Photocatalysis for Water Pollutant Removal. Evaluation of electrospun fibers in a microreactor

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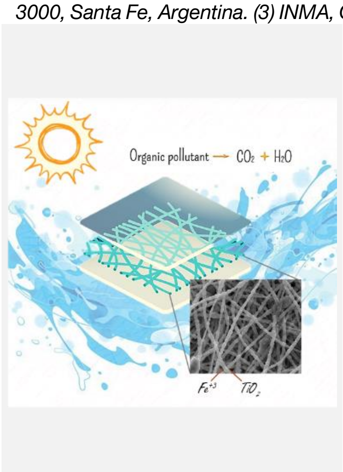

In this work, novel hybrid fiber membranes were synthesized using mesoporous TiO_2 nanoparticles as the photocatalytically active material and polyacrylonitrile (PAN) as the polymer that provides stability and chemical resistance. Carbon and iron were employed as doped materials and different thermal post-treatment were tested. As observed by SEM images, the resulting material is composed of tubular fibers with nanoparticles dispersed on the surface, forming a highly porous three-dimensional matrix. The photocatalytic activity of the fibers was evaluated in a continuous flow microreactor under simulated sunlight, employing 4-chlorophenol as the model pollutant. Significant improvement in the activity of the fibers was verified by the simultaneous presence of carbon and iron, and a post-treatment at 150 °C, due to the generation new electronic states in the TiO_2 particles that enhances the catalyst activity.

Introduction

Growing water pollution requires the development of novel technologies capable of removing recalcitrant compounds that cannot be eliminated by conventional water treatment processes. Photocatalysis with electrospun titanium dioxide (TiO_2) fibers offers several advantages for environmental remediation [1]. This technique can produce nanofibers with high surface area-to-volume ratios, enhancing the contact between TiO_2 and pollutants, and leading to more efficient adsorption and photocatalytic degradation. Additionally, the TiO_2 fibers can be synthesized in various forms, including membranes, mats, and coatings, offering flexibility in the design of pollutant removal systems. Also, TiO_2 fiber membranes can be easily functionalized or doped with different materials to enhance the overall efficiency of the process. In this work, we present the synthesis, characterization and photocatalytic evaluation of electrospun fiber membranes that contain polyacrylonitrile (PAN) as matrix polymer and mesoporous TiO_2 doped with iron and carbon as photocatalytic active materials. The performance of the membranes was assessed in a novel microreactor, specially designed for the purpose, employing 4-chlorophenol as the model pollutant under simulated sunlight

Material and Methods

The titanium oxide photocatalysts were synthesized using an eco-compatible sol-gel method previously reported [2] that generates carbon autodoped and iron doped mesoporous solids without the need of surfactants. The photocatalytic fibers were synthesized using an electrospinning equipment belonging to INMA, Zaragoza, Spain. This equipment, shown in Figure (1), consists of an injector pump, a source of high electrical voltage generation and a collecting surface where the fibers are deposited. For the preparation of the synthesis gel, mesoporous TiO_2 nanoparticles were combined with N,N-Dimethylformamide. This suspension was heated to 60°C to then incorporate the PAN (polyacrylonitrile). The fibers thus obtained were called FB:MT (mesoporous TiO_2), FB:FeMT (TiO_2 with the addition of Fe), and FB:FeMT-150 (TiO_2, Fe and a post treatment at 150 °C).

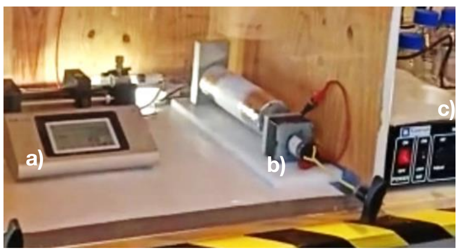

Figure 1. Photograph of the electrospinning system. a) injection pump, b) collector and c) high voltage generator.

