Development and Evaluation of a Photoreactor Based on Supported Nanostructured TiO_2 Photocatalysts for Treatment of Pollutants in Water

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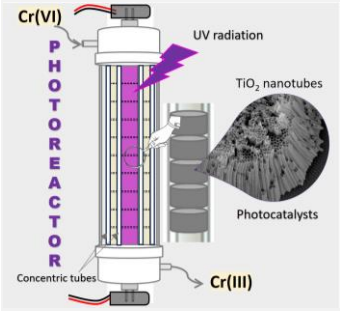
A. Dwojak[1], *M. Vera*[1], *H. Traid*[1], *M. Rosenberger*[1], *C. Schvezov*[1], *M. Litter*[2]. *(1) Instituto de Materiales de Misiones, IMAM (CONICET-UNaM), Félix de Azara 1552, (3300) Posadas, Misiones, Argentina, anabelanataliadwojak@gmail.com . (2) Instituto de Investigación e Ingeniería Ambiental IIIA (CONICET-UNSAM), Escuela de Hábitat y Sostenibilidad, Universidad Nacional de General San Martin, Campus Miguelete, Av. 25 de Mayo y Francia, (1650) San Martin, Buenos Aires, Argentina.*



The study focused on the design, construction and operation of a photoreactor using supported nanostructured TiO_2 photocatalysts for degradation of pollutants in water. Glass was used as the construction material, with concentric tubes housing a UV lamp and TiO_2-coated rings. The rings were prepared by anodic oxidation of titanium tubes, being composed of anatase nanostructures confirmed by SEM, XRD and DRS analyses. To evaluate the performance of the photoreactor, the Cr(VI)/EDTA system (0.4 mM $K_2Cr_2O_7$ and 1 mM EDTA) at pH 2, was used. The photoreactor operated under recirculation and was evaluated by reduction of Cr(VI) in the presence of EDTA, achieving 100% Cr(VI) transformation in 180 min, the kinetics fitting well to a pseudo-first-order model. These findings underline the successful development and promising performance of the designed photoreactor.

Introduction

Numerous research studies have been conducted on the design of photochemical reactors for use in advanced wastewater treatments. These studies seek to design efficient reactors for the treatment of small and medium volumes of aqueous effluents. Key factors include effective contact between the pollutants and the solid photocatalyst, maximizing the surface area and its exposure to useful light. Other important aspects are mixing, mass transfer and flow distribution within the reactor.

The design and construction of photoreactors based on the heterogeneous photocatalysis (HP) process, which use immobilized TiO_2 for the treatment of contaminated water, is of great relevance for the transfer of this technology. Anodic oxidation of titanium alloys using mixtures of ethylene glycol and fluorine ions as electrolytes is an economical and versatile technique to synthesize TiO_2 coatings with nanotubular morphologies.

The objective of this work was to achieve the design and construction of a photoreactor based on immobilized nanostructured TiO_2 photocatalysts for use in transformation of pollutants.

Material and Methods

To ensure efficient utilization of light by the photocatalyst, glass was chosen as the construction material for the photoreactor. A UV light fluorescent tube (GE, F8T5 BLB) emiting in the 350-380 nm range was selected as the radiation source (2800 $\mu W\ cm^{-2}$); this lamp configuration is suitable for the adopted concentric annular reactor design.

The photoreactor includes two concentric glass tubes vertically positioned. The UV lamp was placed inside the inner glass tube, and titanium rings coated with TiO_2 nanotubes were positioned in the annular space along the column, where the contaminant solution also circulated. The photocatalysts were fabricated from commercial grade 2 titanium (TiG2) tubes of 31.75 mm outer diameter, and a wall thickness of 0.89 mm. Rings of 20 mm height were etched with a mixture of $HF:HNO_3:H_2O$ 1:4:5% v/v for 120 s. Then, the rings were potentiostatically anodized at 40 V for 2 h using 50 mL of a solution of ethylene glycol containing 0.27 M NH_4F and 3.5% v/v demineralized water; this coating was named according with the anodization conditions as: E-0.27M-40V-2h-Dec., where "E" corresponds to the organic base ethylene glycol, "0.27 M" to the concentration of NH_4F, "40 V" to the anodizing voltage, "2 h" the anodizing time and "Dec" the chemical stripping used for the surface preparation of the substrate prior to anodizing. Finally, thermal treatments were conducted at 450 °C for 2 h [1]. Due to the design and dimensions of the photoreactor, nine TiG2 rings coated with TiO_2 were required. The coatings obtained on the rings were characterized using SEM, XRD, and DRS. Previous research determined that the substrate geometry does not significantly affect the overall morphology of the coatings [3]. Nanotubes with a length of 5 µm, an internal diameter of 85 ± 5 nm, and a wall thickness of 7 ± 2 nm were obtained. The coatings exhibited a crystalline anatase phase (XRD patterns not shown) and bandgap values ranging from 3.2 to 3.3 eV, characteristic of the TiO_2 crystalline phase (DRS spectra not shown).

