographic analyses an ACE C18 column ($2.1 \times 50 \text{ mm} \times 3 \text{ mm}$ diameter of a particle) was used. Water (A) and methanol (B) was employed as mobile phase at a flow rate of 0.2 mL min^{-1} . The gradient program started with 30% B, rising to 50% B in 4 min, then to 100% B in 3 min, which was hold until 10 min. At the end of the chromatography run, the column was re-equilibrated to the initial conditions and stabilized for 4 min, which led to a total run time of 14 min. The injection volume was 5 μL . The same conditions as described above were employed for the mass spectrometer.

Biological tests

Toxicity tests were carried out by exposing the solutions arising from the degradation processes against brine shrimp (*A. salina*). The ecotoxicity tests were carried out following a protocol presented by Mclaughlin and coworkers [23]. Hence, an aqueous solution of sea salt (at 38 g L^{-1}) was prepared, filtered and added to a small (15 cm diameter) round plastic container. Subsequently, many *A. salina* eggs were added in only one half of this container, which was kept protected from light for 24 h, whereas the opposite half was continuously irradiated by a 100 W incandescent lamp. After the eggs hatched, the *A. salina* organisms migrated to the lit side, then a small portion of this solution with adult individuals could be collected and transferred to a cylindrical glass vial (3 cm diameter) and the volume completed to 1.0 mL by adding the above-mentioned sea salt solution. Afterwards, 4.0 mL of a reaction aliquot, collected from the degradation experiments, were put into the vial, and the volume was completed with water to 5.0 mL. The vial was then left to stand under light for 48 and 96 h and the percentage of immobilized organisms determined. The assays with each aliquot were carried out in triplicate to estimate the toxicity of the target molecules (ATR, DFC and IC) and by-products.

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