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PHOTOCATALYTIC EFFICIENCY OF N-TIO$_2$ APPLIED ON COTTON KNIT – PART 2

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Abstract: *The objective of this work was to demonstrate the treatment durability at washing of N-TiO$_2$ layers applied on cotton fabrics by padding and to investigate the particle adherence and morphology of the textile surface. After 5 washing cycles, the cotton fibers are covered with a high number of particles, which demonstrate that the particle adherence to the substrate is high, most of them being present as large clusters. Also, the washing process does not affect in an important manner the polymer layer, only from place to place the cotton knit beeing disrupted. To evaluate the photocatalytic effect of the materials after washing treatment, samples were exposed to ultraviolet and visible light. The trichromatic coordinates of the exposed and non-exposed samples were measured on Hunterlab spectrophotometer. The contradictories values are determined by the non-uniformities of the materials which don't allowed a uniform dyeing of the fabrics. The obtained results showed that after 5 washings, the particles adherence to the substrate is still high and the photocatalytic effects are not significantly impaired. The photocatalytic efficiency of cotton knit treated with N-TiO$_2$ nanoparticles is higher under visible light than under UV light demonstrating the extension of the TiO$_2$ absorption in the visible range.*

Key words: *nitrogen-doped TiO$_2$, photocatalysis, textiles, washing durability, nanoparticles*

1. INTRODUCTION

Majority of the researches evaluate the photocatalytic effects of N-TiO$_2$ on the pollutants solutions [13-15] and none on the N-TiO$_2$ immobilized on textiles. Even the photodegradation efficiency in liquids is high, the results could be unreliable if the photocatalyst is fixed on solid substrates which acts as a barrier limiting the mass transport of pollutants to reduced surface of the adsorption sites. In addition, due to non-uniformity of the textile surfaces and the traditional methods used in the textile industry [16,17], the immobilized photocatalysts are randomly dispersed as clusters lowering the surface exposed to light. Our study was focused on the analysis of the photocatalytic effects of N-TiO$_2$ deposited on textile materials under visible, UV and solar light and their durability at washing.

1.1. Photocatalytic effect of the fabrics treated with N-TiO_2

The photocatalytic efficiency of the fabrics treated with N-TiO_2, stained with methylene blue (MB), and exposed to visible, UV and solar light is shown in the Tables 1 – 6.

***Table 1**: The aspect of the cotton knit exposed to UV (λ=365 nm) light*

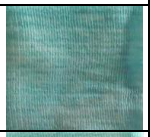
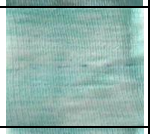
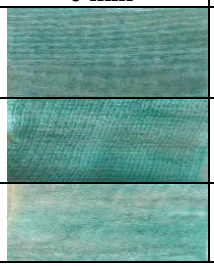
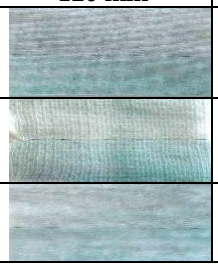
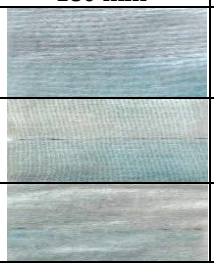
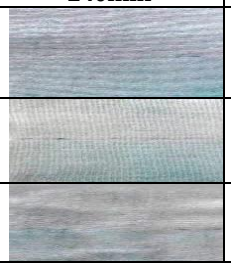
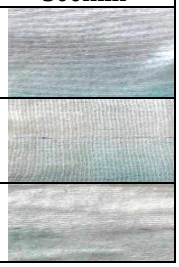
Time (min)	Blank	1Na	1 Nb	2N	2Nbis	3N bis
0						
120						
360						

***Table 2:** Trichromatic coordinates of the cotton knit treated with N-TiO_2, stained with MB and exposed at UV light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	Tone	% Strength SUM
Blank	83.33	-8.85	-8.02	1.67	3.65	3.83	5.55	-5.28	2.50	74.23
1Na	86.05	-11.86	-4.85	**3.43**	2.63	4.56	6.28	-4.47	2	66.83
1Nb	81.46	-9.62	-6.29	2.23	3.21	6.24	**7.36**	-6.44	2	79.63
2N	82.64	-7.59	-4.26	-1.90	-0.79	0.12	2.06	0.61	4	124.04
2N bis	85.15	-10.65	-3.35	2.04	3.27	5.13	6.41	-5.13	2	76.84
3N bis	84.71	-11.41	-3.63	0.55	2.80	4.67	5.47	-4.49	2.5	88.14

