

Sustainable Bleaching Process of Raw Cotton by TiO₂ Light-Activated Nanoparticles

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Abstract

Nanoparticles (NPs) of titanium dioxide (TiO₂) are promising for the photocatalytic degradation of organic compounds, arising as an excellent alternative to conventional bleaching processes. Within this background, aqueous suspensions of TiO₂ NPs were impregnated by the pad-dry method in raw cotton. The hydrophilic properties and whiteness index (WI) of Berger were the main parameters examined before and after the TiO₂ treatment. In the absence of water, using a UV-Vis lamp, high hydrophilicity was found for raw cotton. Diversely, under UV-LED radiation, the presence of water molecules in the coated cotton was revealed to be a crucial parameter in enhancing its whiteness. A comparable WI of Berger with conventional bleaching methods was obtained using 0.5 g L⁻¹ TiO₂ suspension under UV-LED radiation, suggesting that the impregnation of TiO₂ NPs can be a promising alternative for the industrial bleaching methods, as it proves to be more sustainable and with low operating costs.

Author Keywords. Titanium Dioxide, Cotton, Photocatalysis, Bleaching, Cleaning.

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1. Introduction

In the textile industry, there are different processes to remove impurities from raw cotton, making it more hydrophilic and whiter. Scouring, mercerization and bleaching are the main pre-treatments, so that the resulting cotton has the necessary conditions for the following finishing and dyeing treatments. All these treatments are major water consumers in the industrial textile processes, spending between 250-350 kg_{water}/kg_{textile}, and, consequently, spending the highest amount of energy, between 55-60 % ([Karmakar 1999](#)). In addition, during these treatments, different types of waste can be generated being harmful to the environment. For instance, during the scouring process solvents such glycol esters are used, releasing volatile organic compounds to the atmosphere as well residues of detergents (fats,

oils, pectins and ashes), which will end in the water sources; in the mercerization step, residual sodium hydroxide can be delivered, enhancing the effluent pH; the bleaching process generally leads to effluents with high pH, trace amount of H₂O₂ and stabilizers (Babu et al. 2007). Therefore, with the increasing cost of chemical products, equipment, workers, effluent control and chemicals recovering, there has been an increasing need to find alternatives to these conventional textile treatment processes.

Heterogeneous photocatalysis is one of the most promising technologies due to the low cost, non-toxicity and reusability of the semiconductor photocatalyst, and the fact that the sun can be used as a source of radiation, which is an inexhaustible source and does not add costs to the process (Beydoun et al. 1999; Pera-Titus et al. 2004). The semiconductors commonly used to catalyse a wide range of chemical reactions include titanium dioxide (TiO₂), zinc oxide (ZnO), zinc sulphide (ZnS), tungsten trioxide (WO₃) and cadmium sulfide (CdS) (Abid et al. 2017a; Abid et al. 2017b; Beydoun et al. 1999; Lima et al. 2014; Montazer and Pakdel 2010; Pakdel et al. 2014a; Pera-Titus et al. 2004). TiO₂ with a band gap energy \approx 3.0-3.3 eV (Jovic et al. 2015) has been established as one of the most promising photocatalyst in the degradation of organic compounds due to its physicochemical properties and high photoactivity when exposed to ultraviolet (UV) radiation (Abid et al. 2017a; Haji et al. 2014; Hashemikia and Montazer 2012; Jovic et al. 2015; Lima et al. 2014; Montazer and Morshedi 2014; Pakdel et al. 2014a; Wu et al. 2009). Furthermore, this semiconductor is white, which is an advantage when the purpose is to bleach the substrate on which it is applied (Montazer and Morshedi 2012). Commercial TiO₂ Aeroxide[®] P25 (80 % of anatase and 20 % of rutile), is highly used in the industry because it allows the obtention of the best compromise between the high photocatalytic performance of the anatase phase and the more intense absorption in the solar spectrum of the rutile phase (Jovic et al. 2015).

Montazer and Morshedi (2012) tested the photocatalytic activity of TiO₂ nanoparticles (NPs) in the degradation of the hydrophobic impurities and natural dyes of raw cotton fibres, to obtain whiter and hydrophilic cotton. In this study, it was found that a higher concentration of TiO₂ lead to increased bleaching and tissue hydrophilicity. Furthermore, it was verified that these textiles had antibacterial properties and UV protection. Likewise, Daoud, Xin, and Zhang (2005) and Wu et al. (2009) coated cotton textiles with TiO₂ to induce antibacterial and self-cleaning properties. It was found that this coating allows the formation of a biofilm of adsorbed bacteria which activity is inhibited after UV exposure. Wu et al. (2009) still observed bleaching due to the degradation of natural cotton dyes.

Hashemikia and Montazer (2012) managed to get functional features such as anti-pilling, hydrophilicity, self-cleaning, UV protection and antibacterial properties in cotton and polyester (35/65) textiles functionalized with TiO₂. The use of this semiconductor was also studied on wool surfaces by Montazer and Pakdel (2010) and Montazer and Morshedi (2014), to add functional properties. Montazer and Morshedi (2014) described how to bleach and increase the hydrophilicity of wool, after functionalization with TiO₂ and exposure to UV and visible (Vis) radiation. Montazer and Pakdel (2010) reported the decrease of yellowness of wool induced by UV exposure, through the incorporation of TiO₂ NPs, increased photostability, and UV protection.

