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Treatment of real wastewater with TiO_2-films sensitized by a natural-dye obtained from *Picramnia sellowii*

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ABSTRACT

A natural dye extracted from *Picramnia sellowii* (Chokanari) was used to prepare sensitized TiO_2 films. Dyes and heterotrophic microorganisms present in wastewater were treated by photocatalysis using visible light. A factorial design 2^3 was employed to select the operational conditions to sensitize TiO_2 films. The combined treatment using a concentration of 0.03% w/v of sensitizer (natural dye), 700 rpm (spin-coating) and 300 color units of wastewater showed interesting results, removing close to 60% of the color and 60% of Chemical Oxygen Demand. Kinetic experiments using the best coated films showed that Total Organic Carbon abatement was higher using sensitized films, conversely, no statistical differences were found in color removal when comparing sensitized and non-sensitized films. Heterotrophic microorganisms were completely inactivated following 12 h of treatment with sensitized films. Films can be used up to 5 operational cycles with loss of catalytic activity close to 10%.

1. Introduction

Photocatalysis with TiO_2 has been extensively used for oxidative-reductive degradation of organic pollutants and microbial inactivation [1–4]. The functional advantages of TiO_2 are related to its physicochemical stability, affordable price and low-toxicity. However, the treatment of great volumes of water can be burdensome, since a source of ultraviolet radiation is necessary to trigger electronic transitions through photoelectric phenomena of excitation. This requirement represents a serious problem in terms of energetic cost [5]. In order to cope with this problem, several strategies have been developed to modify the material at structural or surface level to expand light absorption of TiO_2 into the visible radiation region, those methods include: transition metals ion doping, non-metals ion doping (including doping of nitrogen, carbon, sulfur and iodine, ion implantation) and photosensitization [6]. The photosensitization is a promising method for improving the photocatalytic activity of TiO_2 and represents a viable alternative to modify the surface of a semiconductor [7–9]. Sensitizers can be adsorbed by semiconductor surface either by chemisorption (formation of chemical bonds) or physisorption (charge attraction). These compounds possess chemical structures formed by conjugated double bonds (π-π^*) that absorbed visible radiation (400–800 nm); those are known as chromophoric groups. After being irradiated with visible light, the electrons that form chromophoric groups are excited and injected to the conduction band of TiO_2, triggering the photocatalytic process and thus, the production of ROS (Reactive Oxygen Species) which according to different reports are responsible for the abatement of organic matter and microbial cell destruction [4,10–12].

Photosensitizers should possess some characteristics like being strongly attached to the semiconductor surface either by chemical bonds or physical attraction, broad absorption spectra in the visible region and chemical stability when expose to visible radiation [13].

Generally, dyes used as sensitizers can be obtained from synthetic or natural sources [14,15]. Artificial dyes and coordination complexes of noble metals are frequently used to sensitize TiO_2 films in order to produce solar cells or photocatalysts.

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However, these substances are costly and can derive in environmental problems after being discarded. In contrast, natural dyes are relatively easy to obtain, low-cost and bio-degradable. In this regard, plants are an excellent source of natural colored compounds that can be utilized as promising TiO_2 sensitizers. Some studies have obtained colored compounds from plants (leaves, fruits, seeds or flowers) in order to characterize and evaluate them as potential photosensitizers of TiO_2 [9,15,16]. In fact, South America is an enormous reservoir of millions of species of plants that indigenous groups have utilized for thousands of years as natural medicines and powerful dyes. *Picramnia sellowii* is a plant that naturally grows in the Amazonian (Colombia, Brazil and Perú) forest and nowadays it has been adapted in order to be cultivated in other regions of the continent. This plant may represent a promising source of natural photosensitizers.

Another point that should be highlighted is the use of TiO_2 films. Out of the main disadvantages of photocatalysis wherein the catalyst is in powder is further separation of TiO_2 nanoparticulates after the process that increases the turbidity of the water; despite the low toxicity of TiO_2, the quality of water decreases. TiO_2 thin films have promoted its extensive application in photocatalytic water treatment mainly by avoiding agglomeration of the catalysis during operation and the leaching of nanoparticles. We previously reported a simple method to obtain TiO_2 films based on sedimentation with a uniform deposition on a glass-type substrate [17].

This study used TiO_2 films modified with a natural compound extracted from the Amazonian plant *Picramnia sellowii* and prepared according to our published protocol for treating a real laboratory wastewater containing microbial populations (bacteria and yeasts) and chemical compounds (dyes, solvents, mordant). The main objectives of this work are: *i).* To determine the variables for TiO_2-films sensitization using the dye extracted from *Picramnia sellowii*, *ii).* To characterize the dye extracted from *Picramnia sellowii* and sensitized films, *iii).* To assess the discoloration, Total Organic Carbon removal and inactivation of heterotrophic microorganisms found in actual wastewater under visible radiation using sensitized TiO_2-films, *iv).* To determine the stability of the films after several cycles of operation.

