

HYBRIDS OF CELLULOSE-TiO<sub>2</sub> FOR ENVIRONMENTAL  
APPLICATION*Lucas G. P. Tienne*<sup>1, 2</sup>, *Fernanda D. P. B. Santos*<sup>1</sup>, *Maria de Fátima V. Marques*<sup>2</sup>, ✉<https://doi.org/10.23939/chcht14.01.093>

**Abstract.** This work is based on the combination of the acid treated-cellulose and chemically adsorbed titanium(IV) oxide on its surface to obtain a hybrid material for application in water treatment to degrade organic compounds. The photocatalytic property was evaluated in the degradation of the methyl orange dye. The photodegradation activity was higher using the hybrid obtained from the cellulose whose hydrolysis was conducted at higher acid concentration, which resulted in smaller fiber diameter, as suggested by scanning electron microscopy. Thermogravimetric analysis and X-ray diffraction confirmed that this hybrid has lower thermal degradation temperature and the size of the cellulose nanocrystals is lower in the more hydrolyzed sample. This allowed the increase of surface area and therefore, the fixation of more nanoparticles of TiO<sub>2</sub>, which is responsible for the photodegradation activity, observed by the bleaching of a dye solution.

**Keywords:** cellulose, acid treatment, hybrid of cellulose-TiO<sub>2</sub>, degradation of organic material.

## 1. Introduction

Cellulose is a high molecular weight linear polysaccharide biopolymer with cellobiose as repeating unit linked by means of beta-1,4 glycosidic bonds. Its molecular weight is variable, with empirical formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, with the minimum value of  $n = 200$  (typically 300 to 700, may be greater than 7000) [1]. It is the most abundant polymer on Earth and it causes less impact on the environment and is less detrimental to human health, giving the reason to consider it as a green polymer. The major source of cellulose is vegetable fiber, which is a composite containing linear semicrystalline cellulose and amorphous components as lignin, hemicellulose and pectin. Cellulose is fibrous and moist, with multiple

hydrogen bonds established between hydroxyl groups of the distinct chains, rendering them impenetrable to water and therefore insoluble, giving rise to compact fibers. However, lignin, hemicellulose and pectin are branched complex polysaccharide molecules, which are extracted from cellulose, making it possible to isolate the linear structure of the cellulose, thereby providing several possibilities of applications of this natural material.

Nanocrystalline cellulose (CNC) can be generated by acid hydrolysis from various plant sources, with transverse dimensions as small as 3–30 nm, giving a high surface to volume ratio. It is a promising material for advanced applications. It is strong, light and relatively resistant to temperature, wear, erosion and corrosion [2, 3]. CNC is inexpensive, sustainable, biocompatible, and biodegradable. It also has tailored hydro/oleophilic equilibrium; has good optical transparency as well as mechanical properties of films and gels [4]. Crystallinity index (CI) is a parameter to describe the relative amount of crystalline material in cellulose. There are both crystalline (ordered) and amorphous regions in the traditional two-phase cellulose model. However, it has been found that the CI varies significantly, depending on the choice of measurement method [5].

Among different hydrolysis parameters that affect the size, size distribution and the aggregation degree of the CNC suspension are: the nature of the raw material, time, temperature, acid-to-pulp ratio and type of acid used. Size, polydispersity, morphology of the CNC, aggregation, and particle-density of suspension are key properties determining the functionality and prospective application of the material [6].

The exposed –OH groups on CNC surfaces can be readily chemically modified to achieve different surface properties and have been used to adjust CNC self-assembly and dispersion for wide range of suspensions, to control interfacial properties [7]. In addition, this biopolymer may have different morphologies with totally different characteristics, like micro or nanofibrillated cellulose, microcrystalline or nanocrystalline cellulose. Thus, a modification of the cellulose structure by means of acid hydrolysis can add other utilities, such as to

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increase its mechanical resistance and thermal stability providing multiple innovative technologies.

Functionalization of cellulose surfaces is done by changing the hydroxyl functional unit of (1,6) $\beta$ -D-anhydroglucopyranose. Apolar groups must be attacked by covalent bonds [8]. The hydroxyl groups in C2 and C3 consist of secondary alcohols and in C6 acts as primary alcohol. Esterification reactions at C6 hydroxyl groups of glucose units in cellulose can occur ten times faster than in C2 and C3 groups. Sulphuric and hydrochloric acids are the most widely reported but phosphoric acid [9] and hydrobromic acid [10] were utilized as well.

Titanium(IV) oxide has excellent chemical stability, non-toxicity, high thermal stability and photocatalytic properties, and is still environmentally friendly in water treatment [11]. Titanium(IV) oxide can vary from amorphous to different crystal structures [12] and all forms have photocatalytic activity. The crystalline form anatase has high activity [13], however, the mixture of anatase and rutile exhibits synergistic effect and increases photocatalytic activity [14]. Another approach to decrease cost, and to produce more sustainable photocatalysts is to use amorphous materials. Since high temperature treatments for crystallization are not required, amorphous materials can be potentially much cheaper to synthesize and easier to adapt for large-scale preparation [15]. One way of highlighting TiO<sub>2</sub> activity is to maximize the surface area of the amorphous material.

