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Mixed oxide-polyaniline composite-coated woven cotton fabrics for the visible light catalyzed degradation of hazardous organic pollutants

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Abstract

Clean water and sea free of organic pollutants are among the 17 United Nation Sustainable Development Goals (SDGs). In this global concern, the design of efficient, stable and recyclable catalytic materials remains challenging. In this context, we designed a series of mixed oxide-modified cotton fabrics and their related composites and interrogated their propensity to catalyze the degradation of methyl orange (MO) (a model pollutant). More specifically, functional cotton fabrics (CF) coated with RuO₂-TiO₂ based-photocatalysts were obtained by dip-coating method at neutral pH. A layer of Polyaniline (PANI) was prepared by in situ oxidative polymerization of the aniline monomer on 4-diphenylamine diazonium salt (DPA) modified-RuO₂-TiO₂ nanoparticles (NPs) coated-CF. The modified CFs catalyzed photodegradation and mineralization of MO under visible light, which depended on polyaniline mass loading. The CF/RuO₂-TiO₂/DPA@PANI obtained by in situ polymerization was the best catalyst due to DPA adhesive layer for polyaniline to RuO₂-TiO₂, and the strong attraction force between cellulose OH groups and anilinium during polymerization. The photodegradation rate constant was 0.101, 0.0532, 0.0775 and 0.0828 min⁻¹ for RuO₂-TiO₂/DPA@PANI, RuO₂-TiO₂, RuO₂-TiO₂/PANI and RuO₂-TiO₂/DPA/PANI coated-CFs, respectively. The catalytic activity is favored by the photoactive species (OH[•], O₂^{-•}) which are formed by the excitation of electrons under visible light but also by the electronic exchanges at the RuO₂//TiO₂, RuO₂-TiO₂//PANI and RuO₂-TiO₂/PANI//CF interfaces. CF/RuO₂-TiO₂/DPA/PANI photocatalyst was stable under simulated sunlight and reusable three times. A mechanism is proposed to account for the efficient CF catalytic properties.

Keywords:

Cotton fabric, RuO₂-TiO₂, diazonium salt, polyaniline, photocatalysis.

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1. Introduction

There is an ever growing demand for specialty textile with one specific or multiple functions. Indeed, much has been achieved recently in this domain, namely textiles with odour elimination property (Wang et al., 2019; Zhu et al., 2019), textiles for tissue engineering (Augustine et al., 2017) and wound healing (Kim, Cha and Gong, 2018), specialty textiles for military applications (Revaiah, Kotresh and Kandasubramanian, 2019), textiles for wearable electronics (Zhou et al., 2019), or catalytic applications (Fujii and Nakamura, 2013). Either woven or non-woven, cotton fibers remain the most used for clothing or specialty textiles due to the biodegradability, strong absorption capacity and porosity of these cellulosic fibers. (Ahmad, Kan and Yao, 2019)

One of the most common modifications of textile surfaces is dyeing. The process has been known for over 2000 years. It is based on textile surface chemistry in which the dye molecules react with a functional group of the textile surface (Mayer-Gall, Lee, Opwis, List and Gutmann, 2016).

Various strategies have been developed not only for the dyeing but also to give the fabric other functionalities namely the antibacterial activity, UV protection, self-cleaning, antifouling (Uddin et al., 2008; Wu, Ma, Pan, Chen, Sun., 2016; Avila Ramirez, Suriano, Cerrutti and Foresti, 2014; Hassan, 2017) and new properties such as better electrical conductivity, (Xu et al., 2016) hydro/oleo-phobia and ease of ironing (Zhou et al., 2019) The strong growing demand for functional textiles necessitates the development of inexpensive synthetic methods based on sustainable raw materials (cotton) while preserving the environment and the ecosystem. The easiest and most direct method for the development of functional cotton fabrics is the dip-coating method, which consists of incorporating the nanoparticles on the surface by direct immersion, leading to the formation of a fibrous surface loaded with NPs.

Yang et al. (2013) have prepared a functional textile by assembling several positively charged NPs of Au on the surface of cotton fabric, by electrostatic interactions between the metal NPs and the surface of the textile. It has been found in the same study that the prepared materials exhibit excellent catalytic properties.

In situ synthesis was also described by (Xi et al. 2016) who developed catalytic cotton fabric loaded with palladium NPs composite material in the presence of polydopamine, acting as a reducing agent for the formation and the growth of palladium NPs on the textile surface.

Recently, another method has been developed and seems to be adopted in the preparation of functional textile surfaces; it is the photo-grafting approach, which generates superficial

radicals by exposing the textile surface to ultraviolet light. The radicals thus generated are able to fixing different types of organic molecules on the textile surface (Mayer-Gall et al. 2016).

TiO₂ nanoparticles are widely used in the coating of fabric surfaces, designed for photocatalytic applications, thanks to these spectacular catalytic properties and its ability to increase the hydrophilic character of the fibrous surface. (Mishra and Butola, 2019) studied the degradation of rhodamine B under UV light using cotton fabric coated with TiO₂ NPs prepared via in situ solvothermal method.

The catalytic efficiency of the TiO₂-coated fabric is negligible under visible light, due to the low protonation of TiO₂ under visible radiation (Nosrati, Olad and Najjari, 2017).

Various components such as metal/non-metal, organic complexes and conductive polymers essentially polypyrrole and PANI have been used as sensitizers of TiO₂ impregnated on the textile surface, under visible light.

(Wang et al., 2019) have developed fabric-based materials loaded with TiO₂/g-C₃N₄ powder, with a simple layer-by-layer self-assembly strategy. They found that the materials are very photo-active in the degradation process of Rhodamine B and toluene under visible light, unlike TiO₂-laden tissue pieces.

Ag-doped TiO₂ coated cotton fabric was the subject of the study conducted by Mishra et al. (Mishra and Butola, 2019) the silver was added as TiO₂ dopant after depositing the latter in situ by sol gel on the textile surface. Their study highlights the interest of the addition of Ag by studying the degradation of Rhodamine B, it significantly improves the catalytic performance of the material under the UV light and visible.

The modification of the cotton fibers with TiO₂ and conducting polymer-based nanocomposite catalysts imparts new properties to the material, ensuring other applications to the cotton fabric support. However, despite the interest raised by the numerous strategies of making specialty catalytic textiles we found they are time consuming to be designed, employ expensive chemicals, require high temperature, and harsh conditions or aggressive chemicals that destroy the surface of the fabric. For these reasons, some authors classify the methods of modifying the fabric surface in two groups: chemical modification which has an impact on the composition of the fibers, and physical methods which rather alter the structure of the fibers (Shahidi, Wiener and Ghoranneviss, 2013). In the light of the advantages and limitations of the previously reported methods, we were motivated to design new catalytic textiles while maintaining the chemical composition as well as the starting structure of the fabric. This is

possible provided one operates under mild chemistry conditions, ensuring efficiency, robustness and high catalytic performances of materials.

In this work, we report a detailed study on the development of a functional cotton fabric modified with a nanocomposite catalysts based on $\text{RuO}_2\text{-TiO}_2$ NPs functionalized by diazonium salt and coated with polyaniline, active in darkness, and the evaluation of the degradation kinetics of Methyl Orange dye in an aqueous medium under visible light at multiple catalyst interfaces.