In the present study, TiO₂ NPs were used to investigate the photocatalytic degradation of hydrophobic compounds and natural pigments of cotton. TiO₂ was impregnated on the surface of raw cotton, without using crosslinking agents, and exposed to radiation sources with different ranges of wavelengths. Following exposure to UV (390 nm) and UV-Vis radiation (300-700 nm), the main objective is that the cotton samples become whiter and hydrophilic,

in a procedure alternative to the conventional cleaning and bleaching processes. In this way, a more sustainable, environmentally friendly, and less costly process that can replace conventional methods can be obtained.

2. Materials and Methods

2.1. Chemicals and materials

The textile substrate used was 100% of raw cotton without any treatment. This textile sample was impregnated in an aqueous suspension containing TiO₂ Aeroxide® P25 from Evonik Industries. Briefly, aqueous suspensions containing different TiO₂ loads (0.5, 4.0, 6.0, 10 and 15 g L⁻¹) were prepared by sonication for 30 min at 30 °C.

The impregnation was conducted by pad-dry method using a foulard (Werner Mathis AG, HVF 27291). The cotton fabric samples were padded under 3 bar pressure at speed rate of 2 m min⁻¹ using the previously prepared TiO₂ suspensions. Finally, the TiO₂-coated fabrics were dried at 100 °C for 2 min in a thermofixation furnace (Werner Mathis AG, DHE 51991).

2.2. Fabrics characterization

The above-mentioned fabrics were characterized by their whiteness index (WI) of Berger, CIE ("CIE", n.d.). The whiteness and tone were analysed by UV-Vis spectroscopy using a colorimeter (Spectraflash SF 450, Datacolor). Additionally, for comparison purposes, a commercial bleached cotton sample was also analysed.

The hydrophobicity and water repellency of the coated TiO₂ fabrics were analysed by measuring the cosine of the contact angle ($\cos \theta$) and wet-out time, respectively. For that, the standard test ISO 23232:2009 (ISO 2009) was used. In the case of the water repellency tests, 3 drops (50 µL total volume of each) of standard liquid consisting of different proportions of water and ethanol were dispersed on the fabrics for 10 seconds (Morgado 2013). The level of repellency is established by the droplets remaining on the substrate surface.

The contact angles were examined in a goniometer Theta Basic+Attenuin, with Navitar lens. In a typical analysis, 3 µL of water was dropped on the cotton surface, and sequential images were recorded using a fixed camera. The measurements were performed at room temperature (≈ 25 °C), and 6 repetitions were conducted at different sites of the cotton pieces. The contact angles were calculated through the equipment software, and the resulting value corresponded to the average value of the contact angles measured.

Diffuse Reflectance Ultraviolet-Visible Near-Infrared (UV-Vis-NIR) analyses were conducted to verify the presence of TiO₂ NPs on the cotton surface by using a spectrophotometer (Cary 5000 UV-Vis-NIR) equipped with an integrated sphere. Reflectance values were acquired between 200-1000 nm with a 1 nm interval. The measurements were performed in triplicate for each sample.

The morphology of the TiO₂ coated raw cottons was evaluated by scanning electron microscopy (SEM) using a Phenom ProX apparatus.

2.3. Photocatalytic bleaching of cotton

The bleaching of the uncoated and coated cotton samples was conducted under different experimental conditions. Firstly, the cotton fabrics were exposed to two types of radiation sources in the absence of water: i) Ultraviolet Light-Emitting Diode (UV-LED, Chanzon, $\lambda_{max} = 390$ nm, 90 W m⁻²) located 7 cm from the fabric; and ii) Ultraviolet-visible lamp (UV-Vis, Ultra-Vitalux 300 W) with a wavelength range between 300-700 nm located 20 cm from the cotton samples. The fabrics were exposed to light for 0, 1, 2 and 5 h. Then, the fabrics were irradiated in the presence of water. In these experiments, distinct reaction systems were used

depending on the radiation source. When Light Emitting Diodes (LEDs) were used as light source, the coated and uncoated fabrics were placed in a cylindrical borosilicate reactor and immersed in 230 mL of water, and a four-LED system (λ_{max} of 390 nm) was placed 5 cm from the reactor wall. The irradiation power of each LED reaching the sample was c.a. 400 W m⁻², which was determined using a UV-vis spectroradiometer (USB2000+, OceanOptics, USA). By using the UV-Vis lamp, the fabric samples were immersed into a Petri plate containing 70 mL of water.

3. Results and Discussion

Different TiO₂ loads were impregnated at the surface of raw cotton in order to study its photocatalytic efficiency for the degradation of hydrophobic compounds and natural cotton pigments. The cotton substrates were analysed before and after exposure to different radiation light sources.

3.1. Fabrics characterization

Raw cotton is mainly composed of α -cellulose but also contains impurities such as waxes and pectins which give it a yellow colour and a hydrophobic nature (Hsieh 2007). This yellow colour is essentially due to the protoplasmic residues of proteins and the flavonoid pigments of cotton flowers (Karmakar 1999). In terms of whiteness, the raw cotton used in this study presented a WI of 11.1 ± 0.1 on the Berger scale. Its hydrophobic nature was proved by the water repellency test and by measuring the contact angle ($134.7 \pm 0.5^\circ$).