Hybrids of cellulose and titanium(IV) oxide are polymer-inorganic composites, which combine different properties. The nanostructure of the hybrids is controlled by adsorption of titanium(IV) oxide nanoparticles on the cellulose surfaces. They are materials with high optical transparency, Young's modulus and hardness. The hybrid will also have characteristics of TiO<sub>2</sub> such as inherent high refraction index and UV absorbing properties. Therefore, the combination will allow photoactivation to photocatalytic degradation. Water resistance and thermal stabilization could be also observed [16]. Photocatalytic and photoelectronic properties of nanosized TiO<sub>2</sub> particles make them very attractive in application areas such as catalysis, gas sensors and solar energy conversion. Moreover, the morphology of TiO<sub>2</sub> particles has a great influence on their performance, and they are synthesized in several shapes such as spheres, rods, needles, *etc.* [17, 18].

Hard and transparent films formed by cellulose-TiO<sub>2</sub> nanoparticles have already been prepared [19]. The authors described the method as facile and the production of the hybrid nanoparticles with high inorganic content by the adsorption of TiO<sub>2</sub> (anatase) nanoparticles on wood-derived nanofibrillated cellulose. However, in general, it is difficult for diffusing molecules to penetrate the crystalline parts of cellulose fibrils [20]. Due to relatively

high crystallinity [21], in combination with the ability of the nanofibers to form a dense network held together by strong inter-fibrillar bonds, it has been hypothesized that it might act as a barrier material [22].

After the preparation of a film, the researchers revealed that the material has enhanced UV-Vis light absorption and has potential application as transparent mechanical-resistant material for protective coats or paper industry, as well as the possibility of forming the desired shape [23]. The authors did not evaluate this material for any specific application.

In the present work, commercial microcrystalline cellulose (Arbocel BC 1000) was treated with sulfuric acid solution (55 and 65 %), producing two samples that reacted with titanium(IV) isopropoxide, and therefore TiO<sub>2</sub> nanoparticles were synthesized directly on the surface of cellulose in slightly acid dry isopropanol medium. Therefore, hybrids of cellulose and TiO<sub>2</sub> were obtained and used in industrial water treatment. The hybrid was characterized by thermal, mechanical and morphological techniques and was evaluated as photodegradation catalyst for the treatment of wastewater due to degradation of organic material. There is no previous work reporting the use of this hybrid in environmental purification area.

## 2. Experimental

### 2.1. Materials

Commercial cellulose Arbocel BC 1000 with average fiber length of 700  $\mu$ m was used. Titanium(IV) isopropoxide was purchased from Sigma-Aldrich; sulfuric acid, methanol and isopropanol were purchased from Vetec Quimica.

### 2.2. Synthesis of TiO<sub>2</sub> by the Sol-Gel Method

To synthesize titanium(IV) dioxide nanoparticles, a solution containing 5 ml of titanium(IV) isopropoxide in 20 ml of isopropanol was prepared. This solution was slowly added to a flask containing 10 ml of isopropanol, acidified to pH 3 with HCl, under vigorous stirring for 1 h. After that time, the system was transferred to ultrasound equipment with 180 ml of distilled water. Then, the product was filtered, washed with distilled water (three times) and dried to obtain powder with 66 % yield. Part of the powder was heated at 773 K for 1 h. This procedure was necessary to promote crystallization from the amorphous oxide to the anatase phase [24]. Besides, the other part of the obtained powder was heated at 423 K for 24 h to dry the amorphous phase.

### 2.3. Acid Treatment of Cellulose

In order to carry out the acid hydrolysis, 10 g of pure commercial cellulose Arbocel were added at 273 K under stirring while the solution of sulfuric acid and distillate water at different concentrations was slowly added to cover the fiber, producing Sample 1 (treated with 55 % H<sub>2</sub>SO<sub>4</sub>) and Sample 2 (65 % H<sub>2</sub>SO<sub>4</sub>). After the addition, the suspension was stirred for 30 min at 318 K. The resulting suspension was washed with 500 ml of cold water, then, it was subjected to centrifugation (15 min, 3500 rpm), resuspended in distilled water and the process was repeated to remove excess acid until pH achieved 6–7. The resulting cellulose suspensions were poured into a Petri dish and left at 313 K to dry.

### 2.4. Preparation of Cellulose-TiO<sub>2</sub> Hybrid

After the cellulose treatment with acid (Samples 1 and 2), each material was resuspended in 200 ml of isopropanol under ultrasound and transferred to a flask being maintained under stirring. Two drops of hydrochloric acid were added and then 20 ml of isopropanol solution containing 5 wt % of titanium(IV) isopropoxide (in relation to cellulose) were added very slowly under vigorous stirring for 1 h. After that time, ethanol was added to interrupt the reaction, and it was kept for 24 h. Then, the suspension was washed with water, resulting in Sample A (from Sample 1) and Sample B (from Sample 2).

### 2.5. Methods of Analysis

The original Arbocel, the resulting hydrolyzed cellulose and the obtained cellulose-titanium oxide hybrid were characterized by scanning electronic microscopy, X-ray diffractometry, thermogravimetric analysis, and infrared spectroscopy.