2. Experimental

2.1. Materials

$\text{RuO}_2\text{-TiO}_2$ nanoparticles (NPs), $\text{RuO}_2\text{-TiO}_2$ /diphenylamine diazonium salt (DPA), $\text{RuO}_2\text{-TiO}_2$ /polyaniline (PANI) and $\text{RuO}_2\text{-TiO}_2$ /DPA/PANI nanocomposites were prepared as described in our previous paper (Mousli et al., 2019 (b)), H_2O_2 (14%), ethanol (Sigma-Aldrich, 99.9%), ammonium persulfate (APS, Aldrich, 98% purity), nitric acid (Carlo Erba, 60% purity), aniline (Aldrich, 99.5% pure), Methanol (Sigma-Aldrich, 95%), Methyl Orange (Sigma-Aldrich). Woven, bleached, and scoured cotton fabric (CF), Deionized water was used in the preparation of all solutions and samples.

2.2. Fabrication process

Several hybrid materials based on textiles have been prepared. To start, pieces of cotton fabric (2×2 cm) were simply soaked for 2h in suspensions of $\text{RuO}_2\text{-TiO}_2$ nanoparticle prepared by sol-gel, $\text{RuO}_2\text{-TiO}_2$ /DPA, $\text{RuO}_2\text{-TiO}_2$ /PANI and $\text{RuO}_2\text{-TiO}_2$ /DPA/PANI nanocomposites in an equivalent mixture of di-ionized water and ethanol. The mass/volume ratio is 3g/l. These suspensions were ultrasonicated for 10 min before dipping the textile in order to well disperse the nanomaterials and reduce their aggregation in solution. This process was carried out at room temperature. The cotton fabrics samples were then extracted from the solution, rinsed several times with distilled water, sonicated for 5 min to remove any nanoparticles that were not impregnated between the fibers of the fabric, rinsed one last time with water and finally dried at room temperature for 12h. The obtained samples were denoted as CF/ $\text{RuO}_2\text{-TiO}_2$, CF/ $\text{RuO}_2\text{-TiO}_2$ /DPA, CF/ $\text{RuO}_2\text{-TiO}_2$ /PANI and CF/ $\text{RuO}_2\text{-TiO}_2$ /DPA/PANI.

The CF/ $\text{RuO}_2\text{-TiO}_2$ /DPA sample was used for the preparation of an hybrid material denoted CF/ $\text{RuO}_2\text{-TiO}_2$ /DPA@PANI by the in situ oxidative polymerization of the aniline monomer on the surface of the fabric impregnated with $\text{RuO}_2\text{-TiO}_2$ mixed oxide already functionalized with diphenylamine diazonium. A solution containing 0.15g (1.61 mmol) of aniline monomer

and 0.05 g (0.75 mmol) of nitric acid is stirred for 60 min to form the anilinium cation. The CF/RuO₂-TiO₂/DPA sample was then emerged into the mixture and kept under stirring for 60 min in order to have the anilinium cation on the surface of the modified fabric and to form the polymer on the surface. 0.2 g (0.87 mmol) of APS dissolved in 5 ml of distilled water were added dropwise to the solution, the mixture is stirred for 2h. Once the polymer began to form (appearance of a dark green color) on the surface of the modified fabric, we waited 15 min before stopping the reaction of the polymerization by separating the sample from the solution containing the monomer. The sample is then rinsed several times with methanol and water to remove the un-reacted monomer and dried at room temperature for 24h.

2.3. Characterization methods

Infrared spectra of pristine and printed cotton fabrics were investigated using a Bruker apparatus in the scan range of 4000-400 cm⁻¹, the analysis was to determine all the functional groups that are on the surface of the textile.

The Raman spectra were recorded on a Nicolet Raman 960 spectrometer operating at 633 nm.

The surface and the composition of the cotton modified with the different nanomaterials were performed with Merlin Carl Zeiss scanning electron microscope (SEM) fitted with an energy dispersive X-ray (EDX) analyzer.

X-ray photoelectron (XPS) measurements were carried out on K Alpha apparatus (Thermo Fisher Scientific, Al X-ray source $h\nu = 1486.6$ eV; spot size = 400 μm). Charge compensation was achieved using a flood gun. The composition was determined using the manufacturer's sensitivity factors.

2.4. Photocatalytic activity

To study the catalytic behavior of the various hybrid materials obtained (CF/RuO₂-TiO₂, CF/RuO₂-TiO₂/PANI and CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI, we have studied the photo-degradation reaction of Methyl Orange (MO) under visible light. The study was conducted in the presence of pristine textile and functional RuO₂-TiO₂ based catalysts coated-cotton fabrics pieces (1×2 cm). In a typical experiment, each sample was tramped in flasks containing 10 ml of MO aqueous solution (50 mg/l) and shaken in the solutions before being stored in the dark for 1h to reach the equilibrate adsorption. After this time and before visible light was turned on, 3 drops of H₂O₂ (14%) were added to each flask enhance the reaction rate by the formation of cation radicals in the solutions under irradiation

during the degradation reaction. The pH of MO solutions is 6.5 and the tests were carried out at room temperature under visible light generated by UV CUBE (Honle UV technology).

2.5. Durability test

2.5.1. Washing, Washing/ironing and sunstroke test

The durability test of the modified cotton fabric is very important; it allows to study the effect of cleaning, ironing and exposure to sunlight on the reuse of the modified fabrics.

i). Cleaning: the test was carried out on two samples of cotton fabric with a same size, modified with RuO₂-TiO₂/DPA/PANI nanocomposite. The test was realized in a standard washing machine in the presence of a detergent.

The samples were washed at 40°C for 2h. After that, the samples were dried in ambient air.

ii). Ironing: one of the two samples already cleaned was ironed, making 10 passes on both sides at T = 200 °C.

The RuO₂-TiO₂/DPA/PANI nanocomposite content in the washed/washed and ironed cotton fabric was measured to determine the loss of the catalyst during washing and also after ironing.

iii). Sunstroke: this test is to study the effect of visible light rays on the catalytic activity of a sample modified with RuO₂-TiO₂/DPA/PANI nanocomposite.

The test consists of leaving the cotton fabric under irradiation for 1h before subsequently using it in the decomposition of MO solution (50mg/l). The distance between the lamp and the sample is 26 cm. The kinetics of the degradation reaction was determined and compared to that of a similar non-irradiated sample.

3. Results and discussion

3.1. Design and physicochemical characterization of catalyst-loaded cotton fabrics

Figure 1 presents a schematic summary of the protocol adopted for the preparation of modified cotton fabric with the various nanomaterials already synthesized.

The scheme highlighted the simplicity and efficiency of the strategy for making functional catalysts cotton fabrics. The different hybrid materials were prepared by dipping pieces of fabric into the suspensions containing the catalyst. This method leads to the formation of modified textiles with a fairly large amount of nanomaterials on the surface; Washing with distilled water and ethanol allowed to lose the excess powder not fixed between the fabric fibers and also to have a homogeneous surface.