The morphology of the cotton samples was examined by SEM (Figure 1), for comparison purposes, a SEM image of the uncoated fabric is also shown (Figure 1a).

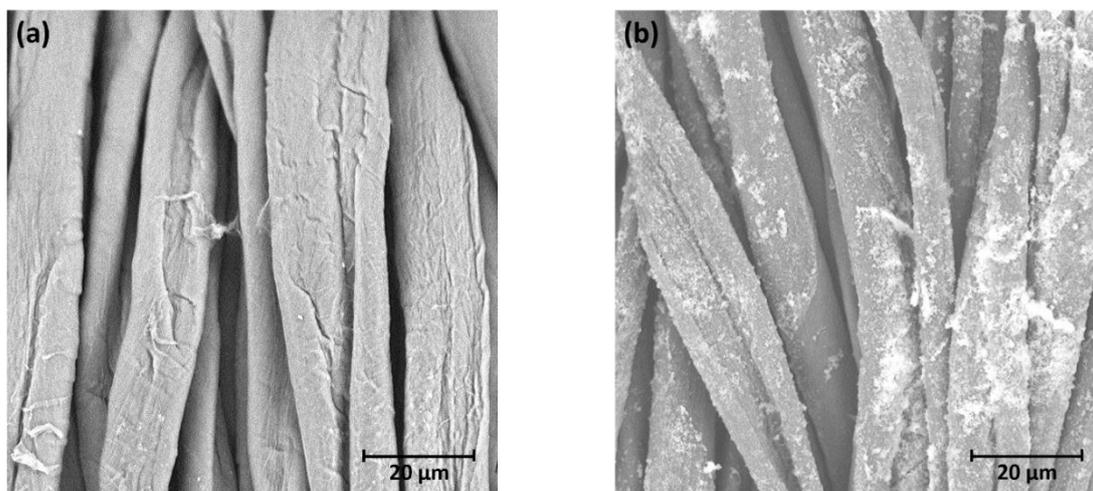


Figure 1: SEM analysis of raw cotton (a) and (b) raw cotton treated using a 10 g L⁻¹ TiO₂ suspension

As displayed in Figure 1(a), raw cotton without pre-treatments presented great amount of impurities on its surface, as well as showed fibres which were quite aggregated and misaligned. After impregnating the TiO₂ NPs on this substrate, Figure 1(b), relative homogeneity of the catalysts on the cotton surface was observed, despite some TiO₂ aggregates.

To understand the effect of the TiO₂ loads, aqueous suspensions containing 0.5, 4.0, 6.0, 10 and 15 g L⁻¹ of TiO₂ were used during the impregnation procedure. By UV-Vis-NIR spectroscopy, as shown by Figure 2, an enhancement in the absorption intensity with the increase of the TiO₂ load was observed.

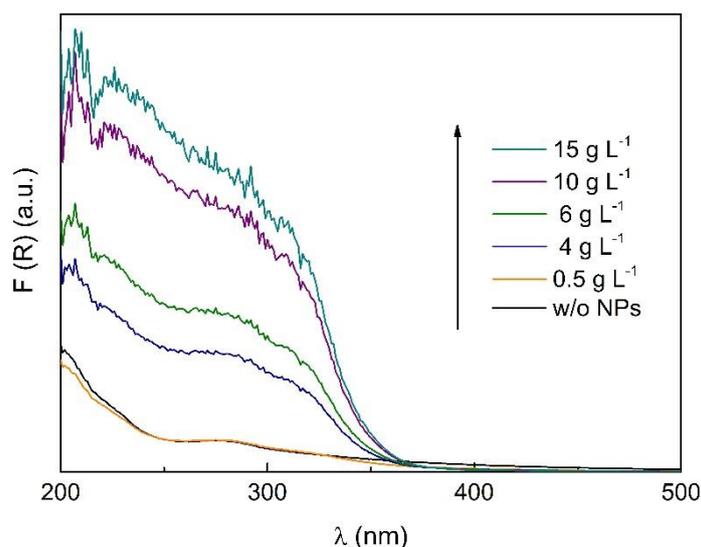


Figure 2: Diffuse reflectance of raw cotton without NPs and with different TiO₂ loads

The uncoated cotton has a specific absorbance spectra that can be observed in [Figure 2](#) ([Batool and Shah 2018](#); [Jovic et al. 2015](#); [Moreira et al. 2019](#); [Zhang and Yang 2012](#)). The UV-Vis-NIR spectra suggest that the TiO₂ NPs were successfully impregnated in raw cotton, without the need to use a crosslinking agent. It was also observed that the increasing the TiO₂ concentration seems to be proportional to the intensity of the TiO₂ absorption band.

Through UV-Vis spectroscopy, [Table 1](#), it was also possible to confirm the presence of TiO₂ on the cotton surface and to verify the influence of using suspensions with different TiO₂ loads.