The XRD analyses were performed to observe the crystallinity of cellulose and eventually of TiO<sub>2</sub>. The samples were analyzed in powder. The X-ray diffractometer worked with a potential difference across the tube of 30 kV and 15 mA. The sweep was carried out in the range of 2θ from 2° to 40°, while the goniometer speed was 0.05°/min and the radiation used was CuK<sub>α</sub>. To characterize the effect of TiO<sub>2</sub> coated nanoparticles on the crystalline structure of cellulose, the average crystallite size ( $L_c$ , nm) in the direction perpendicular to the set of lattice planes (mean crystallite length along  $c$ -axis) was calculated by the Scherrer equation [25].

$$L_c = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where  $\beta$  is full width at half maximum (FWHM) of the related peak;  $K \sim 0.9$  is the constant crystal lattice;  $\lambda = 0.154$  nm is the X-ray wavelength of CuK<sub>α</sub>, and  $\theta$  is Bragg angle.

The space between different diffraction planes ( $D$ , nm) was obtained by Bragg's equation [26]:

$$2D\sin\theta = n\lambda \quad (2)$$

where  $D$  is interplanar distance between layers, nm;  $\lambda$  is the wavelength of X-ray;  $\theta$  is Bragg angle.

*Thermal gravimetric analysis* (TGA) was performed using TA Instruments Series Q, Model 500 analyzer. The samples were heated in the range from room temperature to 973 K under inert atmosphere, at the heating rate of 10 K/min.

*FTIR spectra* were obtained on the Perkin Elmer model L160000X using ATR accessory at a scan of 4000–600 cm<sup>-1</sup> using 100 scans and 4 cm<sup>-1</sup> resolutions.

*Scanning electron microscopy* (SEM) was used to assess the size and morphology of the fibers after chemical treatment, and to observe the incorporation of TiO<sub>2</sub> on the fibers surface. Analyses were carried out with an FEI Quanta 200 microscope. The fibers and TiO<sub>2</sub> were fixed on the specimen holder with carbon adhesive tape and metalized with gold.

*Analysis of methyl orange degradation.* Experiments at different concentrations were performed using both produced cellulose-TiO<sub>2</sub> hybrids (Samples A and B). The concentration of each hybrid in methyl orange solution varied from 10 % to 20 % and 30 %. The neutralized samples were placed under observation for one-week, one month and two months. The samples were compared with the pure methyl orange solution, equally submitted to sunlight. The decrease in color of the dye shows the photocatalysing effect of the hybrid.

*UV-Vis spectroscopy analyzes* were performed to measure the absorption related to the dye solution in order to monitor the absorbance values between each interval to demonstrate photocatalytic activity by the decrease in color with the organic molecule degradation.

## 3. Results and Discussion

Two samples of hydrolyzed cellulose were prepared: Sample 1 (318 K, 30 min and 55 % H<sub>2</sub>SO<sub>4</sub> in the acidic solution) and Sample 2 (the same temperature and time, with 65 % H<sub>2</sub>SO<sub>4</sub> concentration). Both samples were reacted with titanium isopropoxide to chemically adsorb TiO<sub>2</sub> nanoparticles on cellulose surface, producing hybrid Samples A and B, respectively.

### 3.1. Characterization of Cellulose-TiO<sub>2</sub> Hybrids

#### 3.1.1. Scanning electron microscopy (SEM)

From the microscopic images of the hybrids (Fig. 1) in Sample B the cellulose particles in the form of very fine fibers can be identified. Moreover, the structure observed in Fig. 1c was identified as titanium(IV) oxide nanoagglomerated particles with spherical shape anchored on cellulose surface.

On the other hand, Sample A, which was obtained after milder acid treatment of cellulose, still presented microfibrils.

#### 3.1.2. X-ray diffraction

Insights of the cellulose and the formed TiO<sub>2</sub> phases nature were obtained from the XRD diffraction pattern. As seen from Fig. 2, the four characteristic peaks

located at  $2\theta = 14.5, 16.6, 22.5,$  and  $34.9^\circ$  in the original cellulose show that it is a typical XRD pattern of cellulose with the main diffraction signals assigned to the (101), (101), (002), and (040) diffraction planes, respectively [27, 28]. After the cellulose was hydrolyzed and coated with TiO<sub>2</sub>, the intensities of these peaks become weaker and inconspicuous. In fact, this pattern reveals a noticeable decrease in the crystallinity of cellulose. According to the literature [29], this can be related with the use of sol-gel process for the generation of TiO<sub>2</sub> nanoparticles since they were mostly in amorphous state without any additional heat treatment. Thus, the decrease of the crystallinity in the hybrid is related to the incorporation of amorphous TiO<sub>2</sub> nanoparticles into the hydrolyzed cellulose.

The crystallite size  $L_c$  related to cellulose was calculated from the Debye-Scherrer equation and is presented in Table 1, showing a sharp decrease in the crystallite length in Samples A and B. Besides, the space between diffraction planes ( $D$ ) also decreased.