Under the UV light, except 2N and 3Nbis fabrics, the treated samples are more decolorized than the untreated fabric (blank) as the grades on gray scale demonstrate. The highest lightness difference (dL*, + = lighter, - = darker than blank) and the lowest % strength SUM is found on sample 1Na, proving that the methylene blue is more intense decolorized on this fabric than on the other materials after the exposure to UV light. What is important to notice is the behavior of sample 2N, which shows the shade darkening, the color being shifted to green (da* negative) and yellow (db* positive) contrary to the rest of fabrics which colors are shifted to red-yellow.

***Table 3**: Aspect of the knit cotton exposed 5hr to solar light*

Time	0 min	120 min	180 min	240min	300min
Blank					
1Na					
1 Nb					

2N					
2N bis					
3N					
3N bis					

Table 4: *Trichromatic coordinates of the materials treated with N-TiO_2 stained with MB and exposed to solar light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	85.76	-2.70	-4.15	0.69	1.34	1.51	2.14	-2.01	3.5	93.80
1Na	90.69	-3.78	1.47	3.96	3.21	4.94	7.10	-3.74	2	71.50
1Nb	87.69	-3.77	0.53	3.15	1.37	4.79	5.90	-2.87	2	80.01
2N	88.05	-3.48	-0.11	**5.23**	3.06	5.03	7.87	-4.83	2	77.73
2Nbis	89.05	-3.25	1.32	3.08	3.04	5.97	7.37	-4.31	2	88.63
3N	91.09	-2.39	2.66	4.49	3.68	4.77	7.52	-2.86	2	55.20
3Nbis	87.44	-3.66	1.31	3.43	3.03	7.33	8.64	-5.11	1.5	104.76

Sun exposure leads to faster degradation of methylene blue on treated materials than on blank sample, the difference being 1.5 tones compared to untreated material exposed to UV light. Degradative action of sunlight is more intense on 1Na on which surface a higher amount of TiO_2 (4.08 wt% TiK) exists than on 1Nb knit (3.73 wt% TiK) as demonstrated by the lightness (dL*) and color differences (dE*) values and confirmed by % Strength Sum. Also, in the case of 2N and 2N bis, 3N and 3Nbis, it is clear that higher amount of N-TiO_2 existing on the 2N material leads to a faster degradation of the dye.

Table 5: *Aspect of the cotton knit treated with2N, 2Nbis, 3N, 3Nbis exposed 4 h to visible light*

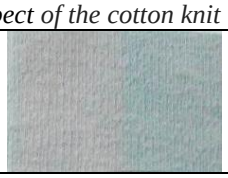
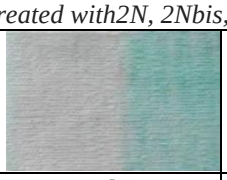
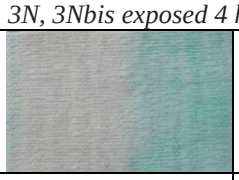
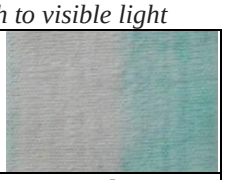
				
Blank	**2N**	**2N bis**	**3N**	**3N bis**

Table 6: *Trichromatic coordinates of the materials treated with N-TiO_2 stained with MB and exposed to 4hs visible light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	84.16	-3.05	-5.62	0.68	8.01	4.97	9.45	-8.92	1.5	79.95
1Na	89.13	-4.93	-0.02	10.42	14.04	15.40	23.30	-19.52	1	25.00
1Nb	85.73	-4.58	-3.95	4.18	7.28	7.36	11.16	-10.34	1.5	56.00
2N	86.48	-2.92	-0.26	1.30	5.14	4.47	6.93	-6.41	2	92.33
2Nbis	88.33	-2.53	2.05	5.68	12.63	10.90	17.63	-14.29	1	48.00
3Nbis	88.72	-3.05	2.99	5.51	9.63	10.43	15.23	-10.42	1	61.76