2. Material and methods

2.1. Plant material

Leaves of *Pricramnia sellowii* (also commonly known as Chokanari) were collected from Viotá, Department of Cundinamarca, Colombia (latitude 4°26′19.79″N, longitude 74°31′20.65″O). *Pricramnia sellowii* has been cultivated and adapted to humid conditions above 80% and temperatures rising to 25 °C. 400 g of leaves were crushed and dried (20 °C) during 7 days.

2.2. Natural dye extraction

10 g of leaves were treated with 400 mL of petroleum ether during 5 min. Non-polar extract was discarded and the remainders were sonicated with absolute ethanol during 20 mins. Then, the ethanolic extract was concentrated by rotary evaporation during 1 h, and after vacuum dried, dried extract was stored in dark conditions at room temperature. In this study, the dried extract was considered as the sensitizer.

The natural dye was characterized using UV–VIS spectroscopy and ^{1}H RMN. UV–VIS spectra were evaluated in a spectrophotometer CARY VARIAN. ^{1}H NMR analysis were performed in a BRUKER ADVANCE III apparatus operating at 300 MHz. Dried extract samples were dissolved in d-DMSO for ^{1}H NMR analysis.

2.3. TiO_2 films preparation

TiO_2 films were prepared using soda lime glasses (26 × 20 mm) as substrate. The substrates were previously washed with a mixture of H_2SO_4 and H_2O_2 (3:1). A suspension of TiO_2 USP (United States Pharmacopeia) for pharmaceutical use (0.05% w/v), and $Na_4P_2O_7$ (0.01 M) was prepared, and pH of the suspension was adjusted to 9.0 with NaOH (1 M), then the suspension was irradiated with microwaves (700 W) during 20 min.

The variables used in this study were selected as discussed in our previously published results [17]. Because of its isoelectric point, TiO_2 is charged negatively at alkaline conditions, this cause charge repulsion between TiO_2 particles. At this pH, sodium pyrophosphate is ionized as a multi-charged ion, increasing the medium ionic strength, which interferes with particle aggregation. Moreover, the electromagnetic field created by microwave radiation cause collisions between TiO_2 aggregates leading to their fragmentation. This process was performed in order to guarantee a uniform film by avoiding aggregates formation [18].

Films were prepared by gently dropping the suspension (5 mL) over the substrates. Afterwards, films were left into the oven at 70 °C until dryness. This process was carried out twice. Then, films were thermally treated at 450 °C for 2 h to increase the adhesion of the particles to glass surface and remove volatile residues.

2.4. Dye-sensitized TiO_2 films preparation

Conditions of films coating with the sensitizer and photoreactor operations parameters were selected using a 2^3 Factorial design. The experiments were carried out using real laboratory wastewater obtained from cell staining wastewater; this allowed setting the suitable conditions for the following photocatalytic experiments. The following factors were evaluated: Sensitizer concentration (% w/v), spin coating speed (rpm), laboratory wastewater color expressed as color units (adjusted by diluting with distilled water according to experimental factors). A total of eight experiments were set from the factorial design. The characterization of the wastewater, the catalytic reactor and the conditions of reactions will be described later in this paper.

The experiments were evaluated in triplicate. The photocatalytic experiments were carried out during 14 h under visible radiation (λ=450 nm). At the end of the process (only one point), the samples were collected and color removal and Chemical Oxygen Demand (COD, Standard Method 5222D) were assessed as response parameters. Table 1 displays the combinations of the evaluated factors for the eight experiments. The results were analyzed statistically using the software Design Expert® and SAS®.

2.5. Dye-Sensitized TiO_2 films characterization

Films were characterized before and after sensitization. Topography was analyzed using Atomic Force Microscopy (AFM) (Asylum Research model MFP3D-BI) in contact mode. Scanning Electron Microscopy (SEM) was performed in a JEOL JSM 6490–LV electron microscope. UV–VIS diffuse reflectance spectra were determined using a quartz tungsten–halogen lamp (Lamp Newport 6333, continuous spectra between 240 and 800 nm). Interface Lab view software® was used to process the data. Fourier Tansform Infrared Spectrsocopy (FTIR) measurements were performed in a Shimadzu 8300 equipment using the KBr pellets method.

2.6. Mechanical stability of sensitized films

Mechanic resistance experiments were performed to evaluate the films resistance under stressful conditions (stirring and long periods of operations). This experiment was performed under the