The photocatalytic effects of textile materials treated with TiO_2 and Fe/TiO_2

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REZUMAT – ABSTRACT

Efectele fotocatalitice ale materialelor textile tratate cu TiO_2 și Fe/TiO_2

*Lucrarea de cercetare a avut drept scop determinarea activității fotocatalitice a materialelor textile tratate prin impregnare-uscare-condensare și cationizare-impregnare-uscare-condensare cu TiO_2 si TiO_2 dopat cu fier. Eficiența fotocatalitică a fost evaluată prin măsurarea diferențelor de culoare (dL*da*db, dE*, dC*, dH*) ale materialelor expuse și ne-expuse la lumina vizibilă și UV pe un spectrofotometru Hunter lab. Activitatea antifungică s-a evaluat conform standardului ISO 20743:2007. Rezultatele demonstrează că sub lumina vizibilă, independent de metoda de tratare, cea mai intensă decolorare se produce pe țesătura de poliester tratată cu TiO_2-Fe. Sub lumina UV, cea mai intensă decolorare este indusă de TiO_2-Fe pe materialele cationizate. Tratamentul de cationizare nu are efecte pozitive asupra fotodegradarii MB, diferențele de culoare și luminozitate fiind similare sau mai mici decât cele obținute în cazul tratării materialelor doar prin impregnare. Gradul de decolorare al țesăturilor din PET si PET/co pătate cu MB este mai mare sub lumina vizibilă decât sub lumina UV. Toate probele demonstrează o foarte bună reducere a Candida a., de 100% în cazul probelor tratate prin impregnare. Ratele de reducere ale Epidermophyton f. variază între 46,87% (D-V1-Fe) și 99,18 % pentru A-V2-Fe.*

Cuvinte-cheie: *TiO_2 dopat cu fier, fotocatalizatori, textile, anti-fungice, impregnare-uscare-condensare*

The photocatalytic effects of textile materials treated with TiO_2 and Fe/TiO_2

*The research has been focused on the photocatalytic activity of the textile materials treated with TiO_2 and TiO_2 iron doped by pad-dry-cure and cationization – pad-dry-cure. The fabrics have been exposed to UV and visible light. The photocatalytic efficiency was evaluated by measuring the color differences (dL*da*db, dE*, dC*, dH*) of the exposed and un-exposed samples on a Hunter lab spectrophotometer. The anti-fungal activity was assessed according modified ISO 20743:2007 standard. The results show that under visible light, independent of treatment used (padding or cationization – padding), the highest discoloration is produced by TiO_2-Fe on polyester. Under UV light, the highest discoloration is produced by TiO_2-Fe only for the cationized materials. The cationization pre-treatment has no positive effect on MB photodegradation, the colour and lightness difference being similar or smaller than those obtained in the case of padding treatment without cationization. The degree of discoloration of PET and PET/co fabrics stained with MB is higher under visible light then under UV light. In the case of cotton, a slightly higher discoloration under UV light is noticed. All samples yielded very good reduction rates of Candida a., with 100% reduction for samples treated by padding. The reduction rates of Epidermophyton f. varies between 46.87% (D-V1-Fe) and to 99.18 % for A-V2-Fe.*

Keywords: *Fe doped TiO_2, photocatalysts, textiles, anti-fungal, pad-dry-cure*

INTRODUCTION

Many attempts have been made to create photocatalytic textiles by the incorporation of titania with cellulose or cotton surfaces [1], graft nano TiO_2 on cotton fabrics using cross-link method [2–4], pad-dry-cure method [5, 6], using SiO_2 as binder [7], automated spray technique [8], sputtering [9].

Unfortunately, due to the low efficiency of TiO_2 under visible light and recombination between the photogenerated electrons and holes, the photocatalytic effect is almost non-observable. To increase the photocatalytic efficiency, TiO_2 was doped with metals [10, 11] and non-metals [12, 13]. Even a multitude of doped photocatalysts have been described by different authors, few data are found about the their deposition on textiles and the photocatalytic effects. In this research, TiO_2 and Fe^{3+} doped TiO_2 nanoparticles were deposited on three types of fabrics by padding and cationization–padding. The textiles coated as previously described were characterized by SEM, EDX, contact angles. The photocatalytic activity of the fabrics under UV and visible light was evaluated following the degradation of methylene blue.