[TiO ₂] (g L ⁻¹)	WI (Berger)
0	11.1 ± 0.1
0.5	12.1 ± 0.1
4.0	16.3 ± 1.2
6.0	17.0 ± 0.4
10	21.7 ± 0.4
15	22.5 ± 1.3

Table 1: Variation of WI Berger with the increase TiO₂ load in the raw cotton before irradiation

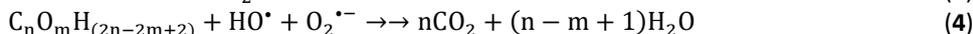
TiO₂ is a white pigment thus, when this material is impregnated on the fabrics' surface it is expected that the resulted coatings assume its white colour, with an increase in the WI Berger values until a plateau is reached. In addition, by water repellency test, was found that, before irradiation, raw cotton coated with TiO₂ NPs maintains its hydrophobic nature, for all catalyst loads studied.

3.2. Photocatalytic results

During the photocatalytic tests, raw cotton samples coated with 0.5, 4.0 and 10 g L⁻¹ of TiO₂ suspensions, were exposed to the UV-Vis lamp and to the UV-LED system, in the presence or absence of water, for 1, 2 and 5 h.

It is known that when TiO₂ is exposed to UV radiation, with energy ($h\nu$) equal to or higher than its band gap, electrons are excited from the valence band to the conduction band, producing electron/hole pairs (e^-/h^+). These e^-/h^+ pairs, move to the particle surface and engage in redox reactions, [Equation 1](#). Positive holes react with water (H₂O) producing HO• radicals, while electrons react with oxygen (O₂) producing O₂•⁻ radicals, [Equation 3](#) and [Equation 2](#), respectively. Then, the produced hydroxyl and superoxide radicals decompose the organic compounds (C_nO_mH_(2n-2m+2)) producing intermediate compounds that can be converted into

carbon dioxide (CO₂) and water, Equation 4 (Conceição et al. 2017; Costa et al. 2013; Daoud, Xin, and Zhang 2005; Haji et al. 2014; Li et al. 2014; Lima et al. 2014; Montazer and Morshedi 2012; Pakdel et al. 2014a; Pakdel et al. 2014b; Pakdel, Daoud, and Wang 2013; Wu et al. 2009).



Therefore, organic compounds present in raw cotton, namely pectins and waxes, are expected to be degraded by exposing TiO₂ to UV radiation, making raw cotton whiter and more hydrophilic (Hsieh 2007). To confirm these assumptions, the WI of cotton samples was analysed under different reaction conditions (Figure 3).