The CF/RuO₂-TiO₂/DPA/PANI hybrid material can be prepared by dipping (Fig 1B) and by in situ oxidative polymerization of the aniline monomer, on the surface of the textile impregnated with diazonium modified-RuO₂-TiO₂ NPs (Fig 1C). The diazonium salt is used as a coupling agent; it serves to improve the adhesion of the PANI on the surface of the RuO₂-TiO₂ mixed oxide, hence the formation of a thick layer of PANI on the fabric surface. In addition to the covalent bond between the mixed oxide and polyaniline through the aryl group, attachment of PANI to the fabric could be harnessed by hydrogen bonds between secondary amine >NH from PANI and OH groups (primary and secondary alcohols) from cellulose, as depicted in Figure 1D (Gopakumar et al. 2018; Rogalski et al., 2018). The thickness of the polymeric layer must be controlled; a large thickness blocks the catalytic effect of RuO₂-TiO₂ NPs (Fig 1C). The acidity of the media during the in situ polymerization of aniline has a detrimental effect on the resistance of the fabric (Onar et al., 2009); this type of synthesis is therefore not recommended if the sample will be used as functional conductive textiles.

233

234 **Fig. 1.** Schematic view of preparation process of RuO₂-TiO₂ based catalysts functional cotton
 235 fabrics: (A) general, (B) in the presence of RuO₂-TiO₂/DPA/PANI nanocomposite and (C) in
 236 situ polymerization of aniline onto CF/RuO₂-TiO₂/DPA; (D) provides a molecular view of
 237 reactions and interactions at materials interfaces.

Figure 2 provides digital photographs of the cotton fabric modified with RuO₂-TiO₂ NPs, RuO₂-TiO₂/DPA, RuO₂-TiO₂/PANI and RuO₂-TiO₂/DPA/PANI nanocomposites. The images display a color change of the fabric comparing to the pristine cotton fabric. The color of the samples depends on the color of the catalyst which is in suspension. After impregnation of the nanomaterials, the fabric turns from its original white color to gray in the presence of RuO₂-TiO₂ NPs (Fig 2b) but also in the presence of RuO₂-TiO₂/PANI nanocomposite (Fig 2c) because of the negligible amount of PANI polymerized on the RuO₂-TiO₂ surface. In the presence of RuO₂-TiO₂/DPA/PANI (Fig 2e), the color is rather black because of the color of the nanocomposite and the amount of polyaniline attached to RuO₂-TiO₂ NPs, thanks to the diazonium salt used as a coupling agent. The cotton fabric is brown in the presence of RuO₂-TiO₂ functionalized with diphenylamine diazonium salt (Fig 2d), this same sample passes to very dark green color, obtained by in situ polymerization of aniline; this last sample is completely covered with PANI layer in both sides (Fig 2f). The catalytic powders are well impregnated between the fibers of the fabric. After washing and drying, the distribution of the nanoparticles on the surface appears to be homogeneous. The color of the CF/RuO₂-TiO₂/DPA@PANI (Fig 2f) depends on the polymerization time; the color becomes darker with the increase of the reaction time.

Fig. 2. Digital photographs of functional cotton fabric obtained by dipping: pristine cotton fabric (a), CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂/PANI (c), CF/RuO₂-TiO₂/DPA (d), CF/RuO₂-TiO₂/DPA/PANI (e) and CF/RuO₂-TiO₂/DPA@PANI (f).

3.2. Morphology analysis of modified-cotton fabrics

The morphology as well as the chemical composition of the cotton fabric before and after modification were studied. Figure 3 shows SEM images and EDS spectra of pristine and RuO₂-TiO₂ based-catalysts cotton fabric. The control sample (Fig. 3 ab) exhibits a spun yarn with fiber sizes between 5 and 10 μm, these fibers are more or less organized in a compact woven texture. After modification, the images show the presence of small particles

agglomerated on the fibers of the fabric (Fig. 3 cd,ef,gh). The color of the RuO₂-TiO₂ NPs and the RuO₂-TiO₂/PANI nanocomposite attached on textile surface (Fig. 3 cd, ef) is light gray, while that of the RuO₂-TiO₂/DPA/PANI nanocomposite is dark, which is due to the dark green color of PANI which coats the RuO₂-TiO₂/DPA (Fig. 3gh).

During the preparation process, the samples did not undergo any thermal or chemical treatment which resulted in oxidation of the cellulose; this oxidation leads to the destruction of the fibers constituting the fabric and thus modifying the crystalline structure of the cellulose (Shahidi, Wiener and Ghoranneviss, 2013; Faruk and Ain, 2013).

The immersion of a surface in a solution containing the aniline monomer leads to the total coverage of the surface with the PANI. The thickness of the polymeric layer strongly depends on the contact angle of the substrate with the solution containing the monomer as well as the polymerization conditions. SEM images of CF/RuO₂-TiO₂/DPA coated PANI obtained by in situ polymerization of aniline in an acidic medium (Fig. 3 j), indicates the formation of a porous and very adherent coating on the surface, covering all RuO₂-TiO₂/DPA NPs and all the fibers. The coating consists of porous clusters as well as tubular shapes of nonmetric diameter that are randomly oriented on the fabric fibers (Fig. 3 j). It is to note that the mixed oxide is confined to the surface of the fibers and fixed by PANI over layer. This is expected to induce efficient catalytic effect as it will be discussed later.

Knowledge of the thickness of the PANI film formed either on the surface of the mixed oxide RuO₂-TiO₂ or on the fibers is important. SEM could be used to define this thickness as in the case of the images of CF-RuO₂-TiO₂-DPA@PANI (Fig. 3 i-j). Visible isolated particles are covered with a film of 100 to 200 nm. However, there are agglomerates PANI of a few microns. The deposit is not strictly uniform on the surface of the fibers, it is therefore impossible to give a single valid thickness over the entire surface of the fabric.

PANI nanofibers deposited by in situ polymerization on cotton fabric were obtained by (Tissera, Wijesena, Rathnayake, de Silva, de Silva, 2018), they demonstrated that the nanofibrous forms are obtained only in acidic medium (pH = 2) and that these nanofibers shows a slight fusing behavior once in higher pH.

EDS analysis confirms the elementary composition of the samples after modification. The fibers of the fabric contain more oxygen than carbon. The RuO₂-TiO₂ nanoparticles present on the surface of the fabric are manifested by the appearance of Ti and oxygen on the spectrum with a significant percentage in the case of the RuO₂-TiO₂ and RuO₂-TiO₂/PANI coating fabric (Fig. 3 b', c'). The Ru has a very weak and even negligible signal compared to that of Ti, which means that the analyzed zone is devoid of Ru (Fig. 3 b', c').

The modified textile with RuO₂-TiO₂/DPA/PANI nanocomposite shows no Ti and Ru signal; they are replaced by the carbon and nitrogen of PANI, which covers the entire surface of RuO₂-TiO₂ mixed oxide (Fig 3 d').

The coverage of RuO₂-TiO₂/DPA NPs by the PANI obtained by in situ polymerization is confirmed by the corresponding EDS spectrum (Fig 3 e'). The coating consists of a large amount of carbon, oxygen, nitrogen and sulfur, which is a precursor of the SO₄²⁻ doping anion; these elements make the composition of PANI film and cellulose. The absence of Ti and Ru peaks account for a PANI thickness of at least 5 micrometers as the sampling depth of EDS is in the 1-5 microns [Ebnesajjad et al. 2011). The spectrum indicates also the presence of a small percentage of Al corresponding to the fluorescence of the sample holder during the analysis.

