

Titanium Dioxide onto Polyethylene for Water Decontamination

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Abstract:

TiO₂ aqueous suspensions under illumination of UV range (310-400 nm UV-A) have demonstrated a big potential for water decontamination and disinfection for human consume. Separation of TiO₂ from the process is not easy. Supporting TiO₂ to a proper substrate avoid the separation step after the photocatalytic treatment. This procedure results very interesting for the manufacturing of economic decontamination devices, which could be made with lightweight and flexible materials, bringing much versatility for the design of reactors for water decontamination. Based on those requirements, supporting TiO₂ over polyethylene results ideal for that purposes due to its physico-chemical properties, good transparency and low cost. In this work we evaluated different methods to support titanium dioxide nanoparticles onto polyethylene. The catalyst was characterized by X-ray diffraction and transmission electron microscopy (TEM) for structural analysis. TEM was also used for morphology characterization. UV-Visible and infrared spectroscopy were used to study the inter band and molecular absorptions respectively. Material ability to perform photocatalytic degradation of rhodamine and bacteria (*E-coli*) in water, were studied. Obtained results suggest a very promissory applicability of the catalyst for water purification application in rural areas.

Keywords: Titanium oxide, Photocatalysis, disinfection, bacteria, Polyethylene

Introduction

Use of TiO₂ nano-particles in suspension is an efficient method for decontamination due to the large surface area of catalyst available to perform the reaction. It has, however, some drawbacks before its scaling up to industrial level, e.g., the necessity of removing the catalyst from the solution after decontamination using filtration increases the cost and time of the cleaning process. Using filtration process becomes costly and time consuming, besides, the need of a filtration step is a serious problem for the design of portable and economical devices for water purification.

An alternative procedure is based on supporting the catalyst on an inert matrix. Several substrates have been used to support the catalyst; cellulose non-woven paper (1), fiberglass beads; metal fibers; steel mesh; steel plates; aluminum; and ceramics such as alumina, silicon carbide, and many types of plastics (2, 3). Systems based on a coating of titanium oxide nanoparticles deposited onto a substrate of polyethylene (PE) are currently of great interest, due to the versatility of PE for the construction of flexible supports with high geometrical area and different shapes. Besides PE is almost transparent to UVA radiation, which improve

almost transparent to UVA radiation, which improve the use of the light. The first attempt to fix a catalyst onto a polyethylene foils (2), involve an even spreading of the powdery catalyst all over the support film by rubbing with a cotton wool, a subsequent ironing (with an iron plate at 74 °C), followed by rinsing with sodium hydroxide, and washing out loosely bonded particles.

Due to the lower thermal stability of plastics, it is not possible to applied high temperature thermal treatment on TiO₂/plastic systems. Consequently, the crystalline degree of the material that will form the films should be adequate for photocatalytic applications. It means that pre-crystallized precursors must be used to prepare photocatalytic TiO₂ films on plastics. Recently, several sol-gel alternatives methods have been implemented to allow the synthesis of crystalline TiO₂ nanoparticles. Anatase crystalline phase of TiO₂ has been obtained from amorphous aqueous solutions of TiO₂ (4), TiCl₄ (5-7) or TiOCl₂ (8), following by a hydrothermal treatment. Titanium alcoxides had also successfully used as TiO₂ precursor for hydrothermal synthesis (9-11) and by precipitation-peptization process (12, 13). They reported that anatase and rutile crystalline phases were obtained by neutralization of TiCl₄ or acidic hydrolysis of Ti(OC₂H₅)₄ with HCl (13), however, hydrolysis of Ti(OC₄H₉)₄ at high acidic conditions with

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HNO₃ has been reported to generate either rutile (14) or anatase (15) crystalline phases.

In this work Titanium dioxide films were deposited onto polyethylene due its flexibility, low toxicity and to be easy to obtain. Its low cost and manipulability make this material very useful for the construction of cheap and disposable equipment for water purification. Several approaches were compared to obtain TiO₂ deposits onto a polyethylene surface, having in mind that rough films are required, because these have shown better photocatalytic behavior than smooth ones (16, 17). A comparison has been performed for its ability to water photocatalytic disinfection and decontamination.