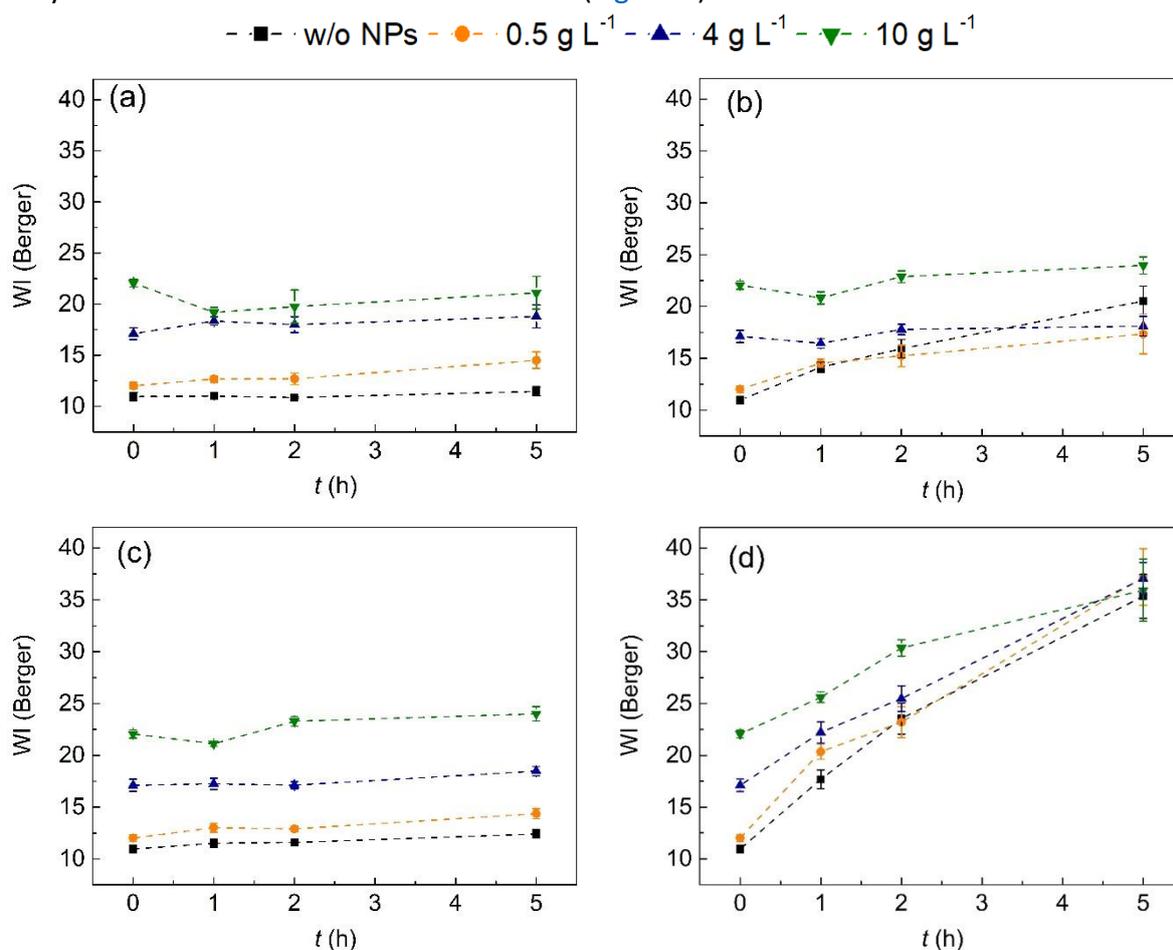


Figure 3: WI variation with time for samples without NPs and with 0.5, 4.0 and 10 g L⁻¹ of TiO₂ in the different reaction conditions. UV-Vis lamp: (a) in the absence of water (b) with water; UV-LED system: (c) in the absence of water, (d) with water

As previously mentioned, before irradiation ($t = 0$ h), an increase in the TiO₂ load promotes an increase in the WI Berger due to the white colour of the photocatalyst. Nevertheless, when the coated TiO₂ fabrics were exposed to the photocatalytic treatment, in the absence of water, and by using both the UV-Vis lamp and the UV-LED, a negligible variation in the WI Berger was detected. The results displayed in Figure 3(a) and Figure 3(c), respectively, suggest that the degradation of the organic compounds was not achieved, since the yellow colour characteristic of the raw cotton remained after the photocatalytic treatment.

On the other hand, in the presence of water molecules and using the UV-Vis lamp, Figure 3(b), a slight increase in the WI Berger value was observed for uncoated fabric as well for the coated

fabric impregnated with a 0.5 g L⁻¹ of TiO₂ suspension. An increment of the WI Berger value from 12.0 ± 0.3 to 17.3 ± 1.9 was observed when the fabrics were treated with 0.5 g L⁻¹ of TiO₂ suspension. This enhancement was also noticed in the uncoated fabric with WI increasing from 11.0 ± 0.4 to 20.5 ± 1.4, suggesting that the presence of dissolved oxygen under light radiation augmented the efficiency of the process by decomposing the organic compounds attached in raw cotton samples (Ferrero, Migliavacca, and Periolatto 2016; Fynn and Dean 1951; Hon 1979; Yatagai and Zeronian 1994). When great TiO₂ loads were used in the coating procedure (4.0 and 10 g L⁻¹), the WI Berger did not change significantly over the reaction time. This seems to be attributed to the existence of a surplus amount of TiO₂ which blocks UV radiation, decreasing the efficiency of the reaction (Conceição et al. 2017; Lima et al. 2014; Pera-Titus et al. 2004).

When the UV-LED system was used as light source in the presence of water, Figure 3(d) after 5 h of irradiation, the fabric sample treated with 0.5 g L⁻¹ of TiO₂ showed the highest WI (37.2 ± 2.7). This corroborate with the results found using UV lamp in presence of water, suggesting that 0.5 g L⁻¹ of TiO₂ could be the optimal catalyst load for the photocatalytic degradation of the compounds which colour cotton. For comparison purposes, the WI of a commercial bleached cotton sample treated be conventional methods was measured, obtaining a value of 57.8 ± 0.1 on the Berge scale. Although the WI value found for the coated TiO₂ treated by photocatalysis was lower than the obtained for the commercial cotton, it is expected that if the exposure time was extended, then the WI values would be closer to those obtained using conventional methods.

To verify the occurrence of photocatalytic degradation of the compounds which make cotton hydrophobic, water repellency tests were carried out on the samples exposed to the different irradiation systems, with and without water. It was found that only the use of the UV-Vis lamp without water was efficient in the degradation of the hydrophobic compounds of raw cotton. In this system, raw cotton with 4 g L⁻¹ of TiO₂, which was initially (t = 0 h) hydrophobic, became hydrophilic after 1 h of irradiation, without being possible to measure its contact angle. The same was found for the sample with 10 g L⁻¹ of TiO₂.

Comparing the two sources of irradiation, the results suggest that the UV-Vis lamp, which presents different emission peaks between 300 and 700 nm, Figure 4(a), is more efficient in the photodegradation of the hydrophobic compounds of cotton. The UV-LED system, with an emission peak at 390 nm, Figure 4(b), proved to be efficient in the photocatalytic degradation of the compounds that give colour to cotton. In addition, the presence of water seems to be crucial in the degradation of compounds, promoting the photodegradation and photooxidation of α-cellulose.