Fig.3. SEM images and elemental spectra of pristine cotton fabric (a, b, a'), CF/RuO₂-TiO₂ (c, d, b'), CF/RuO₂-TiO₂/PANI (e, f, c'), CF/RuO₂-TiO₂/DPA/PANI (g, h, d') and CF/RuO₂-TiO₂/DPA@PANI (i, j, e').

3.3. XRD

Figure 4 illustrates the XRD patterns of the control cotton fabric and the coated cotton RuO₂-TiO₂/PANI hybrid. The diffractogram of cellulose has peaks at 14.9°, 16.7° and 22.9° corresponding to the Miller indices of β cellulose (1-10), (110) and (200), respectively (Fig 4 a) (French., 2014). The presence of RuO₂-TiO₂ on the surface results in the appearance of the characteristic peaks of TiO₂ anatase at 25.45°, 36.9° and 48.07° and a peak at of 37.84° corresponding to RuO₂ rutile (Fig 4 b, c, d). The presence of PANI in the RuO₂-TiO₂/DPA/PANI powdery nanocomposite and in the hybrid material CF/RuO₂-TiO₂/DPA@PANI caused the attenuation of RuO₂-TiO₂ peaks (Fig 4 e, f). The peaks of the cellulose in the treated cotton fabric are slightly shifted towards the lower values of 2 θ , indicating the diffusion of RuO₂-TiO₂/PANI, RuO₂-TiO₂/DPA/PANI and RuO₂-TiO₂/DPA@PANI nanocomposites and RuO₂-TiO₂ NPs into the amorphous and paracrystalline regions of cellulose, without affecting the its crystallinity (Savitha and Gurumalles Prabu, 2013). These results are similar to those reported by Savitha and Prabu

(2013) in the case of coated cotton, for polyaniline–TiO₂ hybrid (Bhat et al. 2004) and (Muthukumar and Thilagavathi, 2012) in the case of polyaniline coated cotton fabric.

Fig. 4. XRD patterns of uncoated cotton fabric (a), CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂/DPA (c), CF/RuO₂-TiO₂ /PANI (d), CF/RuO₂-TiO₂/DPA/PANI (e) and CF/RuO₂-TiO₂/DPA@PANI (f).

3.4. FTIR

Figure 5 depicts the IR spectra obtained for all different nanocomposite materials. The spectrum (a) corresponding to pristine cotton fabric has several peak characteristics of pure cellulose., the vibration band located at 898 cm⁻¹ is attributed to the asymmetric out-of-phase ring stretch C–O–C. (Chen and Jakes, 2002; Gilbert, Kokot and Meyer., 1993; Tao et al, 2018; Carrillo, Colom, Sunol and Saurina, 2004; Zahran, Ahmed and El-Rafie, 2014; Chung, Lee and Choe, 2004). At 1030 cm⁻¹ is situated the C-O stretching vibration. The bands at 1114 and 1169 cm⁻¹ are assigned to asymmetric bridge C-O-C. The band located at 1318 cm⁻¹ is due to C-H wagging. The pic appeared at 1372 cm⁻¹ is attributed to C-H bending (deformation stretch) and that at 1435 cm⁻¹ is corresponding to C-H in plane bending. The spectrum displays a band at 1642 cm⁻¹ relative to the adsorbed water molecules. The peak appearing at 2913 cm⁻¹ is assigned to C-H stretching band. The spectrum exhibits a broad band between 3100 and 3650 cm⁻¹ which is due to O-H stretch. In addition to the characteristic bands of cotton fabric, some new bands attributed to the nanomaterials inserted on the tissue fibers appear after treatment (Fig 5: b, c, d, e and f).

The modification of the cotton fabric with RuO₂-TiO₂ mixed oxide (Fig 5 b) is manifested by the appearance of a vibration band situated at 690 cm⁻¹ which corresponds to Ru-O and deformation of Ru-O-H (Musić, Popović, Maljković, Furić and Gajović, 2002). It should be noted that the bands of cellulose are stored because of the amount of RuO₂-TiO₂ NPs on the surface. The CF/RuO₂-TiO₂/PANI spectrum (Fig 5 d) shows no significant difference from that of CF/RuO₂-TiO₂ (Fig 5 b). The spectrum shows only the peaks of cellulose and those of RuO₂-TiO₂. The small amount of PANI polymerized on the surface of RuO₂-TiO₂ NPs results in the absence of its signals under IR. The presence of the functionalized nanoparticles on the fabric is manifested by the appearance of certain peaks on the spectrum of CF/RuO₂-TiO₂/DPA (Fig 5 c), include those located at 1580 and 1160 cm⁻¹, which are attributed to the aromatic C=C stretching and C-H benzene ring stretching band, respectively (Leroux, Fei, Noël, Roux and Hapiot, 2010). These bands are associated with other apparent on the spectrum and which are attributed to the cellulose and RuO₂-TiO₂ mixed oxide. The spectrum of CF/RuO₂-TiO₂/DPA@PANI (Fig 5 f) exhibits only PANI bands, they are located at 792, 1026, 1154, 1493, 1574, 3251 and 3488 cm⁻¹ which correspond to C-N⁺ stretching vibration, plane bending of C-H, C-H benzene ring stretching band, N-N stretching vibration. C=N stretching of quinoid vibrations (Yuzhen, Yuan, Liangzhuan Wu and Jinfang, 2013), N-H stretching (Zhang, Liu and Su, 2006) and adsorbed H₂O molecules (Bishop, Pieters and Edwards, 1994) respectively. The absence of the cellulose signs is due to the fact that the thickness of PANI coating is greater than the effective penetration depth of IR radiation as well as the high absorption of polyaniline (Bajgar et al., 2016).

Fig.5. FTIR spectra of pristine cotton fabric (a), CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂/DPA (c), CF/RuO₂-TiO₂/PANI (d), CF/RuO₂-TiO₂/DPA/PANI (e) and CF/RuO₂-TiO₂/DPA@PANI (f).