Materials and Methods

The deposition processes applied in this work involve the use of TiO₂ dispersions with different dispersant phases. Two approaches were considered for the synthesis of the dispersions:

a) *TP process*: TiO₂ dispersed in a solution of polystyrene in ethyl acetate. 0.25g of commercial TiO₂ (P-25 from Degussa) were incorporated to a solution containing 5.00 g of polystyrene in 100 mL of ethyl acetate. The powder was completely dispersed with strong stirring during 6 h and by application of ultrasound for 1 h.

b) *SOL process*: TiO₂ aqueous based sols. TiO₂ sol was synthesized by the precipitation-peptization method at room temperature (18). 15.0 mL of titanium isopropoxide (Aldrich >98%) was rapidly incorporated, under strong stirring, to a solution containing 1.8 mL of nitric acid (Merck AR) in 180 mL of deionized water (18 MΩ, Millipore System). The system was kept under stirring for 48 h, until the white TiO₂ flocks turned to a pale blue translucent sol. The obtained sol was purified by dialysis (Spectra-Pore cellulose acetate membrane, MWCO 3500) up to get a pH of 3.5.

Polyethylene surface was mechanically roughened to increase its roughness, vigorously washed with water and detergent, and rinsed with 18 MΩ deionized water before depositing. The dispersions were deposited on the pretreated polyethylene surface by pneumatic spray. The systems were dried at room temperature. Four different materials were produced, which were named: *TP* (from dispersion "a"); *SOL* (from dispersion "b"); and *TP-SOL* (dispersion "b" applied on a previous film made from dispersion "a"); and *TP-SOL-SOL*, similar than *TP-SOL* but with two applications of dispersion "b". Some *TP* samples were mechanically roughened before application of a layer of dispersion "b"; these samples are named by adding an (L) to the corresponding name.

Material characterization was performed using X-ray Rigaku Miniflex diffraction equipment to determine the crystal structure. A transmission electron microscope Phillips EM 400 was used for morphological and structural characterization. Whereas the study of the inter band and molecular absorption was performed through the ultraviolet, visible and infrared spectroscopy, by using a single beam Biochrom UV-VIS spectrophotometer Libra S22 and a Shimadzu FT-IR spectrophotometer, respectively.

The photocatalytic activity of the different materials was tested with two water contaminants:

a) 0.32 ppm of rhodamine B (Aldrich) dye solution in water. A 13.85 cm² TiO₂-Polyethylene foil was placed in the base of a Petri dish; 10 mL of the rhodamine B solution was added to the Petri dish, covering all the surface of the TiO₂-plastics, with a depth of a few millimeters. The system was illuminated with two 5W black light tubes, placed at 30 cm from the surface of the solution, during a 5 h period. The concentration of rhodamine was measured spectrophotometrically before and after irradiation, with an Agilent 8453 diode array spectrophotometer. Water evaporation was compensated by adding enough water to keep the system mass constant before and after the experiment.

b) 10⁷ *E-coli* colonies form units per milliliter (CFU/mL) in water. A 13.85 cm² TiO₂-polyethylene foil was placed in the base of a 1.0 L beaker; the reaction volume was 400 mL and the reaction time 1.0 h; samples were taken at 30 min periods. The system was illuminated with an OSRAM ULTRAVITALUX 300 W lamp (15 W/m² UV-A, measured with a UDT UV-A sensor).

Several experiments were carried out to test the performance of the photocatalyst in long term using conditions. The systems used to test the catalysts were the same described before for the short term experiments. A constant UV-A irradiation (15 W/m²) impinges on the system during 600 h. Along this period of time, the system was periodically inoculated with *E-coli* to maintain the concentration in c.a. 10⁷ CFU/mL in 400 mL of water, this is stated as initial concentration in Figure 6; from these water conditions and after one hour of UV-A irradiation in presence of the catalyst, samples were taken to evaluate the remaining CFU/mL. In all the cases, control experiments in the dark and under illumination but without photocatalysts (photolysis) were performed.