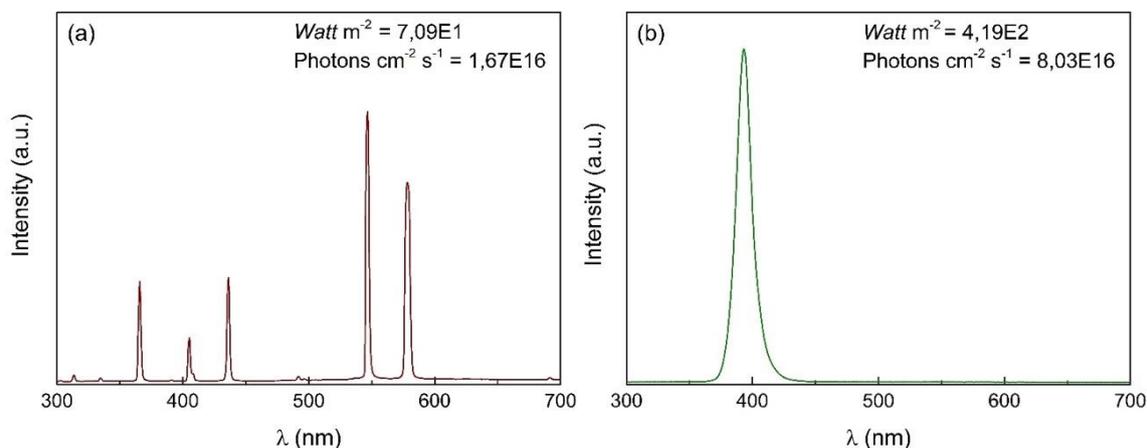


Figure 4: Emission spectra of (a) UV-Vis lamp and (b) the system of UV-LEDs

Since no cross-linking agents were used, it would be expected that the presence of water would cause the detachment of TiO₂ NPs from the surface of the cotton fibres. To verify if this occurred in these reaction systems, SEM analysis was performed [Figure 5](#) on the cotton samples with 10 g L⁻¹ of TiO₂ which were exposed to water and irradiated with UV-Vis lamp and UV-LEDs.

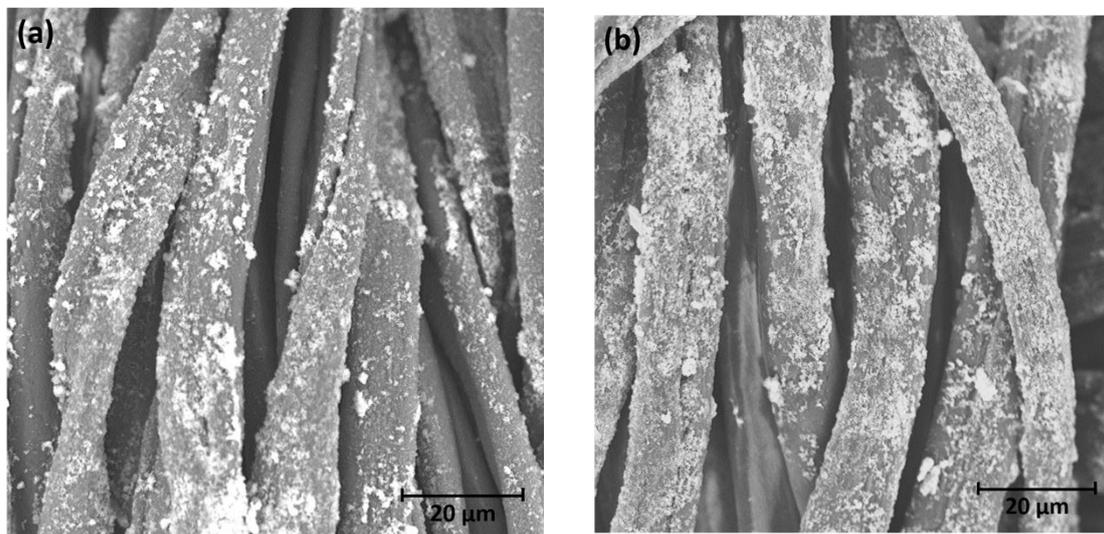


Figure 5: SEM images of raw cotton with 10 g L⁻¹ of TiO₂ exposed to the (a) UV-Vis lamp and (b) UV-LEDs irradiation under aqueous reaction medium

As displayed in [Figure 5](#), a negligible loss of NPs was notice after the 5 h exposure to water and using both irradiation sources. These results suggest a good stability of the coated fabrics without requiring the addition of crosslinking agents.

4. Conclusions

The TiO₂ NPs, activated with a UV-Vis lamp and UV-LEDs, proved to be efficient in the photocatalytic degradation of the compounds which stain and confer hydrophobic nature to cotton, such as pectins, waxes and natural pigments.

Irradiating the raw cotton treated with a suspension of 4.0 g L⁻¹ TiO₂, with a UV-Vis lamp for 1 h, in dry conditions, made it possible to degrade the hydrophobic compounds, rendering it hydrophilic.

In presence of water and the irradiation system of four UV-LEDs, it was possible to make raw cotton three times whiter than it was initially, using a suspension of 0.5 g L⁻¹ TiO₂ and a residence time of 5 h. The water medium plays a critical role in the degradation of compounds that stain the raw cotton, since it favours the photooxidation and photodegradation of α -cellulose, owing to the formation of a higher number of soluble radicals.