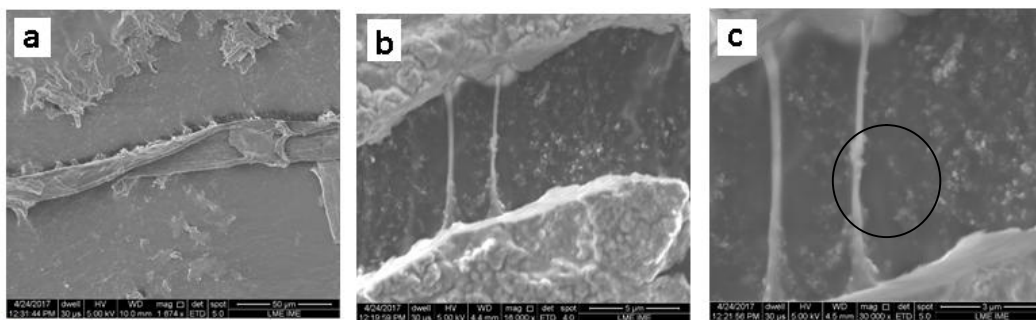


Fig. 1. Scanning electron microscopy images of the hybrids: Sample A (a); Sample B (b) and Sample B (higher magnification) (c)

Table 1

X-ray diffraction results of the original cellulose and both hybrid samples of cellulose-TiO<sub>2</sub>

Samples	$2\theta$ , degree	$D$ , nm	$L_c$ , nm
Original cellulose	24.20	0.38338	2.6864
Sample A	24.10	0.36927	0.1172
Sample B	23.20	0.36770	0.4353

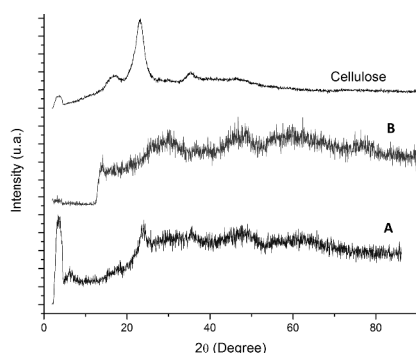


Fig. 2. X-ray diffraction of commercial cellulose and cellulose-TiO<sub>2</sub> hybrids A and B

#### 3.1.3. Thermogravimetric analysis

Higher resistance to thermal degradation can be observed (Table 2) in hybrid A, obtained from cellulose treated at lower acid concentration, as expected. The pyrolysis of the cellulose occurs by the cleavage of glycosidic bonds, C-H, C-O, C-C bonds, and by dehydration, decarboxylation and decarbonylation. This shows that in the most drastic hydrolysis condition there was a greater reduction of the polymerization degree of the cellulose forming smaller chains with less resistance to thermal degradation, possibly due to the smaller size of crystals and to the greater number of free chain terminals.

The residue content at 973 K for both hydrolyzed samples indicates that the carbon amount (char) resulting from cellulose pyrolysis was very high.

According to the literature [2], the pyrolysis residue increases with the smaller particle size of nanocellulose and with the largest number of chain ends. This could be also due to the presence of a high amount of crystalline cellulose, which has an intrinsically flame-resistant property.

In Fig. 3 the thermograms of TG and DTG are presented and two mass losses were detected. The first slight weight loss at low temperature (from ambient to 348 K) is related to cellulose dehydration, attributed to physically adsorbed and hydrogen bonded linked water molecules. The other step corresponds to the thermal degradation ( $T_{max}$ ) that occurred at 593 K for the original cellulose, at 517 K for the hydrolyzed one (samples 1) and at 537 K for the cellulose-TiO<sub>2</sub> hybrid (samples A). It should be noted that the decomposition temperature of the acid treated cellulose and the hybrid material was significantly lower than the original cellulose. This phenomenon can be related to the reduction of cellulose chain length after hydrolyses and to the catalytic property of incorporated TiO<sub>2</sub> nanoparticles in the hybrids.

Additionally, it is observed that in the case of both hydrolyzed and hybrid samples, there is no weight loss after reaching 673 K. The residual mass would be used to calculate the inorganic content in the synthesized hybrids; however, taking into account that hydrolyzed celluloses generate high amounts of char, for synthesized hybrids, the content of TiO<sub>2</sub> nanoparticles could not be detected.

### 3.1.4. Infrared spectroscopy (FTIR)

It can be seen from Fig. 4 that the hybrids show broad and intense band in the region of about 3400 cm<sup>-1</sup>, corresponding to the vibration of the O–H bond, as well as the vibration at 1056 cm<sup>-1</sup> related to C–OH stretching. Bands at 2900 and close to 1450 cm<sup>-1</sup> are draw and flexion characteristics of the CH<sub>2</sub> groups, respectively. The peak at 1630 cm<sup>-1</sup> is primarily due to the bending mode of the absorbed water with some contribution from carboxylate groups, and that at 900 cm<sup>-1</sup> – to the C–H deformation of the cellulose.

The FTIR spectrum of TiO<sub>2</sub> nanoparticles shows the presence of four major absorption bands. The first is the largest, and is observed at 3500 cm<sup>-1</sup>, corresponding to the stretching vibration of the OH group of the nanoparticles surface; the second band is observed at around 1630 cm<sup>-1</sup>, corresponding to water bending modes of Ti–OH (both are overlapped with those of cellulose); the third is a prominent peak at 1380 cm<sup>-1</sup> related to Ti–O vibration modes. A broad band centered at 650 cm<sup>-1</sup> is due to the vibration of Ti–O bonds in the TiO<sub>2</sub> particles.

We synthesized titanium dioxide nanoparticles using the sol-gel method and heated a part of the obtained particles at 423 K for 24 h and another part at 773 K for 1 h. Basically, TiO<sub>2</sub> is amorphous even after treatment at 423 K for a long period. Meanwhile, the sample heated at 773 K presents XRD profile of crystalline anatase-phase TiO<sub>2</sub> exhibiting strong diffraction peaks at around 26° and 48° (Fig. 5). Therefore, it is not possible to transform amorphous TiO<sub>2</sub> into anatase on the cellulose surface by heating process, since cellulose is not stable at 773 K.