MATERIALS AND METHODS

Materials

Fabrics: 100% polyester woven fabric (A), weight – 142 g/m^2, 100% cotton (D), weight – 260 g/m^2 and

50/50% polyester/cotton (G) weight – 201 g/m^2 fabricated by KIVANÇ Tekstil San. Ve Tic. A.S.
Chemicals
- **TiO_2**, rutile and anatase mixture (Aldrich), particles size below 100 nm.
- **TiO_2-Fe**, prepared by Kumoh National Institute of Technology (KIT), South Korea.
- **ITOBINDER AG:** polyacrylic binder (LJ Specialities, UK).
- **Itofix EZF**: polyethylene polyamine resin (LJ Specialities, UK).
- **BIOWET PB**: anionic surface agent.
- **PVP:** Polyvinylpyrrolidone (Aldrich).

Methods

Method to prepare photocatalytic solutions: 1 gram of Fe-TiO_2, respectively, TiO_2 was dispersed in 190 ml of distilled water on ultrasonic bath (US). 10 mL Biowet PB was added and stirred 30 minutes on US, then 1 g of PVP added and stirred for 30 minutes on US bath. 10 ml of polyacrilic binder (ITOBINDER AG) was dropped into above dispersion and intensively mixed by a mechanical stirrer.
Finally, the dispersion was diluted with 388 mL water and stirred for 1 hour on US to get a relatively stable solution with the following composition:
- solution 4: 1.67 g/L TiO_2-Fe, 16.67mL/L BIOWET PB, 1.67 g/LPVP, 16.67mL/L ITO; pH = 5
- solution 5: 1.67 g/L TiO_2, 16.67mL/L BIOWET PB, 1.67 g/LPVP, 16.67mL/L ITO; pH = 6

Methods to treat textiles

Two methods were used to coat the textiles with TiO_2 and TiO_2-Fe:

a. Pad-dry-cure: fabrics were padded 3 times with solutions 4 (**code 4-V2**) and 5 (**code 5 -**V1), and then dried at 120°C for 2 minutes and condensed to 150°C for 4 minutes.

b. Cationization – Pad-dry-cure: materials have been padded (foulard) in a solution containing 10 g/l Itofix EZF then were dried at 120°C for 2 minutes and condensed at 170°C for 1 minute. The dried materials were padded (foulard) with solution 4 (**code 4 - V4**), and respectively, solution 5 (**code 5 -V3**), dried at 120°C for 2 minutes and condensed at 150°C for 4 minutes.

Characterization of treated textiles

Analysis: shape, size and particle dispersion on fabrics' surface were analyzed on a scanning electron microscope (Quanta 200, FEI, Netherlands) equipped with an X-ray energy dispersive spectrometer (EDX) for identification of elements existing on materials. To evaluate the photocatalytic effect the fabrics were immersed in $2x10^{-5}$ mL/L methylene blue solution for 30 minutes, dried under infrared radiation source and exposed to UV (254nm) and in laboratory equipment Xenotest equipped with a xenon lamp that simulates the visible light. The photocatalytic efficiency was evaluated by measuring the color differences (dL*da*db, dE*, dC*, dH*) between the exposed and un-exposed samples on a Hunter lab spectrophotometer, at 10° observer angle and D65 light.