The glass tubes were secured with two caps of polytetrafluoroethylene (PTFE, Teflon®). A closed-loop batch recirculation system with a 400 mL reservoir was adopted. The photoreactor operated

with a recirculation flow rate of approximately 12.5 $cm^3\ s^{-1}$. The total reaction volume of the system was 450 cm^3, with the irradiated volume in the annular section being approximately 120 cm^3. The nine TiO_2-coated rings provided an irradiated photocatalyst area of approximately 170 cm^2. To evaluate the performance of the photoreactor, the Cr(VI)/EDTA system (0.4 mM $K_2Cr_2O_7$ and 1 mM EDTA) at pH 2, was used [2]. Samples of the contaminant solution were periodically taken from a sampling point using the diphenylcarbazide (DFC) spectrophotometric method. The samples were diluted in test tubes with 3 mL of water, to which 100 µL of DFC (0.25 g of DFC in 100 mL of acetone) and 200 µL of H_3PO_4 (1:1) were added.

The solution was stirred, allowed to react for 20 minutes to ensure color stability, and the absorbance value was measured in a spectrophotometer (Shimadzu, UV-2550 or UV-2600i) at 540 nm.

Results and Discussion

The SEM micrographs of the nanotubular coatings on the titanium rings are presented in Figure 1.

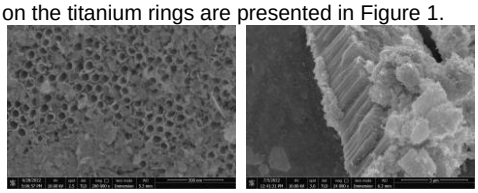


Figure 1. SEM micrographs of the top and side views of the nanotubular coatings obtained on the Ti rings. Anodizing conditions: E-0.27M-40V-2h-Dec.

Figure 2 shows a photograph of the photoreactor operating in a HP test.

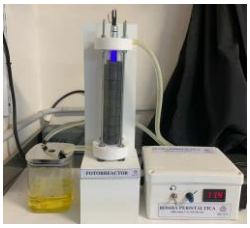


Figure 2. Concentric annular photoreactor.

Figure 3 shows the temporal profile of the Cr(VI) concentration normalized with respect to the initial concentration (C/C_0). A comparison with the system in the absence of photocatalyst (i.e., blank test or photolysis) is also shown. The lines correspond to pseudo-first-order kinetic adjustments and the rate constants (k_1, $R^2 > 0.95$) are presented in Table 1. The fitting curve represents the joint kinetics of the homogeneous transformation (photolytic reaction in the absence of the photocatalyst) and the heterogeneous transformation on the surface of the nanotubes[2].

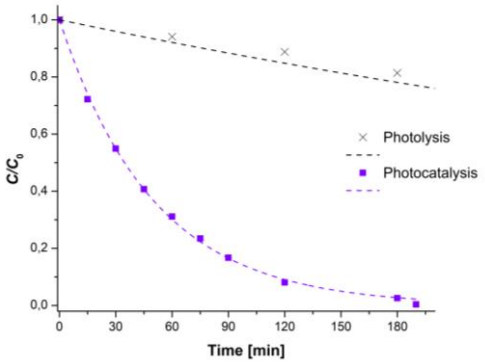


Figure 3. Time profiles of normalized Cr(VI) concentration (C/C_0) on the HP test.

Table 1. Values of k_1, R^2, and percentage of Cr(VI) removal at 180 min of reaction for the photolysis and photocatalytic tests.

Test	$k_1 \times 10^3$ [min^{-1}]	R^2	% Cr(VI) removal at 180 min
Photolysis	1.37	0.95	20
HP	20	0.99	100

After 3 h of irradiation, a 100% transformation of Cr(VI) was observed in the presence of the TiO_2-coated rings, compared to a 20% transformation in their absence (photolysis).

Conclusions

A concentric annular photoreactor using nanostructured TiO_2 coated rings as photocatalysts was successfully designed, built and operated. The results of the performance evaluation of the photoreactor with the Cr(VI)/EDTA system are very promising as a 100% transformation of Cr(VI) was achieved in 180 min, compared to only 20% in the absence of the rings. The transformation was very well adjusted to a pseudo-first-order kinetics.

Acknowledgments

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References

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