3.5. Raman

Generally, the mixed metal oxides are manifested with Raman active modes corresponding to each oxide constituting the mixed material. this has already been demonstrated in our previous study conducted on RuO₂-TiO₂ mixed oxide (Mousli et al., 2019 (b)); the latter, under the Raman laser gives signals that are attributed to each of the two oxide namely the TiO₂ anatase that occurs with seven modes of Raman actives vibration that are E_g (144 cm⁻¹), E_g (197 cm⁻¹), B_{1g} (399 cm⁻¹), A_{1g} (514 cm⁻¹), B_{1g} (514 cm⁻¹) and E_g (639 cm⁻¹) (Arsov, Kormann and Plieth., 1991), and the rutile RuO₂ which absorbs between 400 and 800 cm⁻¹ with the symmetries E_g corresponding to a doublet and A_{1g} and B_{2g} phonons vibrations corresponding to the singlet (Chen, Korotcov, Hsu, Huang and Tsai., 2007), they are they are usually located at 528, 645 and 716 cm⁻¹ respectively (Mar, Chen, Huang and Tiong, 1995). On the CF/RuO₂-TiO₂ spectrum, no signal is attributed to RuO₂. All the peaks are assigned to the anatase, this is due to the analyzed area which is possibly disabled in ruthenium (Fig 5 b). Ditto for the fabric impregnated with RuO₂-TiO₂/PANI, the spectrum is almost the same to that of CF/RuO₂-TiO₂. The negligible amount of PANI inserted on the surface of RuO₂-TiO₂ is not sufficient to be detected in Raman, hence the absence of its peaks on the spectrum (Fig 5 c). A

slight red shift and a widening of the peaks are recorded for RuO₂-TiO₂ NPs already functionalized with diphenylamine diazonium modified cotton fabric samples (Fig 5 d). In the presence of PANI, the bands of RuO₂-TiO₂ mixed oxide are attenuated (Fig 5 e) even masked (Fig 6 f) by PANI which completely covers RuO₂-TiO₂-DPA materials; all the bands appearing on the spectra are corresponding to the PANI, they are located at 1168, 1250, 1335, 1510, and 1595 cm⁻¹; they are assigned to C-H bending of the quinoid and benzenoid ring, C-N⁺ stretching vibration, C=C stretching of the benzenoid ring, and C=C stretching of the quinoid rings (Jlassi et al., 2014; Jin, 2018). It is noted that the Raman response of the cellulose is hidden by TiO₂ which absorbs strongly in the same zone as cellulose.

Fig.6. Raman spectra of pristine cotton fabric (a), CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂ /PANI (c), CF/RuO₂-TiO₂/DPA (d), CF/RuO₂-TiO₂ /DPA/PANI (e) and CF/RuO₂-TiO₂/DPA@PANI (f).

3.6. XPS

Fig.7 XPS survey scans (a-e) and C1s narrow regions (f-j) of pristine cotton (a,f), CF/RuO₂-TiO₂ (b,g), CF/RuO₂-TiO₂/PANI (c,h), CF/RuO₂-TiO₂/DPA/PANI (d,i) and CF/RuO₂-TiO₂/DPA@PANI (e,j).

XPS was used to monitor the stepwise modification of cotton woven fabric by the catalytic materials. For the nanocatalyst XPS spectra, the reader is referred to (Mousli et al., 2019 (b)). Figure 7 displays survey and high resolution C1s spectra from cotton before any surface modification (Figures 7a,f) and after dip coating in aqueous suspensions of RuO₂-TiO₂ (Figures 7b,g), RuO₂-TiO₂/PANI (Figures 7c,h) and RuO₂-TiO₂/DPA/PANI (Figures 7d,i). Figures 7e,j display the survey spectrum and narrow C1s region of cotton fabric dip coated first in RuO₂-TiO₂/DPA suspension and then top coated with PANI prepared in situ by oxidative polymerization.

The composition of RuO₂-TiO₂ mixed oxide surface as well as that of the corresponding nanocomposites RuO₂-TiO₂/PANI and RuO₂-TiO₂/DPA/PANI before impregnation on the fabric surface have already been analyzed by XPS. The high resolution spectra of the materials were exposed and discussed in a previous study (Mousli et al., 2019 (b)).

The survey regions exhibit the main peaks S2p, C1s, N1s, Ti2p and O1s centred at 168, 285, 400, 458 and 532 eV, respectively. Ru3d is too weak to be visible on the survey regions as it is located at the onset of the C1s peak. Ti2p is readily visible after immobilization of the RuO₂-TiO₂ nanocatalyst (Figure 7b) compared to pristine cotton (Figure 7a), but the Ti2p/C1s peak intensity ratio decreases for CF/RuO₂-TiO₂/PANI compared to CF/RuO₂-TiO₂ since the nanocatalyst RuO₂-TiO₂ was first modified with PANI prior to attachment to the cotton fabric by dip coating (Figure 7c). One can note in Figure 7d a total absence of Ti2p due to the

modification of the cotton fabric by RuO₂-TiO₂/DPA/PANI. Indeed, we have demonstrated recently (Mousli et al., 2019 (b)) that the modification of RuO₂-TiO₂ by the DPA diazonium coupling agent permits to achieve much higher PANI mass loading that resulted in the total screening of the RuO₂-TiO₂ nanocatalysts. As a matter of fact, the C1s narrow region displayed in Figure 7i does not exhibit any Ru3d at ~280-282 eV. For CF/RuO₂-TiO₂/DPA@PANI, Figure 7e shows a relatively intense N1s peak at 400 eV due to the in situ synthesis of PANI at the surface of CF/RuO₂-TiO₂/DPA. This coating is deep green (quasi looking as black, see digital photograph in Figure 1C, upper panel) and in line with the detection of an intense N1s peak. Interestingly, and compared to RuO₂-TiO₂/DPA/PANI dip coated on cotton (Figure 7d), one can now see S2p (168 eV) and S2s from the PANI doping. Another interesting feature of the survey region displayed in Figure 7e is the shape of the inelastic background. After the O1s peak at 532 eV and towards the apparent high binding energy (in reality at low kinetic energy side), the survey spectrum in Figure 7e exhibits ever increasing intensity of the inelastic background which is due to inelastically emitted electrons from the buried surface underneath PANI (cotton and RuO₂-TiO₂/DPA). In contrast, the inelastic background between the C1s and O1s peaks is horizontal or slightly decreasing, which is characteristic of a top layer, herein PANI. These aspects contrast markedly with the situation of noted in Figure 7d for CF/RuO₂-TiO₂/DPA/PANI. Indeed, dip coating RuO₂-TiO₂/DPA/PANI on the cotton fabric does not screen the cellulosic substrate, and for this reason one can note the decreasing intensity of the background at higher binding energy side of the C1s and O1s peaks which mainly due to cotton.

For the narrow C1s regions, Figure 7f displays a main peak at 286.5 eV due to C-O and a shoulder at 288 eV due to hemiacetal group O-C-O. Possible COOR groups are present on the cotton as judged from the small shoulder at ~289 eV. After modification with RuO₂-TiO₂, the cotton fabric exhibits Ru3d doublet at ~280-282 eV (Figure 7g) the intensity of which decreases relatively compared C1s in the case of CF/RuO₂-TiO₂/PANI (Figure 7h) since the nanocatalyst RuO₂-TiO₂/PANI does not have much surface immobilized PANI (Mousli et al., 2019 (b)). For CF/RuO₂-TiO₂/DPA/PANI (Figure 7i) there is no Ru3d doublet, but the C1s peak looks like that of pristine cotton except it is slightly broad due certainly due to contribution from PANI. Finally, Figure 7j exhibits distinct C1s spectrum (recorded for CF/RuO₂-TiO₂/DPA@PANI) compared to that shown in Figure 7i and underlines the essential difference between CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI. In the former case, RuO₂-TiO₂/DPA/PANI nanocatalyst is immobilized by dip coating and remains between the cotton fibers, whereas for the latter, PANI is synthesized in situ on

cotton that has been pre-dip coated with RuO₂-TiO₂/DPA nanoparticles. Polymerization occurs on the bare cotton C-OH sites but also on the DPA groups from the immobilized nanocatalyst. This important difference in the processes induces significant differences in the surface compositions as judged from XPS.

