Nanocomposite rGO@TiO2 Supported on Fique Fibers for Photocatalytic Degradation of Dyes

Yeimi Lorena Barajas-Rueda¹, Martha Lizeth Pinzón-Martínez¹, Nelson Gutierrez², German Díaz², Luz Marina Ballesteros-Rueda¹, Rafael Cabanzo², Enrique Mejía-Ospino*²

¹Centro de Investigación en Catálisis (CICAT), Universidad Industrial de Santander, Bucaramanga, Colombia
²Laboratorio de Espectroscopía Atómica y Molecular (LEAM), Centro de Investigación en Materiales y Nanociencias (CMN), Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: emejia@uis.edu.co

Abstract. By means of ultrasonic and cationic treatment, the surface of the fiber was adapted to maximize the support of the nanocomposite rGO@TiO2; which had a previous preparation and subsequent anchoring to the fibers by chemical reduction in times of immersion. The fibers were subjected to characterization by FTIR spectroscopy, while in the nanomaterial obtained was verified the deposition of the nanocomposite by means of scanning electron microscopy SEM, as well as the change in the value of the bandgap for TiO2 by UV-spectroscopy. In order to evaluate the photo-degradative activity of the rGO@TiO2 / Fique catalyst, we used Methylene Blue (MB). The experiments were carried out using sunlight that allowed obtain a degradation efficiency of approximately 99 % in two hours.

1. Introduction

Previous studies have established that around 700,000 tons of dyes are produced every year in worldwide, of which 10 to 15 % are discharged directly to the effluents without any treatment [1]. Nowadays, the increasing environmental awareness has prompted searching new alternatives to eliminate this mixture of contaminants present in the waters of these industries and their high concentrations has hindered the treatment by conventional biological or physicochemical processes.

In order to solve this problem, in recent years, research in this area focused on photocatalytic degradation processes, becoming the main alternative in the treatment of water contaminated by dyes [2], [3]. The formation of highly oxidizing agents (OH- and O2-) by the reduction of oxygen and the oxidation of H2O, are responsible for the rapid reaction and the non-selective form with the pollutant species. From these processes, these pollutants are oxidized until complete mineralization, that is, to CO2, water and inorganic ions. In general, this type of technology involves the use of semiconductor materials of a stable nature, with low toxicity, resistant to chemical corrosion and with suitable thermal and mechanical properties, such as TiO2, ZnO, Ce2O3, etc. [4]–[9]. However, despite the high
efficiency of these systems, there are some limitations related to its use with solar energy and the rapid recombination of the electron-hole. Therefore, different studies have focused on improving the photo-activity of TiO2, proposing the modification of its electronic structure through doping with nanoparticles or other semi-conductors such as graphene oxide (GO). GO is a precursor of reduced graphene oxide or graphene with surface and edges, many oxygenated functional groups (hydroxyls, epoxides, carboxyls and carboxyls) which confer high hydrophilicity and easy interaction with organic pollutants [10]–[13].

On the other hand, Fique is a natural fiber obtained of the leaves of the Fique plant (*Furcraea sp*.), a xerophytic monocot native which is originally from South American Andean regions of Colombia, Ecuador, and Peru. It is also possible to find this plant in Venezuela and the east coast of Brazil. Fique is used in the manufacture of sacks, bags, cloths, shoes, and handicrafts. Fique have also been used as a structural reinforcement of polymeric matrix composites, cements, and concretes composites [14], [15].

In this work, we developed novel method for obtaining bio-nanocomposites of reduced graphene oxide (RGO) and TiO2 nanoparticles (RGO@TiO2) supported on Fique fiber; for the purpose of examining the photocatalytic activity of bio-nanocomposite RGO@TiO2-Fique for degradation of dyes.

2. Experimental

2.1. Materials and reagents
Fique fibers were supplied by Coohilados Del Fonce Ltda. Cooperative located in the municipality of San Gil, Colombia. Graphene oxide was supplied by Laboratorio de Espectroscopia Atómica y Molecular (LEAM) and used without prior purification. Finally, the Methylene Blue (MB) was purchased from Sigma-Aldrich and used without further purification.

2.2. Preparation and treatment of raw Fique fibers
The fibers were cleaned by means of ultrasound using deionized water for 60 minutes to eliminate plant residues such as hemicellulose and lignin, among others. The cationic treatment was carried out as reported by Wang [10]. Briefly, the fibers were immersed in 6 % aqueous HCl solution for 3 hours, then these fibers were washed and immersed in 6 % NaOH aqueous solution for another 3 hours, washed and dried at 60 °C for 12 hours.

2.3. Deposition of the nanocomposite on Fique fibers
An aqueous solution was prepared mixing using 507 mg of commercial TiO2 nanoparticles in anatase phase and average size of 18 nm with 169 mg of GO (weight ratio 3:1) in 25 mL of deionized water. The fiber was impregnated by immersion three times, for 15 minutes each, then chemical reduction of the GO was carried out by submerging the fibers in 1 % calcium chloride and sodium borohydride for 10 minutes, finally washed and dried at 80 ℃ for 1 hour.