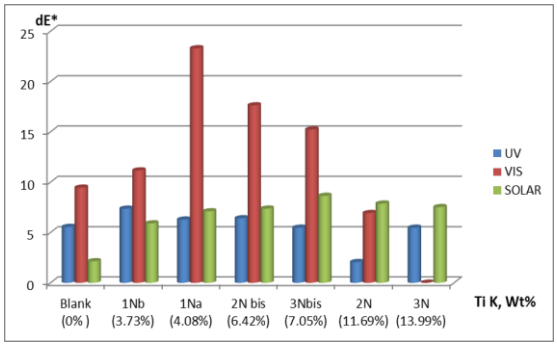


***Fig. 1**: Correlation dE* and TiK*

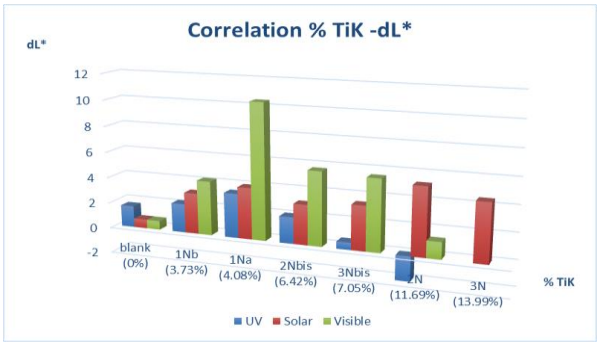


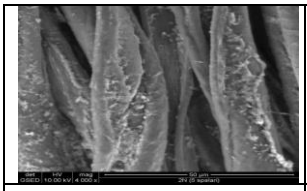
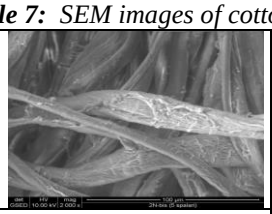
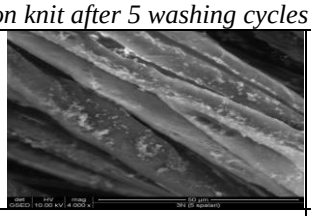
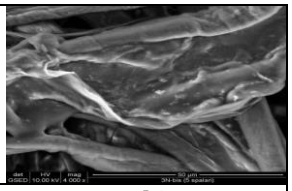
***Fig. 2**: Correlation dE* and TiK*

Under UV and visible light, comparing the values of dL*, dE* and % TiK (Fig. 1 and 2), it is obvious that, the photocatalytic efficiency increases until TiO_2 concentration reaches an optimum value (4.08 wt% TiK), than decreases as the amount of N-TiO_2 increases. Under the solar light, the photocatalytic effects are higher for high amount of TiO_2 deposited on materials.

1.2. The treatments durability (Resistance to washing)

The morphology of the textile surface (Table 7) and the amount of N-TiO_2 (Table 8) remained on the knits after 5 washing cycles were investigated to determine the treatments durability.

***Table 7:** SEM images of cotton knit after 5 washing cycles*

			
2N	**2Nbis**	**3N**	**3N bis**

After 5 washing cycles, the cotton fibers are covered with a high number of particles, most of them being present as large clusters, which dimensions vary from 145.7nm to 2µm. The polymer layers are not much affected by washing, only from place to place being disrupted.

***Table 8:** EDAX spectra of the cotton knit after 5 washing cycles*

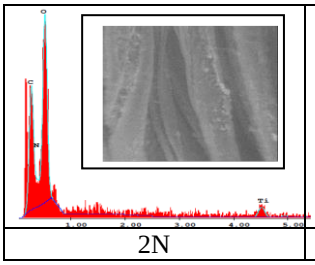
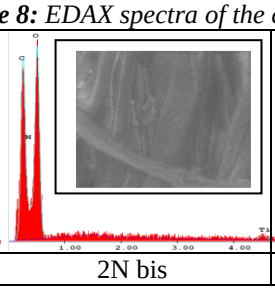
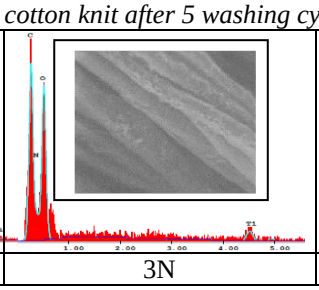
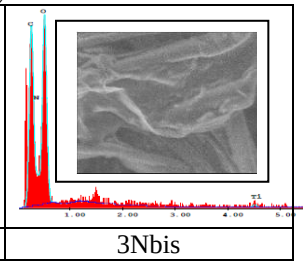
			
2N	2N bis	3N	3Nbis

***Table 9:** Elements founds on cotton knit initial and after 5 washings*

Ti K, Wt, %	2N	2N bis	3N	3N bis
Initial	**11.69**	6.42	**13.99**	7.05
After 5 washings	13.03	5.48	11.90	3.53
Removed, %	+ 10.28	14.64	14.94	49.93

Except the 3N bis cotton knit, the adherence of the particles is very high if we consider the amount found on the fabrics after 5 washings which decreases by 12.57% for 2N, 4.51-6.42% for 2N bis, and 15% for 3N in comparison with the initial fabrics. It seems that addition of Itobinder instead to improve the particle adherence to the textiles surface, remove a large part of them, especially in the case of 3N bis knit (Table 9).