Raw cotton passed from hydrophobic to hydrophilic and became whiter, as in industrial pre-treatments, but without using a large number of chemicals, water, and energy. It is not necessary to use crosslinking agents since the TiO₂ NPs link to the cotton fibres after irradiation in the different reaction systems. Besides, this photocatalytic technology produces less waste, being less harmful to the environment since TiO₂ is not toxic.

This investigation represents a beautiful proof of concept of an alternative to conventional raw cotton cleaning and bleaching processes, which is more sustainable, environmentally friendly, and presents lower operating costs.

References

- Abid, M., S. Bouattour, A. M. Ferraria, D. S. Conceição, A. P. Carapeto, L. F. Vieira Ferreira, A. M. Botelho do Rego, et al. 2017a. "Facile functionalization of cotton with nanostructured silver/titania for visible-light plasmonic photocatalysis". *Journal of Colloid and Interface Science* 507 (december): 83-94. <https://doi.org/10.1016/j.jcis.2017.07.109>.
- Abid, M., S. Bouattour, A. M. Ferraria, D. S. Conceição, A. P. Carapeto, L. F. Vieira Ferreira, A. M. Botelho do Rego, M. Rei Vilar, and S. Boufi. 2017b. "Functionalization of cotton fabrics with plasmonic photo-active nanostructured Au-TiO₂ layer". *Carbohydrate Polymers* 176 (november): 336-44. <https://doi.org/10.1016/j.carbpol.2017.08.090>.
- Babu, B. R., A. K. Parande, S. Raghu, and T. P. Kumar. 2007. "Cotton textile processing: Waste generation and effluent treatment". *The Journal of Cotton Science* 11, no. 3: 141-53. <https://www.cotton.org/journal/2007-11/3/141.cfm>.
- Batool, I., and G. B. Shah. 2018. "Chemical bonding of organic dye onto cotton fibers using silane as coupling agent (I)". *Fibers and Polymers* 19, no. 4: 790-96. <https://doi.org/10.1007/s12221-018-7732-z>.
- Beydoun, D., R. Amal, G. Low, and S. McEvoy. 1999. "Role of nanoparticles in photocatalysis". *Journal of Nanoparticle Research* 1, no. 4 (december): 439-58. <https://doi.org/10.1023/A:1010044830871>.
- "CIE - International Commission on Illumination - Commission Internationale de l'Eclairage - Internationale Beleuchtungskommission." n.d. Accessed May 12, 2020. <http://cie.co.at/>.
- Conceição, D. S., C. A. L. Graça, D. P. Ferreira, A. M. Ferraria, I. M. Fonseca, A. M. Botelho do Rego, A. C. S. C. Teixeira, and L. F. Vieira Ferreira. 2017. "Photochemical insights of TiO₂ decorated mesoporous SBA-15 materials and their influence on the photodegradation of organic contaminants". *Microporous and Mesoporous Materials* 253 (november): 203-14. <https://doi.org/10.1016/j.micromeso.2017.07.013>.
- Costa, A. L., S. Ortelli, M. Blosi, S. Albonetti, A. Vaccari, and M. Dondi. 2013. "TiO₂ based photocatalytic coatings: From nanostructure to functional properties". *Chemical Engineering Journal* 225 (june): 880-86. <https://doi.org/10.1016/j.cej.2013.04.037>.
- Daoud, W. A., J. H. Xin, and Y. Zhang. 2005. "Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities". *Surface Science* 599, no. 1-3 (december): 69-75. <https://doi.org/10.1016/j.susc.2005.09.038>.
- Ferrero, F., G. Migliavacca, and M. Periolatto. 2016. "UV treatments on cotton fibers". In *Cotton Research*, edited by I. Y. Abdurakhmonov, 235-56. IntechOpen. <https://doi.org/10.5772/63796>.
- Fynn, P. J., and J. D. Dean. 1951. "Effect of light on cotton textiles". In *Yearbook of Agriculture 1950-1951*, 436-40. U.S. Department of Agriculture. <https://naldc.nal.usda.gov/download/IND43894097/PDF>.
- Haji, A., A. M. Shoushtari, F. Mazaheri, and S. Ensieh. 2014. "Environmentally friendly pretreatment for enhanced coating of TiO₂ nanoparticles on PET/Wool fabric". Paper presented in International Conference on Chemical, Civil and Environmental Engineering (CCEE'2014), Singapore, November 2014. <https://doi.org/10.13140/2.1.3539.3608>.
- Hashemikia, S., and M. Montazer. 2012. "Sodium hypophosphite and nano TiO₂ inorganic catalysts along with citric acid on textile producing multi-functional properties". *Applied Catalysis A - General* 417-418 (february): 200-08. <https://doi.org/10.1016/j.apcata.2011.12.041>.