The evaluation of cultured *E-coli* bacteria used as contaminant indicator in the experiments was performed by using the Oxfam-DeLAgua Portable Water Testing Kit. The kit is designed to provide information about the bacteriological quality of water supplies. The

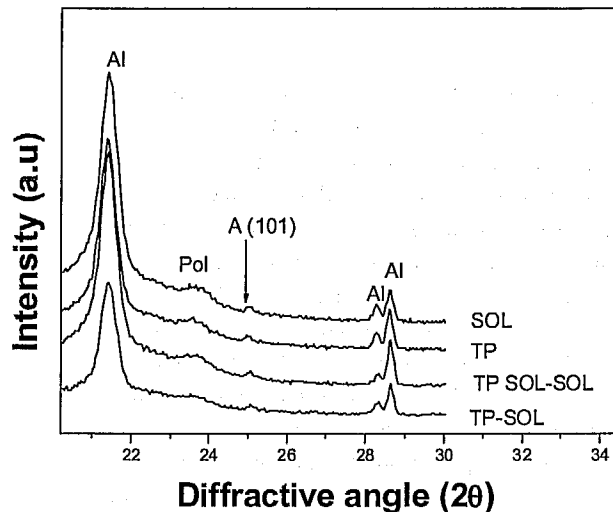


Figure 1. X ray diffractograms of sample TP+SOL.

analysis of water samples for total coliform bacteria is carried out by passing a measured quantity of water through a sterile filter. Any bacteria present in the water are caught in the filter. The filter is then placed onto a paper pad soaked in a liquid growth medium (Luria Broth) which feeds coliform bacteria, but inhibits the growth of any other bacteria caught in the filter. The system after incubation at 37 °C for 18 h will give the possibility of counting E-coli.

Results and Discussion

Structural Characterization

The crystalline structure of sample TP-SOL determined by X-ray diffraction (XRD) is shown in Figure 1. The films have anatase structure, with an observed diffraction peak at 25.06°. The mean grain size D was estimated from Scherrer's formula, i.e.,

$$D = \frac{0.9\lambda_x}{\beta \cos\theta}, \quad (1)$$

where $\lambda_x = 1.54 \text{ \AA}$ is the X-ray wavelength of the CuK_α radiation, 2θ is the diffraction angle, and β is the full width at half maximum of diffraction peak. Applying Scherrer's formula to (101) peaks TiO_2 films, the main grain size was calculated to be around 45 nm. Additional peaks are associated to the polyethylene (Pol) and the aluminum substrate (Al). These results are remarkable because show that all the samples prepared have certain degree of crystallinity, in spite that no thermal treatment was used. The films have to be crystalline (at least in some extension) to display any photocatalytic activity (19).

The materials were also studied by transmission electron microscopy, where the sample was taken by scratching the surface of the material. Figure 2 shows

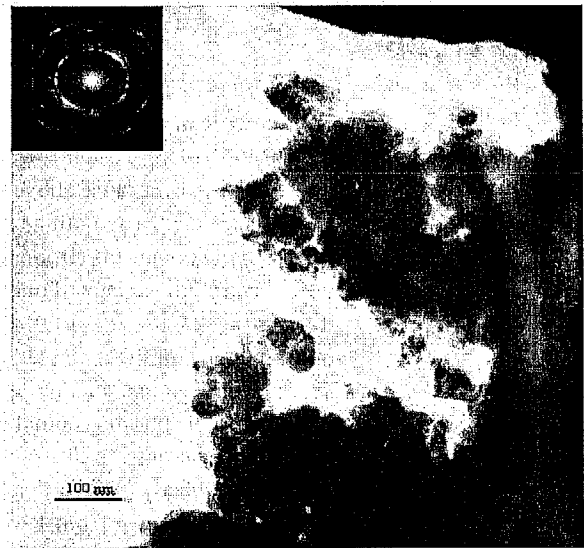


Figure 2. TEM micrograph of TP+SOL film, scratched from the surface of the plastic sample. The inset shows the electron diffraction pattern of the TiO_2 film.