For the final, PANI-rich surface CF/RuO₂-TiO₂/DPA@PANI, the C/N atomic ratio is 7.4 higher than the theoretical value of 6 for PANI and that reported by (Barthet, Armes, Chehimi, Bilem and Omastova, 1998) for PANI surface, due to possible contribution of the cotton fabric and presumably some adventitious hydrocarbon contamination. The doping level is given by:

$$D\% = \frac{S \times 2}{N} \times 100\% = 49.4\%$$

where *S* and *N* are the atomic percents of sulfur and nitrogen. The factor 2 stands for double charge born by the SO₄⁼ dopant. This D% is matching 50%, the doping level for conductive PANI.

3.7. Stability of catalytic textiles.

3.7.1. SEM monitoring of the morphology of washed and washed/ironed-cotton fabrics

After washing, the RuO₂-TiO₂/DPA/PANI nanocomposite deposit on the fabric surface has become much more homogeneous. All the powder agglomerated on the surface is gone during the washing, remains only the particles that are impregnated between the fibers and that are well attached to the surface (Fig 8 a, b).

The SEM images show that the washing has disordered the fibrous structure of the samples and the surface contains very few nanoparticles comparing to the unwashed sample (Fig 8 cd, fg). The presence of the nanoparticles on the fabric and the complete composition of the surface have been confirmed by EDS. It is noted that the surface analyzed is crippled in Ru (Fig 8 e, h).

Visually, washing as well as washing followed by ironing does not destroy the nanocomposite RuO₂-TiO₂/DPA@PANI. PANI film appears to be persistent and fairly adherent to the fibrous surface (Fig 8 I, j). The morphological analysis as well as the composition of the surface carried out by SEM/EDS show images and composition almost similar to those of the same sample before the adhesion tests. The fibers are completely loaded with PANI, hence the appearance of a porous surface, made up of non-homogeneous agglomerates (Fig 8 k-m and n-p).

Fig.8. Digital photographs of CF/RuO₂-TiO₂/DPA/PANI (a) and CF/RuO₂-TiO₂/DPA@PANI (i) as prepared, and after washing (j) and (b) respectively. SEM images and elemental spectra of washed CF/RuO₂-TiO₂/DPA/PANI (c-e) and CF/RuO₂-TiO₂/DPA/PANI (k-m) and cleaned and ironed CF/RuO₂-TiO₂/DPA/PANI (f-h) and CF/RuO₂-TiO₂/DPA@PANI (n-p) respectively.

3.7.2. XPS after washing/ washing and ironing

Fig. 9. XPS-determined N/C atomic ratios for untreated, machine washed, and washed/ironed samples of CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI. For the sake of clarity, RuO₂-TiO₂ is noted MO for mixed oxide in the labels.

The cotton textile catalysts CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI were also examined by the surface sensitive XPS in order to check any subtle change in the surface composition as a result of fastness tests conducted by machine washing using industrial detergents at standard dose (75 ml for 5 kg clothes, T°=40 °C, cotton program). We have selected herein the most efficient catalytic textiles prepared using diazonium compounds. PANI was loaded on the diazonium modified catalyst prior to dip coating or prepared in situ as mentioned above in the presence of CF/RuO₂-TiO₂/DPA.

Despite the presence of DPA and covalent bonding of PANI in either cases, we have noted decrease of the surface N/C atomic ratios for both catalytic textile. However, ironing the washed textile does not induce any additional change.

It follows that XPS can provide deep insight in the surface composition particularly for CF/RuO₂-TiO₂/DPA@PANI textile which remains very dark even machine washing. In contrast, for CF/RuO₂-TiO₂/DPA/PANI, one could note leaching of the catalyst even with the naked eye as the nanocatalyst has been removed partially after washing, and the result is confirmed by XPS.

The essential difference between the surfaces comes from the N/C ratio which is even higher for washed CF/RuO₂-TiO₂/DPA@PANI compared to the untreated CF/RuO₂-TiO₂/DPA/PANI. Obviously, in situ polymerization of aniline is important in providing a continuous PANI top layer that withstands machine washing.

These surface composition aspects will be correlated to the catalytic activity of the textiles.

4. Photocatalytic activity

The catalytic efficiency of RuO₂-TiO₂ NPs, RuO₂-TiO₂/PANI and RuO₂-TiO₂/DPA/PANI powdery nanocomposites with respect to the MO degradation reaction under the same conditions as the present work ([MO]=50 mg/l, pH=6.5, T=T_{amb}) was reported in a previous study (Mousli et al., 2019 (b)). It is noted that the RuO₂-TiO₂/PANI and RuO₂-TiO₂/DPA/PANI nanocomposites are effective catalysts in the darkness (Mousli et al., 2019 (b)), the amount of the catalysts coated on cotton fibers is very small compared to the volume of the volume of MO solution and its concentration, hence the choice to use visible light to activate the nanocatalysts and to accelerate the degradation reaction of the MO.

The study found that the presence of PANI improves the catalytic properties of RuO₂-TiO₂ mixed oxide, namely: the catalysts containing PANI are very active in the dark, while pristine RuO₂-TiO₂ is an effective catalyst under visible light; in addition, the catalytic effect of the catalyst increases with increasing the amount of PANI in the nanocomposite. Whereas the use of PANI alone in photocatalytic processes has a negligible effect under irradiation and this has been claimed by several researchers (Xiong et al., 2012, Eskizeybek et al. 2012). This is due to the low adsorption of the pollutant by PANI which requires its association with another material in order to improve the kinetics of the photocatalytic process.

Despite the fact that they are the same powders that are impregnated on the surface of the fabric and used in MO degradation process, the materials are not catalytically active in the dark because of the small amount of catalyst inserted on the surface and between the fabric

fibers (0.4 mg). The solutions are therefore exposed to visible light for 45 min. The decomposition of the dye is controlled by the transition from its orange color to the colorless followed by the absorption spectra measured at regular time intervals. Under visible light, the MO solution containing RuO₂-TiO₂, RuO₂-TiO₂/PANI, RuO₂-TiO₂/DPA/PANI and RuO₂-TiO₂/DPA@PANI nanocatalyst-modified cotton fabrics became completely colorless after 45 min as compared with the solution containing the pristine sample. This is strong supporting evidence for the effect nanocatalysts loaded on the fabric surface (Fig 10).

Fig. 10. Digital photographs of Methyl Orange under visible light.

The photo-activity of the different materials (pristine CF, CF/RuO₂-TiO₂, CF/RuO₂-TiO₂/PANI, CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI) was evaluated and compared by measuring the concentration of the dye in solution by UV-Vis at different time intervals. Figure 11 shows the recorded spectra.

Fig.11. UV-vis absorption spectra of Methyl Orange solutions (50 mg/l) for various periods: pristine cotton fabric (a), CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂/PANI (c), CF/RuO₂-TiO₂/DPA/PANI (d) and CF/RuO₂-TiO₂/DPA@PANI (e).

The MO is characterized by a band in the visible region attributed to the azo form and located between 400-500 nm and which monitors the effect of the photocatalysis on the degradation of MO; and another band situated between 250-300 nm which is due to the phenyl group in the dye.