Table 2

TG and DTG of cellulose materials

Samples	H <sub>2</sub> SO <sub>4</sub> , % (v/v)	TiO <sub>2</sub> , %	$T_{onset}$ , K	$T_{max}$ , K	Residue, %
Original cellulose	–	–	593	617	8.8
Sample 1	55	–	517	543	48.1
Sample A	55	5	537	565	47.8
Sample 2	65	–	–	–	67.8
Sample B	65	5	495	521	66.8

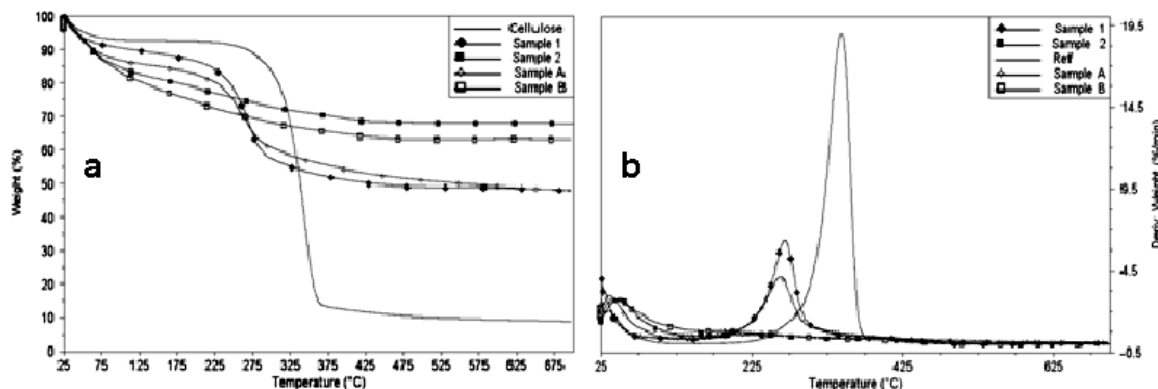


Fig. 3. TG (a) and DTG (b) of original cellulose, Samples 1, 2, A and B

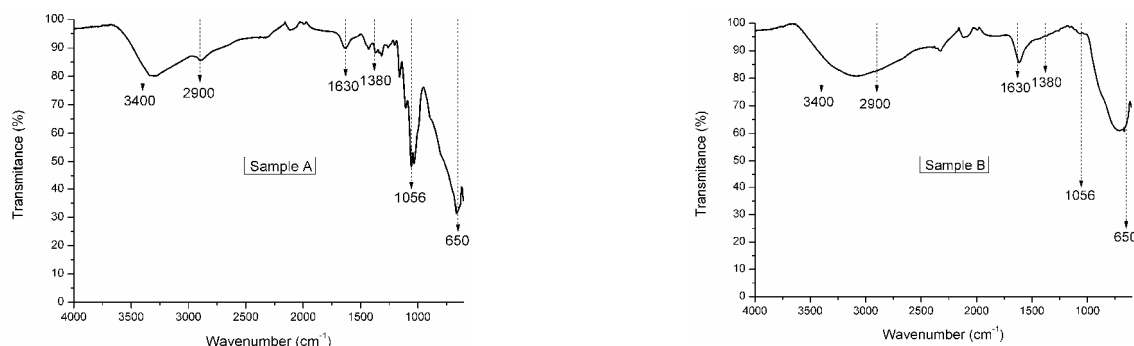


Fig. 4. FTIR spectra of Samples A and B

### 3.3. X-Ray Diffraction of TiO<sub>2</sub>

We synthesized titanium dioxide nanoparticles using the sol-gel method and heated a part of the obtained particles at 423 K for 24 h and another part at 773 K for 1 h. Basically, TiO<sub>2</sub> is amorphous even after treatment at 423 K for a long period. Meanwhile, the sample heated at 773 K presents XRD profile of crystalline anatase-phase TiO<sub>2</sub> exhibiting strong diffraction peaks at around 26° and 48° (Fig. 5). Therefore, it is not possible to transform amorphous TiO<sub>2</sub> into anatase on the cellulose surface by heating process, since cellulose is not stable at 773 K.

### 3.4. Visual Evaluation of Methyl Orange Degradation

From the solutions prepared as described in the experimental section, Samples A and B were evaluated in three different proportions of cellulose-TiO<sub>2</sub> to methyl orange: 10, 20 and 30 %. Thereafter, the solutions were neutralized and placed under daylight for one week. Then, they were submitted to daylight for one-month more and the discoloration of the organic dye was evaluated as a result of its degradation by the photocatalytic action of TiO<sub>2</sub> nanoparticles on the hybrid. To exclude the possibility that the staining was caused by the light itself, we did blank experiments where only methyl orange solu-

tion in the absence of TiO<sub>2</sub> photocatalyst was submitted to the same conditions as the samples.

The pH value of dye solution with the hybrid has a significant influence on the percentage of degradation of dye [30]. Therefore, we neutralized all samples before submitting to daylight.

As methyl orange is also a pH indicator, the samples were tested after addition of the hybrids A and B in the dye solution before and after pH neutralization (as shown in Fig. 6).