2.4. Fiber characterization
FTIR spectroscopy measurements were made on the Thermo Scientific Nicolet iS 50 FT-IR Spectrometer, with a spectral range from 400 to 3800 cm-1, equipped with a Polaris Dual Source: Polaris Long-life IR with spectral resolution. A QUANTA FEG 650 microscope integrated with the Genesis Imaging / Mapping software version 6.37 was also used for the SEM to facilitate its management. In addition, with this same equipment, dispersed energy spectroscopy (EDS) was carried out for elementary analysis of the sample, using the EDAX.TSL Advance Microanalysis Solutions software. For UV-Vis DR Spectroscopy, a halogen lamp was used to cover the wavelength range from 250 to 1000 nm.

2.5. Evaluation of the photo-degradative activity
The degradation tests of Methylene Blue were carried out by placing rGO@TiO2 nanocomposite fiber in contact with 20 mL of dye aqueous solution (10, 15 and 20 ppm) for two hours, under sunlight exposure. The reaction was monitored by UV-Vis spectroscopy.
3. Results and Discussion

Figures 1a and 1b show Fique fiber before and after clean treatment, respectively. The clean fibers have homogeneous texture and ease of handling.

![Figure 1. a) Fique raw fibers, b) Fique fibers after ultrasonic cleaning and cationic treatment](image)

Figure 2 shows FTIR spectra of raw Fique fibers and clean Fique fiber. The bands located at 3400, 2800, 1650 and 1250 cm\(^{-1}\) corresponding to functional groups of cellulose [14]. Likewise, those of hemicellulose in 1600 cm\(^{-1}\) and lignin between 1500 and 1800 cm\(^{-1}\). When contrasting the spectrum resulting from raw and treated Fique fiber, the disappearance of the band at the range of 1500 and 1600 cm\(^{-1}\) was observed, which corresponds to the vibrations of the aromatic rings structure, being these the main structural components of lignin after the cationic treatment. Likewise, between the range from 1700 to 1800 cm\(^{-1}\), disappearance of peaks was observed, which was associated to the stretching in tension of carbonyl bonds -C = O associated with ester-type bonds that usually occur in the structure of the hemicellulose. In general, this characterization technique allowed determining that the fibers after the treatment are constituted mainly by cellulose, which provides a chemically more suitable environment for the anchoring of the nanocomposite on these fibers, since the cellulose has more hydroxyl groups that promote a better interaction with the nanocomposite.

![Figure 2. FTIR raw Fique fiber spectrum and Fique fiber spectrum treated](image)

Figure 3 is a photograph of Fique fiber coated with Reduced GO (rGO) TiO2 nanoparticles. The dark tonality is related to the recovery of the graphitic structure of the GO material. The reduction of GO
minimizes the hydrophilic character of the nanocomposite avoiding the re-dispersion of the GO in the aqueous medium and maximizing the anchoring of the nanocomposite to the Fique fibers.

Figure 3. Fique fiber coated with nanocomposite rGO@TiO₂

Figure 4a y 4b show SEM micrograph an EDS micro-analysis of Fique fiber coated with rGO@TiO₂ nanocomposite. According to the micrograph, the Fique fibers present a partial coating with accumulation of nanocomposites on several places of the surface. The nanocomposites have a homogeneous amorphous morphology. EDS results show presence of titanium (Ti), carbon (C) and oxygen (O) corresponding to the elements of the nanocomposite.

Figure 4. a) SEM micrograph Fique fiber coated with rGO@TiO₂ and b) Fique fiber/rGO@TiO₂ EDS elemental microanalysis

Figure 5 shows the photo-degradative activity for Methylene Blue at concentrations form 10, 15 and 20 ppm. This procedure was carried out in order to determine if within this range of concentrations, the nanocomposite showed a decrease in its photo-degradative activity. According to the degradation curves, the concentration does not affect the efficiency photo-degradative of the bio-nanocomposite, rGO@TiO₂/Fique. After 120 minutes, the process reaches 99 % of photo-degradation of MB dye.
Figure 5. Photo-degradative activity of the rGO@TiO2/Fique nanocomposite for the MB dye at 10, 15 and 20 ppm.

4. Conclusions
The anchoring was made effective by modifying the Fique fibers with nanocomposite (rGO@TiO2) with good characteristics in the mechanical mixing preparation. It was possible to confirm the photo-degradative activity of the modified Fique Fiber with values of 99 % for Methylene Blue dye for two hours under the sunlight exposure. The obtained results demonstrated the potential of the bio-nanocomposite in applications related to environmental remediation, because its support is based on a natural fiber, making it environmentally friendly and offering possibilities of recovery and reuse.

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