Under visible light and in the presence of H₂O₂ as oxidant and composite materials (CF/RuO₂-TiO₂, CF/RuO₂-TiO₂/PANI, CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI), the band at 250 nm disappears completely after 15 min, only the band located at 500 nm which remains but decreases with time until its complete disappearance after 45 min indicating the total decomposition and mineralization of MO (Fig 11 b, c, d, e).

In the presence of pristine cotton fabric, the characteristic bands of MO have retained their intensity throughout the irradiation period, which means that the unmodified textile has no role in the photocatalytic degradation process of MO and that the decomposition of the latter is necessarily due to the catalyst inserted on the fabric surface and their interaction with it (Fig 11a).

The concentration of MO in the solution at different degradation times depends on the catalytic efficiency of each material. The degradation extent (%) is calculated by the following relationship:

$$\% = \frac{C^{\circ} - C}{C^{\circ}} * 100$$

Figure 12 shows the percentage of dye degradation as a function of treatment time for all photocatalytic materials. It is found that the effectiveness of the photocatalysis in the presence of the different cotton fabric samples differs markedly.

The decomposition of the dye in the presence of RuO₂-TiO₂-modified fabric already coated with PANI appears to be active compared to pristine RuO₂-TiO₂; this is due to the presence of the polymer and the electronic transfer between the different materials constituting the nanocomposites (PANI, RuO₂-TiO₂ and cellulose).

We have demonstrated in the previous studies that the elimination of MO is better in the presence of PANI and that the catalytic activity of the nanocomposites containing the polymer is directly related to the amount of the conductive polymer in the composite (Mousli et al., 2019 a; b, 2019). In this study, the CF/RuO₂-TiO₂/DPA@PANI sample contains a rather thick layer of PANI compared to the other ones. For this reason, its activity is better, and likely due to the porosity of the cotton fabric and the strong interaction of aniline and OH group of cellulose but also to the presence of the diazonium salt on the surface of RuO₂-TiO₂ mixed

oxide NPs, which acts as a coupling agent and which served for the insertion and adhesion of PANI to the surface of the mixed oxide on the one hand, and on the fabric surface on the other hand.

PANI is an excellent photosensitizer; it acts both as an efficient electron donor and as good hole transporter (Bejbouji et al. 2010, Park et al. 2015, Zhang et al. 2018). The presence of PANI in the heterojunction based-photocatalysts improves the catalytic efficiency as well as the kinetics of the degradation reaction of pollutants, due to the incorporated nanostructure and the synergistic effect between the species (Tanwar and Mandal., 2019)¹]. This makes PANI an attractive element used in the design and development of novel catalytic hybrid materials to progress in the field of heterogeneous catalysis under irradiation and even in the dark (Mousli et al., 2019 (a) and (b) 2019).

Fig. 12. Variation of the percentage of degraded MO as a function of the time in the presence of different catalysts

The studies carried out on the photodegradation of MO indicate that the reaction follows kinetics of order 1 whose integration of the reaction rate is given as follows:

$$\ln \frac{C}{C_0} = -Kt$$

where, C_0 is the initial concentration of the pollutant, K (min^{-1}) is the apparent rate constant and C is the concentration of pollutant at t .

Figure 13 shows the kinetics treatment for an apparent first order for the decomposition of MO under the catalytic effect of the different catalytic materials.

A good linear correlations of $\ln(C/C_0)$ against time ($0.99 < R^2 < 1$) were acquired, suggesting that the catalytic reaction obey pseudo-first-order kinetics. These plots allowed also calculating the rate constant of the MO degradation reaction; they are 0.0532, 0.0775, 0.0828 and 0.101 min^{-1} for the reaction catalyzed by $\text{CF/RuO}_2\text{-TiO}_2$, $\text{CF/RuO}_2\text{-TiO}_2/\text{PANI}$, $\text{CF/RuO}_2\text{-TiO}_2/\text{DPA/PANI}$ and $\text{CF/RuO}_2\text{-TiO}_2/\text{DPA@PANI}$ (Fig 13).

Fig. 13. Kinetics of degradation (a) and first order linear transforms of the decomposition of Methyl Orange solution (50 mg/l) under visible light.

The optimization of the operating conditions (T_{amp} , pH, choice of solvent...) whose the photocatalytic degradation reaction of MO took place has a role in the preservation of the nanocharged fabric surface of and the nanocatalyst. After the photocatalytic process, no undesirable changes in surface color, shape or structure were noticed. All the samples are stable in the reaction medium and can be reused as such in another photocatalytic process (Fig 14).

Fig.14. Digital photographs of pristine cotton (a) fabric and functional cotton fabric after the photocatalytic process: CF/RuO₂-TiO₂ (b), CF/RuO₂-TiO₂/PANI (c), CF/RuO₂-TiO₂/DPA/PANI (d) and CF/RuO₂-TiO₂/DPA@PANI (e).

4.1. Degradation product

Figure 15 shows the original IR spectrum of MO and that after decomposition in the presence of CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI under visible light. The original spectrum (Fig 15 a) exhibits a peak at 3430 cm⁻¹ for N-H stretching vibration. The C-H stretching vibration of -CH₃ are located at 2905 and 2854 cm⁻¹. At 1610 and 1540 cm⁻¹ are located C-C vibrations of benzene skeleton, and the band 1426 cm⁻¹ is attributed to N=N (Shen, 2015). The pic at 1380 cm⁻¹ is assigned to -S=O vibration. The band C-N is observed at 1225 cm⁻¹ and C-H stretching vibrations of benzene ring were pointed at 1030, 847 and 697 cm⁻¹ (Tanwar and Mandal, 2019). Stretching vibration -C-S is manifested by an IR signal at 624 cm⁻¹. The spectra of the degraded products in the presence of both CF/RuO₂-TiO₂/DPA/PANI (Fig 15 b) and CF/RuO₂-TiO₂/DPA@PANI (Fig 15 b) are similar; they illustrate only two bands which were not observed in the original spectrum of the dye. They include a large band at 3300 cm⁻¹ due the H₂O molecules and a peak centred at 1634 cm⁻¹ which is attributed to HCO₃⁻ derived from CO₂ dissolved in water (Babushkina, Nikitina, Goncharov and Ponomareva, 2009; Garand et al., 2009). These spectra reflect the total mineralization of MO under visible light.

Fig.15. IR spectra of Methyl Orange before (a) and after degradation in the presence of CF/RuO₂-TiO₂/DPA/PANI (b) and CF/RuO₂-TiO₂/DPA@PANI (c) under visible light.

The illumination of the RuO₂-TiO₂-coated cotton fabric leads to the excitation of electron positioned on the valence band (VB) of TiO₂ and move towards the conductance band (CB) leaving holes on the VB; the latter migrate to RuO₂ and participate in the formation of OH[•] radicals on the surface of the nanocomposite. In addition, the excited electrons diffuse on the surface and react with oxygen to generate O₂^{-•} anion radicals. These radical species (OH[•], O₂^{-•}) are very powerful oxidants and can destroy several organic molecules. To prove the existence of such active radicals, one could perhaps use radical traps as proposed elsewhere (Buzzetti et al. 2019). The role of the generated photoactive species is explained by the proposed mechanism shown in Fig 16.