According to the results shown in Fig. 7, it was possible to identify that Sample B showed superior photocatalytic activity since at 20 and 30 % concentrations the color faded to transparency. This was possible due to the improved fixation of the titanium(IV) oxide on the surface of Sample 2, as shown by the characteristic FTIR bands. Moreover, this sample has decreased degradation temperature according to TGA and XRD data, which indicates sharper decrease in cellulose molecular mass and crystalline size.

Therefore, based on the methyl orange test, it can be seen that hybrid B has greater degradation rate of the organic substance evaluated by the staining of this dye. In the 20 % and 30 % tests there was total degradation due to visualization of transparency in the solutions. The other tests also clearly obtained the photocatalytic activity, however, with a lower degradation rate.

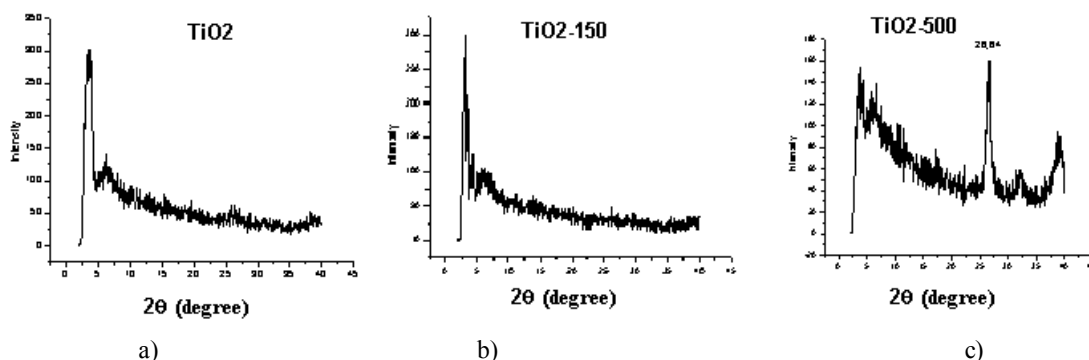
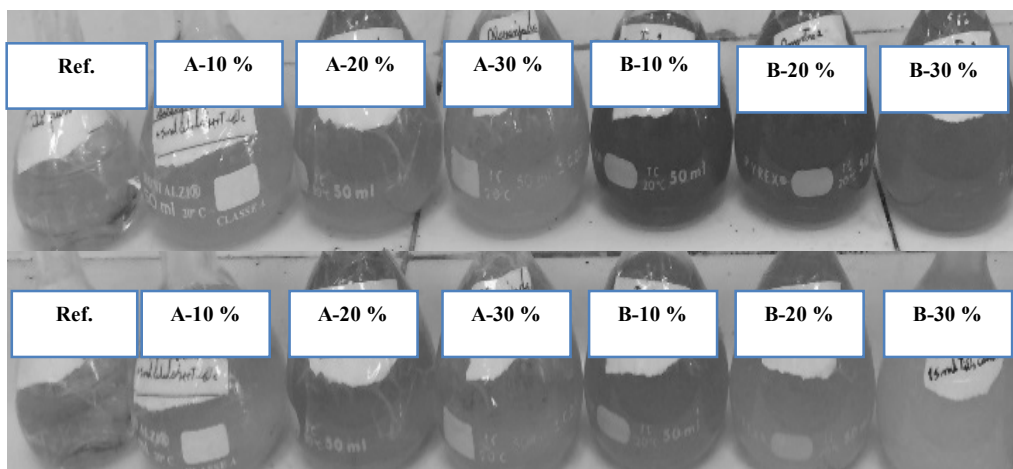
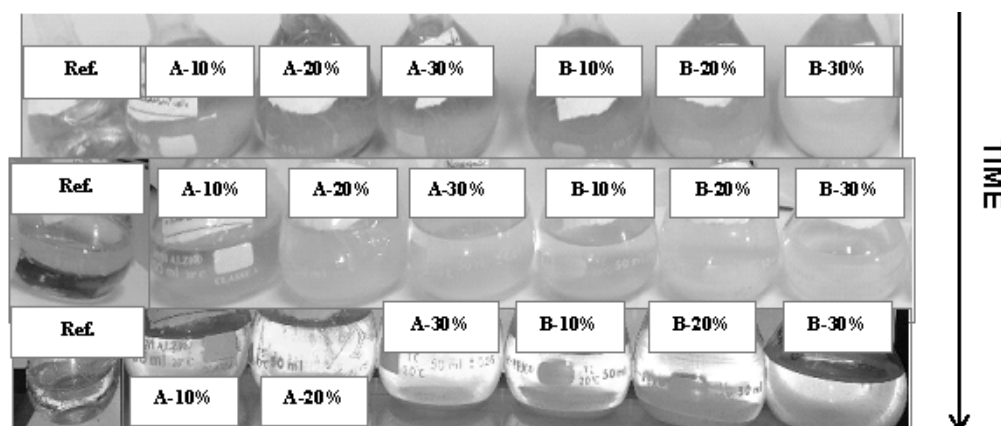


Fig. 5. X-ray diffraction of: titanium dioxide(a); titanium dioxide after treatment at 423 K, 24 h (b) and titanium dioxide after treatment at 773 K, 1 h (c)



**Fig. 6.** Neutralization process of the methyl orange solution with hybrids: Sample A (from Sample 1: cellulose treated with 55 % H<sub>2</sub>SO<sub>4</sub>) and B (from Samples 2: treated with 65 % H<sub>2</sub>SO<sub>4</sub>) with 10, 20 and 30 % (v/v). First row shows samples after immediate preparation, second row – after neutralization and one-week contact under light



**Fig. 7.** Degradation of methyl orange with Sample A and B with 10, 20 and 30 %, after one week, one month and two months

### 3.5. Evaluation of the Dye Decomposition (UV-Vis Spectrometry)

The photocatalytic activity of the synthesized hybrids was evaluated by the photocatalytic decomposition of methyl orange in aqueous suspension under daylight irradiation.