A continuous flow microreactor was employed to test the nanofiber membranes (Figure 2). It is composed by: 1) a PMMA block, that contains the inlet and outlet ports and diffusers; 2) the fiber membrane; 3) a reaction chamber frame made of PTFE with a thickness of 130 µm, with silicone gaskets on top and bottom to seal the chamber; 4) a borosilicate glass window; 5) a top frame and a bottom aluminum plate with 6 screws, employed to assemble the reactor components. Illumination was provided by a solar simulator (Oriel Solar Simulator, model 9600), located at 4 cm from the microreactor. This distance assures uniform irradiation of the reaction space. The irradiated reactor volume was 117 µL (4.5 cm × 2 cm × 130 µm). Degradation experiments were carried out employing 4CP aqueous solutions at an inlet concentration of 100 µM. The pollutant solution was injected into the microreactor by a syringe pump, at a flow rate of 1 mL/h; and collected at the outlet in a glass vessel. Quantification of 4CP was carried out by HPLC.

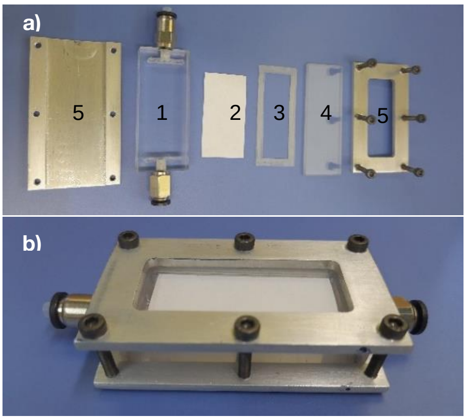

Figure 2. a) Microreactor components. b) Assembled microreactor.

Results and Discussion

Characterization of the fibers. The morphology of the fibers was studied by SEM. They presented tubular shapes, with an average diameter of ~0.65 µm, indeterminate morphology and high porosity, which favors its use as support and adsorbent. The fibers synthesized as a reference only with PAN displayed uniforms diameters, smooth surface and few defects. Instead, when the fibers were synthesized employing mesoporous TiO_2, changes on the surface were observed. All fibers showed more roughness and bulges or widening, which is attributed to the presence of nanoparticles that modify their porosity. On the other hand, the fiber surface has a homogeneous distribution of Ti, C, O, and Fe (when appropriate), which is confirmed by EDS analysis.

Photocatalytic activity. Results of 4CP degradation at a flow rate of 1 mL/h, along with the mass of catalytic material employed, are reported in Table 1. Best performance was achieved with the TiO_2 fibers doped with carbon and iron with a thermal post-treatment at 150 °C (FB:FeMT-150). In this type of fiber, the mild heating temperature of the post-treatment would promote the diffusion of carbon and iron in interstitial and substitutional sites of the titania matrix, generating new electronic states that retard the recombination of electrons and holes in the catalyst and improve its activity [3]. Additional experiments were carried out by adding more layers of fiber membrane FB:FeMT-150 inside the microreactor. As evidenced in Table 1, an increase in the mass of fiber employed results in higher degradation of 4CP, reaching a maximum value of 48.2 %.

Table 1. Photocatalytic evaluation results

Type of membrane	Mass of fiber membrane (mg)	4CP Degradation (%)
FB:MT	15.3	10.2
FB:FeMT	16.3	18.7
FB:FeMT-150	11.4	32.2
FB:FeMT-150	47.3	48.2

Conclusions

A simple and versatile method for the synthesis of TiO_2 fiber membranes is presented. The obtained fibers, based on a hydrophobic polymer such as PAN, constitute a novel hybrid material that can be easily recovered from aqueous media and reused. The functionalization of the fibers with TiO_2 doped with carbon and iron with a thermal post-treatment at 150 °C, allowed us to obtain a highly porous, active and promising photocatalyst for the degradation of water pollutants at large scale.

Acknowledgments

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