Fig. 16. Mechanism of Methyl Orange degradation on $\text{RuO}_2\text{-TiO}_2$ -coated cotton fabric surface.

The modified-fabric has been widely used in heterogeneous catalysis either for degradation of organic pollutants or to enhance antibacterial activity. For an antibacterial application, (Krishnamoorthy, Navaneethaiyer, Mohan, Lee and Kim, 2012) have modified the cotton fabric using graphene oxide (GO) nanostructure by dip coating method for the bacterial quantitative reduction of both Gram-negative and Gram-positive bacteria. In 2019, (Ahmad, Kan and Yao, 2019) evaluated the catalytic performance of cotton fabric impregnated with TiO_2 nanoparticles coupled with phthalocyanine based reactive dye, Reactive Blue-25 used as a visible light absorber for degradation of Rhodamine under visible light. The same experimental process was adopted by (Zhu et al., 2017), who made ZnO nanoparticle substitute with Methylene Blue (MB) dye and coated cotton fabric by dip-pad-dry method for self-cleaning textile application.

The materials that are cotton fabric-based used in photocatalysis often bear TiO_2 nanoparticles which are known as an excellent catalyst under UV light (Stan et al., 2018; Mishra and Butola, 2018; Nosrati, Olad and Najjari, 2017). ZnO nanostructure has also been widely used in the same field of application; it represents an alternative thanks to its wide gap (3.37 eV),

exciton binding energy (60 meV) and its low price (Zhu et al., 2017). Nanocomposites such as TiO₂-PANI-based cotton fabric have also been used in photocatalysis, the materials exhibits better photocatalytic activity thanks to the synergistic effect at the TiO₂//PANI interface. (Nosrati, Olad and Najjari, 2017; Kumar and Pandey, 2018).

4.2. Durability test

In this part and among the cotton fabrics modified with the powdery catalyst (CF/RuO₂-TiO₂, CF/RuO₂-TiO₂/PANI and CF/RuO₂-TiO₂/DPA/PANI), we have chosen the sample CF/RuO₂-TiO₂/DPA@PANI and CF/RuO₂-TiO₂/DPA/PANI which catalyzes better the reaction of the decomposition of MO to study the effect of the adhesion tests (washing and insolation) on the catalytic activity of the catalyst (RuO₂-TiO₂/DPA/PANI nanocomposite). Adhesion tests were performed as described above. The samples were used as catalysts in the degradation of MO under the same conditions as previously ([MO], pH=6.5, T_{amb}, CF size, volume of MO and the source of visible light).

Figure 17 and 18 illustrate the digital photographs of the MO solutions at different irradiation times in the presence of CF/RuO₂-TiO₂/DPA/PANI and CF/RuO₂-TiO₂/DPA@PANI insolated during 1h (Fig 17/18 A), washed (Fig 17/18 B) and washed and ironed (Fig 17/18 C).

Under irradiation, the behavior of MO solutions containing both samples exposed to sunlight is the same as those of the non-irradiated same samples. The MO solution lost completely its orange color after 45 min, which is the case even before sunlight exposure; so the samples are very stable under the visible light rays and the irradiation does not affect its catalytic properties (Fig 17/18A).

Washing and ironing led to a weight loss of 8% and 6.4% of the mass of washed CF/RuO₂-TiO₂/DPA/PANI and washed and ironed CF/RuO₂-TiO₂/DPA/PANI respectively, this loss decreased the catalytic capacities of the samples and the discoloration of MO solution take place after 200 min in the presence of the washed sample and 250 min in the presence of the washed and ironed sample (Fig 17 B, C). However, CF/RuO₂-TiO₂/DPA@PANI seems to be very stable and washing and washing followed by ironing have no effect on the catalytic power of the nanocomposite (Fig 18 B, C). The PANI layer deposited on the surface constitutes a protective layer of the RuO₂-TiO₂/DPA powders nanocatalyst, hens its stability during the catalytic process.

Fig. 17. Digital photographs of MO solutions under visible light in the presence of CF/RuO₂-TiO₂/DPA/PANI insolated (A), washed (B), washed and ironed (C). a, b, c, d, e and f correspond to the sampling times 15, 30, 45, 100, 150, 200 min respectively.

Fig. 18. Digital photographs of MO solutions under visible light in the presence of CF/RuO₂-TiO₂/DPA@PANI insolated (A), washed (B), washed and ironed (C). a, b, c, d, e and f correspond to the sampling times 15, 30 and 45 min respectively.

Although the mass loss of the washed/ironed sample is lower than that of the washed one, which means that ironing has an effect on the catalytic properties of the catalytic materials. The CF exposed to sunlight gives better degradation of MO under visible light. The mineralization took place after 15 min of irradiation. The rate constant of the dye degradation reaction is calculated to be 0.0959, 0.0155 and 0.01302 min⁻¹ in the presence of CF/RuO₂-TiO₂/DPA/PANI fabric exposed to sunlight, washed and washed/ironed samples, respectively (Fig 19).

The degradation rate of MO in the presence of CF/RuO₂-TiO₂/DPA@PANI is constant even after the three tests (insolation, washing, washing and ironing), which confirms that the washing and the heat of the iron do not have any impact on the catalytic properties of RuO₂-TiO₂ and this thanks to the layer of PANI deposited on the surface (Figure 19).

The rate constant is 0.0994 min⁻¹ for the washed sample and 0.1 min⁻¹ for the insolated and the washed and ironed sample while it is 0.101 min⁻¹ before the durability test.

Fig.19. First order linear transforms of degradation of MO solutions (50 mg/l) in the presence of CF/RuO₂-TiO₂/PANI and CF/RuO₂-TiO₂/DPA@PANI: sonicated for 1h, washed, washed and ironed

5. Conclusions

The present work sets a pathway for designing cotton fabric coated with hybrid photocatalysts operating under visible light.

The nanostructure coated-CFs have a significant catalytic activity in the photodegradation and the mineralization of MO dye under visible light. This catalytic activity depends on the PANI amount in the nanocomposite. Indeed, the cotton fabric based on in situ synthesis of PANI exhibits better catalytic performance as compared to other catalysts coated-CFs. The PANI film was uniformly deposited over the entire surface of the fabric and on both sides, trapping a large amount of RuO₂-TiO₂ on the fibrous surface, thanks to the diphenyl amino group from diazonium salt which served as a coupling agent for attaching the PANI to RuO₂-TiO₂ surface but also to the strong interaction between PANI and fabric forming O-N covalent band. The improvement of the degradation kinetics and the catalytic performances could be credited to the strong interfacial interactions between the nanocomposite components that maximizes the interfacial contact between RuO₂-TiO₂ and PANI and the synergistic effect as well as charge transfer at different interfaces of CF/RuO₂-TiO₂/DPA@PANI. It turned out that the washing of the cotton fabrics as well as the washing followed by the ironing affect the performances of the materials but they keep their retain substantial photocatalytic activity under simulated sunlight but do not block the catalytic effect of CF/RuO₂-TiO₂/DPA@PANI hybrid material. In the case of exposure to simulated sunlight, but without any washing, the catalytic textiles

remain very stable and catalytically active. This feature makes them suitable for the design of textile-based structured solar cells, anti-pesticide clothes and for other industrial and outdoor environmental applications.

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