From the cellulose-TiO<sub>2</sub> hybrids A and B solutions in methyl orange at different percentages, UV-Vis spectroscopy (Fig. 8) were also performed to monitor the absorbance values in each interval in order to confirm the lowering of the absorbance after daylight exposure due to the photocatalytic activity.

The UV-Vis spectrum of methyl orange showed two absorption maxima. The first band is observed at 271 nm, and the second band, more intense, under visible region, is located at 465 nm in neutral pH, which was used to monitor the photocatalytic degradation of this dye.

As can be observed, Sample B stands for having less absorption peak at 465 nm, showing greater efficiency in the dye decomposition. Therefore, cellulose hybrid with TiO<sub>2</sub> nanoparticles can act as degradation agent of organic matter with the purpose of polluted waters purification. In order to verify the stability and durability of TiO<sub>2</sub> coating with cellulose after water treatment, FTIR was performed for both hybrids aged 12 months, as shown in Fig. 9. Both spectra are similar to their correspondents in Fig. 4. Therefore, essentially the material did not degrade strongly. However, there are some changes, like the intensity of the carboxylic peak around 1630 cm<sup>-1</sup>, that clearly increased with ageing, especially for Sample B.

## 4. Conclusions

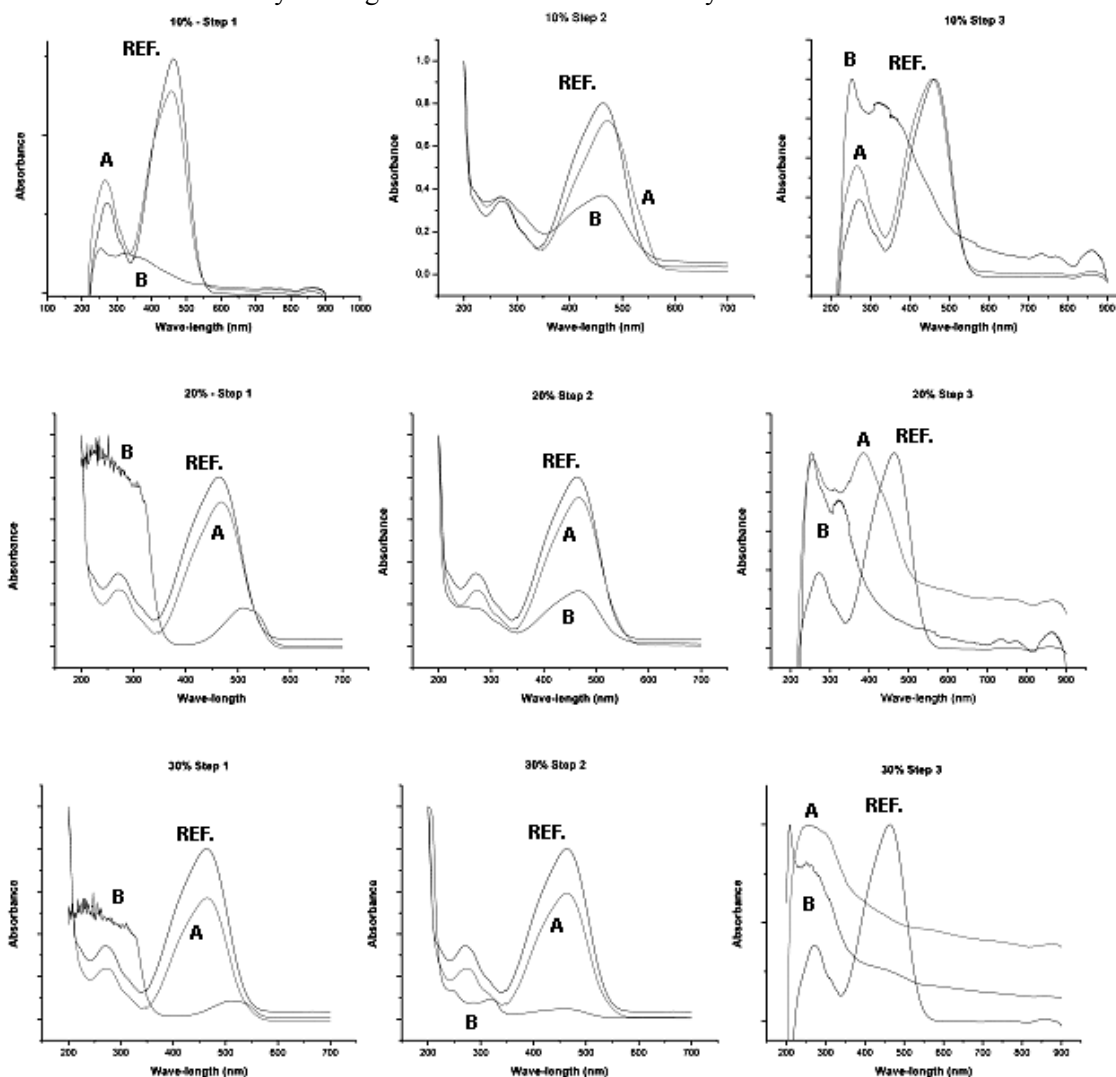
The obtained hybrids are green water-resistant materials, which due to their photocatalyst activity can be used in water treatment.