1.3. Photocatalytic evaluation of the N-TiO_2 cotton knit after 5 washing cycles

Table 10: *Aspect of the cotton knit after 5 washing cycles and exposed 4 hours to visible light*

Blank	2N	2N bis	3N	3N bis

Table 11: *Trichromatic coordinates of the cotton knit after 5 washing cycles and exposed 4 hours to visible light*

Material	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	85.52	-2.94	-4.59	1.19	12.27	5.88	13.66	-13.01	1	54.71
2N	76.25	-8.74	-12.28	**6.17**	10.87	14.85	19.41	-18.40	1	**40.46**
2Nbis	85.14	-4.10	-3.47	5.91	13.29	14.06	**20.23**	-19.32	1	44.81
3N	75.06	-9.02	-12.22	4.64	12.03	13.80	18.88	-18.28	1	42.67
3Nbis	85.51	-4.41	-3.42	5.21	11.06	13.24	18.02	-17.15	1	49.93

According to the tones on greyscale, the methylene blue is decolorized on all the materials, including the untreated ones (Tables 10 and 11). If we consider the lightness values (dL*), the sample 2N shows the most intensive discoloration followed by 2Nbis, 3Nbis and 3N samples. The da* and db* values are positive, meaning that color for all the samples is shifted to longer wavelength (red-yellow). If we consider the color difference values (dE*) the highest discoloration is shown by sample 2Nbis due to higher values of da* and db*, knowing that the total color difference is calculated using the following formula:

$$\Delta E^* = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \quad \textbf{(1)}$$

The contradictories values, especially if we take into account the % Strength SUM, are determinate by the non-uniformities of the materials which don't allowed a uniform dyeing of the fabrics and the dependence of the color measurement by a multitude of parameters (surface texture, uniformity, instrumental geometry, dyes shades, etc.)

Table 12: *Chromatic coordinates of the cotton knit after 5 washing cycles and exposed 9 hours to natural solar light*

Material	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	87.72	-2.02	-1.49	3.18	2.19	3.71	5.36	-4.19	2.50	68.80
2N	72.94	-7.01	-9.91	1.41	5.46	9.57	11.11	-10.99	1.50	85.98
2Nbis	87.82	-1.88	0.81	5.51	6.28	9.77	12.86	-10.07	1.00	65.14
3N	73.00	-7.10	-10.39	8.07	7.16	15.95	19.25	-17.37	1.00	50.01
3Nbis	88.33	-2.09	0.85	**8.89**	7.76	13.20	17.71	-13.54	1.00	44.09

The values of brightness and % Strength SUM (Table 12) demonstrate that the most intensive discoloration is shown by 3Nbis followed by 3N and 2N bis. The color difference is almost double or triple comparing with blank sample.

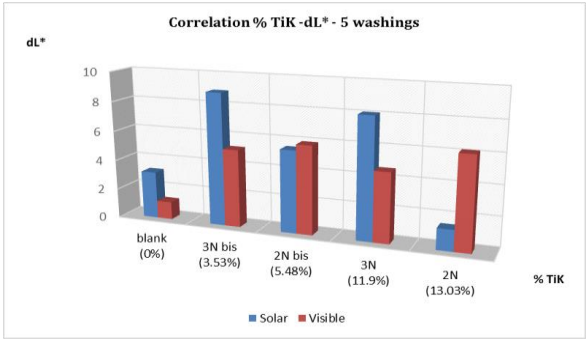


***Fig. 3**: Correlation % TiK -dL* - 5 washings*

Based on dL* values, it can be concluded that, except the sample 2N, the efficiency of N-TiO_2 is higher under the solar light than under visible light (Fig. 3).

2. CONCLUSIONS

The obtained results showed that after 5 washings, the particles adherence to the substrate is high and the photocatalytic effects are not significantly impaired. The cotton knit treated with N-TiO_2 nanoparticles show an improved photocatalytic effects under visible light.

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