the results for a sample containing P-25 and a layer of TiO_2 deposited from a TiO_2 sol prepared in the laboratory (TP-SOL). The film is formed by TiO_2 particles with diameter below 10 nm, which form aggregates of c.a 50-75 nm large. The inset shows the electron diffraction pattern of one of the aggregates. The polycrystalline structure corresponds in this case to a mix of anatase and brookite. These results are in agreement with the XRD analysis, confirming that the film is composed by aggregated TiO_2 crystalline nanoparticles. Brookite is not detected by XRD due to its lower concentration in the sample and the superposition of its principal diffraction peak with anatase (101). Rutile was not detected by electron diffraction, in spite that P-25 has a 20% of rutile in its composition; this result indicates that the amount of the layer containing P-25 and polystyrene removed by scratching the surface was negligible.

Optical Characterization

Specular spectral transmittance for TiO_2 films were recorded in the $200 < \lambda < 900 \text{ nm}$ wavelength range. Figure 3 shows the spectral specular transmittance for TiO_2 films deposited onto polyethylene. A noticeable change in the specular transmittance is observed in the obtained TiO_2 films with respect to the observed from the polyethylene substrate. Deposited films are rough and this is observed as a decrement of the transmittance in the visible range. Below 400 nm an absorption peak associated to the TiO_2 is observed in all the coated samples. The absorption peak observed at 261 nm, is present only in the TP samples and correspond to

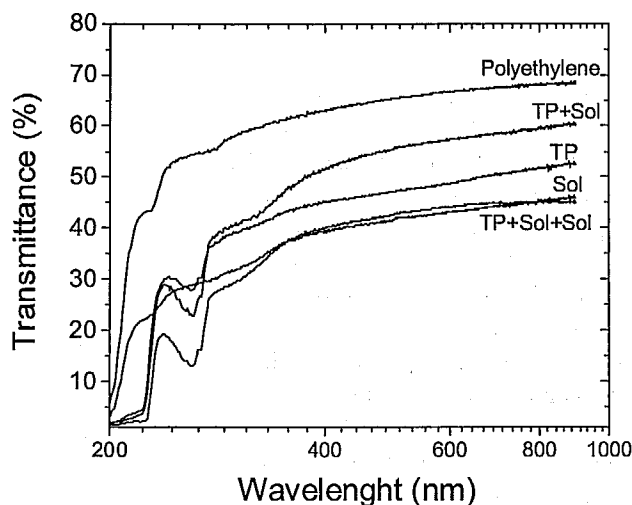


Figure 3. UV-visible spectral measured transmittance of TiO₂/Polyethylene samples.

absorptions due to the presence of polystyrene mixture. This peak remains invariant even after the material was used several times, which indicates that the film containing polystyrene and P-25 remains attached to the polyethylene substrate even after the photocatalytic process. Fourier Transform Infrared Spectroscopy (FT-IR) allows us to study molecular bonds. Figure 4 shows FTIR spectra of polyethylene and coated polyethylene with different TiO₂ mixtures. The spectra mainly show methyl bonds; four absorption peaks domain the spectra showing stretching bonds at 2920 cm⁻¹, 2850 cm⁻¹, 1464 and 719 cm⁻¹. From the ratio of the 731 y 719 cm⁻¹ peaks (1:1), it was determined that polyethylene is crystal at 50%, according to the ASTM D5576. Absorption peak placed at 694 cm⁻¹ correspond to Ti-O-Ti (20) vibrations; and the absorption peak at 536 cm⁻¹ is associated to Ti-O (20). After photocatalytic reaction, the absorption peaks of films do not show any change respect to the new ones. This confirms that the molecular bonds of the film and substrate do not change with the use.

Photocatalytic Degradation of Rhodamine

Once the rhodamine solution is added to the Petri dish containing the TiO₂-plastics in the bottom, the dye is adsorbed on the surface acquiring a light pink color. The amount of Rhodamine adsorbed is c.a 65% of the initial concentration for all the cases studied. The adsorption of rhodamine on polyethylene without TiO₂ was negligible.