- Hon, D. N. 1979. "Photooxidative degradation of cellulose: Reactions of the cellulosic free radicals with oxygen". *Journal of Polymer Science: Polymer Chemistry Edition* 17, no. 2 (february): 441-54. <https://doi.org/10.1002/pol.1979.170170214>.
- Hsieh, Y. L. 2007. "Chemical structure and properties of cotton". In *Cotton*, edited by S. Gordon and Y. L. Hsieh, 3-34. Woodhead Publishing. <https://doi.org/10.1533/9781845692483.1.3>.
- ISO (International Organization for Standardization). 2009. *Textiles - Aqueous liquid repellency - Water/alcohol solution resistance test*. ISO 23232:2009. <https://www.iso.org/standard/50923.html>.
- Jovic, V., K. E. Smith, H. Idriss, and G. I. Waterhouse. 2015. "Heterojunction synergies in titania-supported gold photocatalysts: Implications for solar hydrogen production". *ChemSusChem* 8, no. 15 (june): 2551-59. <https://doi.org/10.1002/cssc.201500126>.
- Karmakar, S. R. 1999. *Chemical technology in the pre-treatment processes of textiles*. Textile Science and Technology, vol. 12. Amsterdam: Elsevier Science B.V. <https://www.sciencedirect.com/bookseries/textile-science-and-technology/vol/12/suppl/C>.
- Li, M. Y., T. T. Deng, S. X. Liu, F. X. Zhang, and G. X. Zhang. 2014. "Superhydrophilic surface modification of fabric via coating with nano-TiO₂ by UV and alkaline treatment". *Applied Surface Science* 297 (april): 147-52. <https://doi.org/10.1016/j.apsusc.2014.01.105>.
- Lima, G. G., C. A. Lima, F. F. Vieira, and E. M. Silva. 2014. "Estudo comparativo da aplicação de nanopartículas de TiO₂ e ZnO na descoloração fotocatalítica de uma solução de corante empregando radiação UV artificial". *Revista Eletrônica de Materiais e Processos* 9, no. 1: 22-27. <http://www2.ufcg.edu.br/revista-remap/index.php/REMAP/article/view/417>.
- Montazer, M., and S. Morshedi. 2012. "Nano photo scouring and nano photo bleaching of raw cellulosic fabric using nano TiO₂". *International Journal of Biological Macromolecules* 50, no. 4 (may): 1018-25. <https://doi.org/10.1016/j.ijbiomac.2012.02.018>.
- — —. 2014. "Photo bleaching of wool using nano TiO₂ under daylight irradiation". *Journal of Industrial and Engineering Chemistry* 20, no. 1 (january): 83-90. <https://doi.org/10.1016/j.jiec.2013.04.023>.
- Montazer, M., and E. Pakdel. 2010. "Reducing photoyellowing of wool using nano TiO₂". *Photochemistry and Photobiology* 86, no. 2 (march): 255-60. <https://doi.org/10.1111/j.1751-1097.2009.00680.x>.
- Moreira, N. F. F., M. J. Sampaio, A. R. Ribeiro, C. G. Silva, J. L. Faria, and A. M. T. Silva. 2019. "Metal-free g-C₃N₄ photocatalysis of organic micropollutants in urban wastewater under visible light". *Applied Catalysis B: Environmental* 248 (august): 184-92. <https://doi.org/10.1016/j.apcatb.2019.02.001>.
- Morgado, J. 2013. "Nanotecnologia aplicada ao processo de fabrico". Support material to the course Têxteis Técnicos e Funcionais from Associação para a Formação Tecnológica e Profissional da Beira Interior.
- Pakdel, E., W. A. Daoud, L. Sun, and X. Wang. 2014a. "Photostability of wool fabrics coated with pure and modified TiO₂ colloids". *Journal of Colloid and Interface Science* 447 (february): 191-201. <https://doi.org/10.1016/j.jcis.2014.10.032>.
- Pakdel, E., W. A. Daoud, L. Sun, and X. G. Wang. 2014b. "Visible and UV functionality of TiO₂ ternary nanocomposites on cotton". *Applied Surface Science* 321 (december): 447-56. <https://doi.org/10.1016/j.apsusc.2014.10.018>.

- Pakdel, E., W. A. Daoud, and X. Wang. 2013. "Self-cleaning and superhydrophilic wool by TiO₂/SiO₂ nanocomposite". *Applied Surface Science* 275 (june): 397-402. <https://doi.org/10.1016/j.apsusc.2012.10.141>.
- Pera-Titus, M., V. García-Molina, M. A. Baños, J. Giménez, and S. Esplugas. 2004. "Degradation of chlorophenols by means of advanced oxidation processes: A general review". *Applied Catalysis B: Environmental* 47, no. 4 (february): 219-56. <https://doi.org/10.1016/j.apcatb.2003.09.010>.
- Wu, D. Y., M. C. Long, J. Y. Zhou, W. M. Cai, X. H. Zhu, C. Chen, and Y. H. Wu. 2009. "Synthesis and characterization of self-cleaning cotton fabrics modified by TiO₂ through a facile approach". *Surface & Coatings Technology* 203, no. 24 (september): 3728-33. <https://doi.org/10.1016/j.surfcoat.2009.06.008>.
- Yatagai, M., and S. H. Zeronian. 1994. "Effect of ultraviolet light and heat on the properties of cotton cellulose". *Cellulose* 1, no. 3 (september): 205-14. <https://doi.org/10.1007/BF00813508>.
- Zhang, H., and L. Yang. 2012. "Imbuing titanium dioxide into cotton fabric using tetrabutyl titanate by hydrothermal method". *Journal of the Textile Institute* 103, no. 8 (august): 885-92. <https://doi.org/10.1080/00405000.2011.621678>.

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