Additionally, Sample 2 (cellulose hydrolyzed with 65 %  $\text{H}_2\text{SO}_4$ ) was more effective than Sample 1 (55 %  $\text{H}_2\text{SO}_4$ ) to obtain the cellulose- $\text{TiO}_2$  hybrid with higher efficiency in organic matter degradation. This is because the surface area in this material is higher possibly due to the smaller cellulose crystal size, assisting the fixation of  $\text{TiO}_2$  on the cellulose surface. The absorption bands in FTIR spectra confirmed the presence of  $\text{TiO}_2$  and identified vibrations of functional groups of cellulose in the hybrid. The decrease in the intensity of the characteristic peak of the cellulose crystal planes in XRD was due to the coating of the cellulose surface by amorphous  $\text{TiO}_2$  nanoparticles. However, due to the smaller dimensions of the cellulose crystals after acid hydrolysis, the hybrid material has lower resistance to thermal degradation than the unmodified cellulose. The visual analysis and UV-Vis spectra of the hybrid in contact with methyl orange showed that

degradation under light was verified, discoloring the dye, especially using the hybrid obtained with cellulose hydrolyzed at higher acid concentration, proving the higher photocatalytic activity.

Therefore, the application of cellulose- $\text{TiO}_2$  hybrid activity in degradation of organic matter and purification of organic polluted water was confirmed. In addition, the hybrid was resistant to degradation during treatment in water.

So, the energy of nanocrystalline surfaces can be better utilized by fixing  $\text{TiO}_2$  nanoparticles with photocatalyst properties. The evaluation of the methyl orange mediated photodegradation showed that the hybrid obtained from cellulose treated at 65 %  $\text{H}_2\text{SO}_4$  is more active, which was evidenced by the greater decrease of the relative absorption to the dye after two months of contact with the hybrid.



**Fig. 8.** UV-Vis spectrometry of hybrids A and B to methyl orange solutions with 10, 20 and 30 % (v/v) after step 1 (one week); step 2 (two weeks) and step 3 (three weeks)



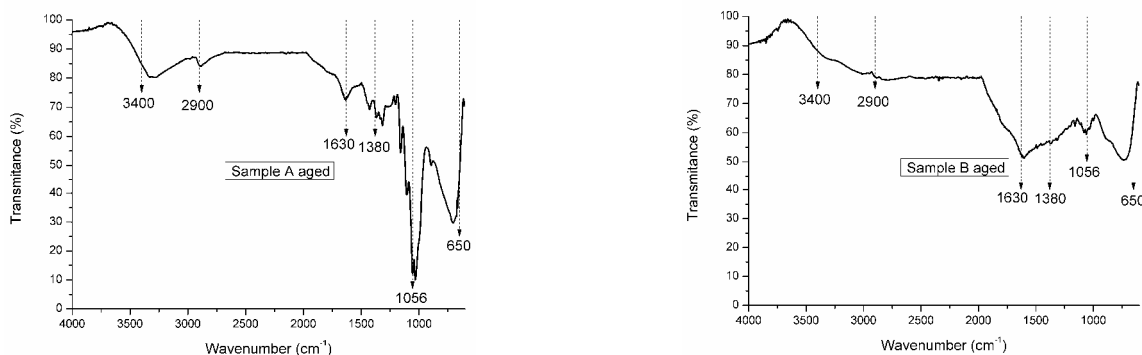


Fig. 9. FTIR spectra of both hybrids aged 12 months

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## ЕКОЛОГІЧНЕ ЗАСТОСУВАННЯ ГІБРИДІВ ЦЕЛЮЛОЗА-TiO<sub>2</sub>

**Анотація.** Комбінацією обробленої кислотою целюлози та хімічно адсорбованого оксиду титану(IV) на її поверхні одержано гібридний матеріал для оброблення води з метою розкладу органічних сполук. За ступенем деградації метилового оранжевого оцінено фотокаталітичні властивості гібриду. Встановлено, що фотодеградаційна активність є вищою для гібриду, отриманого з целюлози, гідроліз якої проводився за підвищеної концентрації кислоти. В результаті діаметр волокон зменшується, що підтверджено результатами скануючої електронної мікроскопії. За допомогою термогравіметричного аналізу та рентгенівської дифракції встановлено, що більші гідролізовані гібриди мають нижчу температуру термічної деградації, і менший розмір нанокристалів целюлози, що дало можливість збільшити площу поверхні, а отже фіксацію наночастинок TiO<sub>2</sub>, які відповідають за фотодеструктивну активність. Збільшення активності фіксувалось через знебарвлення розчину барвника.

**Ключові слова:** целюлоза, кислотне оброблення, гібрид целюлоза-TiO<sub>2</sub>, розклад органічного матеріалу.