Figure 5 shows the absorbance of rhodamine at 552 nm after 5h UVA irradiation, relative to the initial absorbance of the rhodamine solution. The results indicate that more than 98% of rhodamine was discolored after the period of UV illumination. Discoloration

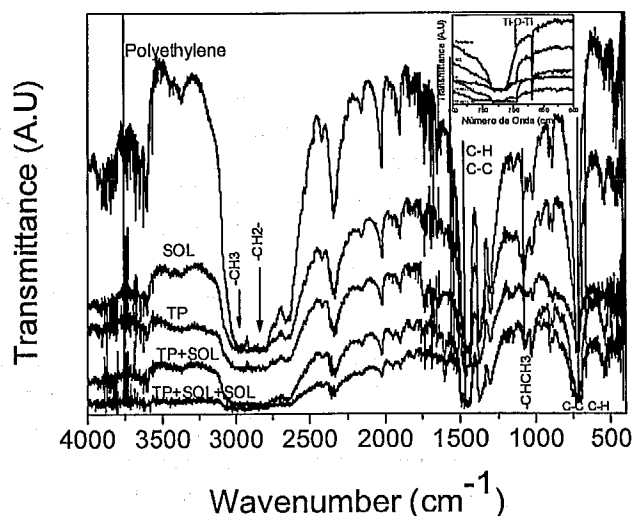


Figure 4. FT-IR spectral measured transmittance of TiO₂/Polyethylene samples.

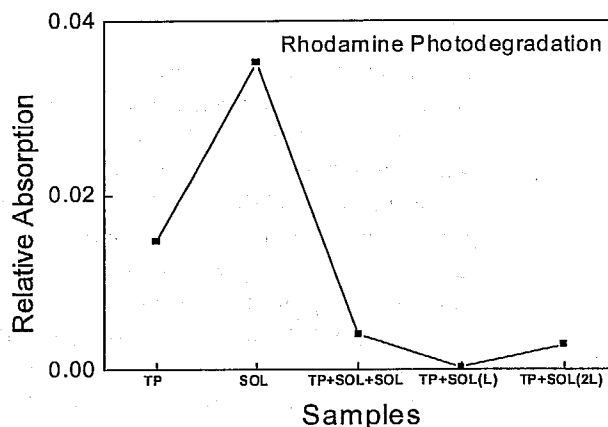


Figure 5. Rhodamine absorbance, relative to the absorbance of the initial rhodamine solution, after different photocatalytic experiments for different TiO₂/Polyethylene samples.

of rhodamine in controls prepared with polyethylene without TiO₂ was not detected, which indicates that discoloration by photolysis is negligible in the studied period. The system coated only with aqueous TiO₂ sol (SOL, in Figure 5) was the less efficient; probably as consequence of the loose of TiO₂ during manipulation. In the other cases the efficiency was similar; no delamination or separation of the layer of polystyrene-TiO₂ was detected during the experiments. It should be mentioned that after irradiation the light pink color of the surface of the TiO₂ plastics was not detected by the naked eyes. This result indicates that most of the dye adsorbed on the surface was also discolored.

Photocatalytic Disinfection Activity

Table 1 shows the effect of UVA irradiation on systems containing suspension of *E-coli*, c.a 10⁷ UFC/mL, and different TiO₂-plastics. Photolysis alone has a

Table 1. *E.-coli* (CFU/mL) in water respect to the irradiation time. Samples name are indicated in the text.

Time (min)	Sample (CFU/mL)				
	photolysis	Polyethylene	SOL	TP+SOL+SOL	TP+SOL (L)
0	8.9×10^6	8.9×10^6	6.0×10^6	8.9×10^6	8.7×10^6
30	$> 10^7$	5.1×10^4	3×10^2	0	0
60	5.9×10^4	3.0×10^3	0	0	0
Dark control	6.8×10^6	8.0×10^6	6.8×10^6	8.0×10^6	$> 10^7$

moderate bactericidal effect; after 30 min of irradiation the amount of bacteria was higher than at the beginning of the experiments and, after 60 min, the concentration was only 2 orders lower than in the dark control. Similar result was obtained when pure polyethylene was placed in the bottom of the recipient. When TiO₂-coated polyethylene was placed in the recipients, the bactericidal effect was notably higher. In the case of photocatalyst SOL, the bacteria count was reduced by two orders after 30 min and total extinction was obtained after 60 min of UV-A irradiation. In the case of TP-SOL and TP-SOL+SOL the bactericidal effect was even higher and total extinction was obtained after 30 min of illumination. The differences between photocatalyst SOL and TP-SOL may be related with the higher amount of TiO₂ coated on the plastic as consequence of the deposition of TiO₂ with polystyrene plus a layer of water based TiO₂ sol. Application of a second layer of water based TiO₂+SOL do not improved the performance of the catalyst. This effect is well known; too thick TiO₂ layers do not have better photocatalytic efficiencies (21).

The TP-SOL photocatalysts was also tested in long term experiments. The results shown in Figure 6 indicate that, as a general trend, it is observed a beneficial influence of the photocatalyst versus photolysis alone, which in average reduced the bacteria concentration in more than two decades. Complete disinfection was reach in the first sample (took after 25 min of irradiation) but, in the follow five samples (taken during the first 100 h of the experiment), the concentration of bacteria fluctuated between 0 and 10² CFU/mL. Afterwards, it is observed a systematic reduction of photocatalyst efficiency, but the positive effect on the elimination of bacteria is still observed up to the eighth test, performed after 250 h of irradiation. It is noticeable that the population of *E.-coli* after the 250 h of irradiation remains in the same level that in the system exposed to UVA light without TiO₂-plastic (see photolysis in Figure 6), so its seems that the TiO₂ layer lost it bactericidal effect after 250 h of treatment. The main reason for

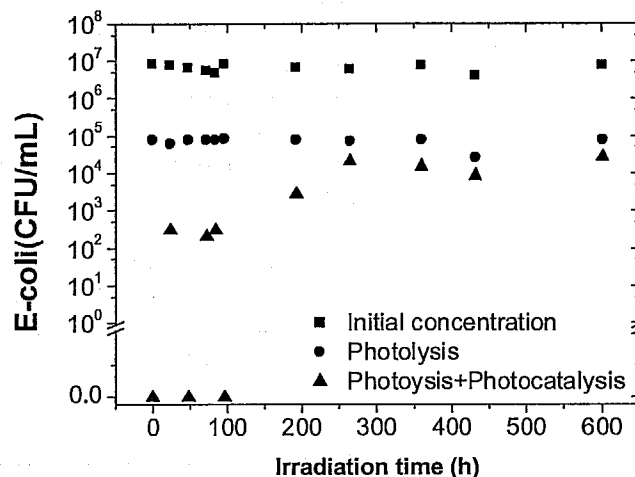


Figure 6. *E.-coli* bacteria counting after different photocatalytic experiments with a TP+SOL sample. Experiments were performed along 600 h of UV-A continuous irradiation of the sample.

this decrement is ascribed to the deposition of the killed bacteria onto the surface of the catalytic film.

Summary and Concluding Remarks

Structural films characterization obtained by X-ray diffraction, showed that the main TiO₂ phase was anatase. Analysis performed by electron diffraction experiments confirm such a result, however some traces of brookite were also identified. TEM images indicate that films are composed by particles with a diameter lower than 20 nm, forming aggregates of approximately 50 nm size.

The photocatalytic activity of the materials was determined by degrading rhodamine B, used as model contaminant. Batch Experiments performed with the photocatalytic material (13.85 cm² cm²) and rhodamine (10 mL, 0.32 ppm) indicated the complete discoloration after 5 h of treatment. Short term disinfection experiments made with an initial concentration of 10⁷ CFU/mL of *E.-coli*, under 15 W/m² irradiation in the UV-A range, indicated that after 60 min the disinfection was complete. Long term disinfection experiments under the same conditions than explained before, showed a

diminution of the efficiency under several hours of continuous use. This effect is ascribed to the deposition of organic materials on the film surface. This novel developed material present, under UV-A irradiation, a positive effect to degrade rhodamine as well as disinfect water contaminated with E-coli, which make it feasible to be used as a possible flexible material for developing a solar disinfection reactor, which is currently under development in our laboratory

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