RESULTS AND DISCUSSIONS

SEM analyses

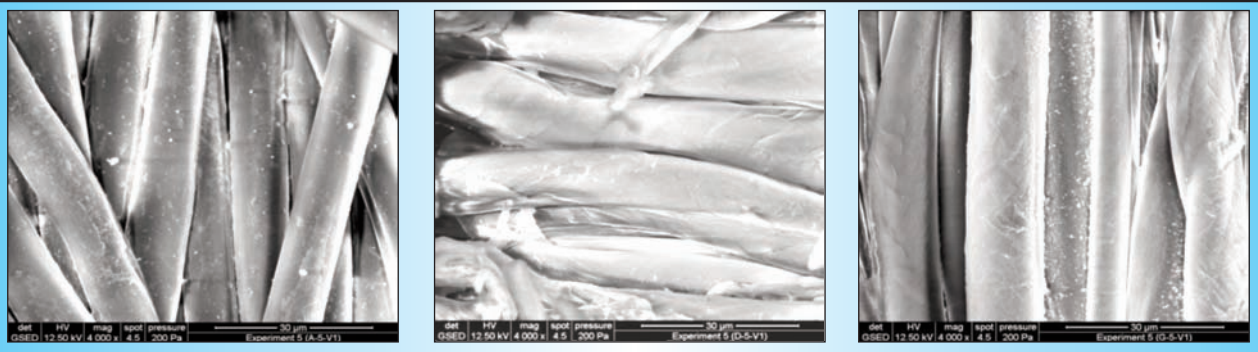
SEM images of treated materials are presented in table 1.
SEM images (table 1) demonstrates that by padding (V1, V2), regardless of used photocatalysts, polyester fibers are coated evenly with a higher number of particles, less agglomerated than those deposited on cotton. This phenomenon could be explained by the two slightly different types of interactions between the particles and materials surface. Thus, in the presence of water, the cellulose and polyester fibres gets a slight negative charge due to ionization of hydroxyl and, respectively ester groups. The polyester being hydrophobic and not having hydrophilic groups, the negative charge is less pronounced compared to the cellulose. The TiO_2/polyacrylate dispersion has a pH around 6–6.5. At this pH, sodium polyacrylate is dissociated into sodium ions and negative carboxyl groups. Sodium ions neutralize some of the negative charges (hydroxyl) of cellulose allowing the deposition of a larger quantity of polyacrylate than deposited on polyester material. In the same time, between the polyacrylate layers covering the textile materials and TiO_2 particles, which are also coated with a thin layer of polyacrylate, electrostatic repulsion forces occur, leading to a decrease of TiO_2 particles on cotton materials.
In the case of TiO_2 deposition on cationized materials (V3), SEM images show that TiO_2 particles are dispersed non-uniformly on all types of fibers, are present in the form of clusters with different shapes and sizes, the smallest being on the fibers polyester. Polyethylene polyamine cationic resin forms a more uniform and thinner layer on polyester fibers than that of cotton. In the case of TiO_2-Fe deposition on cationized materials (V4), Fe-TiO_2 particles are agglomerated, dispersed unevenly, in greater numbers on cotton than on polyester fabrics. The smaller particle clusters are found on polyester.

Quantification of the TiO2 and TiO2–Fe by EDX

The results of metal quantification by EDX are shown in tables 2 and 3.
The highest amount of TiO_2 is deposited by cationization – padding, on polyester fabrics (A5-V3) followed by polyester/cotton and cotton. The amount of TiO_2 deposited by padding (V3) on initially cationized material is ≈ 2.5 times higher on polyester fibers than on cotton fibers. By pad-dry-cure method (V1), the quantity of TiO_2 particles decreases in order polyester/cotton > polyester > cotton. On contrary, except the polyester fabrics, TiO_2-Fe particles are deposited in larger quantity by pad-dry-cure than by cationization-padding. The largest amounts of titanium dioxide doped with iron (V4) are deposited on the

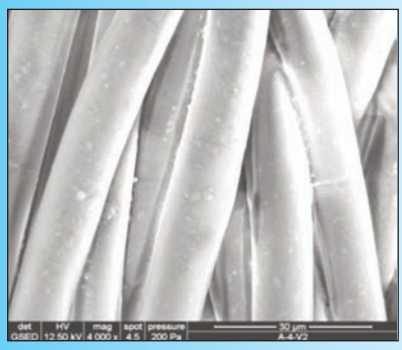
Table 1

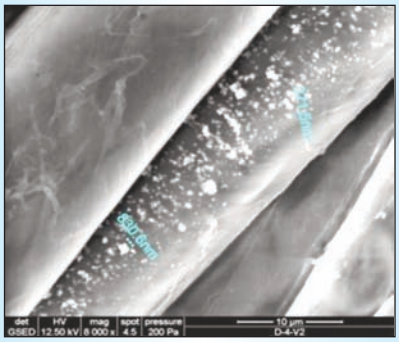
SEM IMAGES OF THE MATERIALS TREATED WITH SOLUTION 4 AND 5

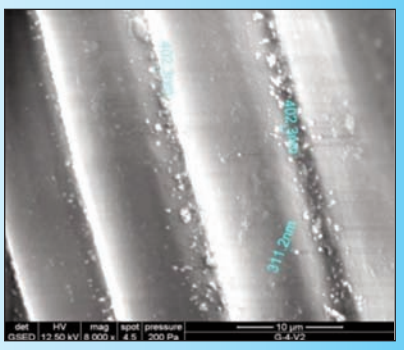

A5-V1

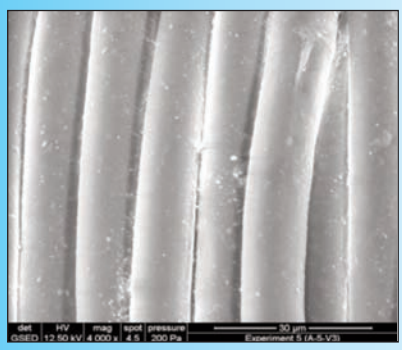
D5-V1

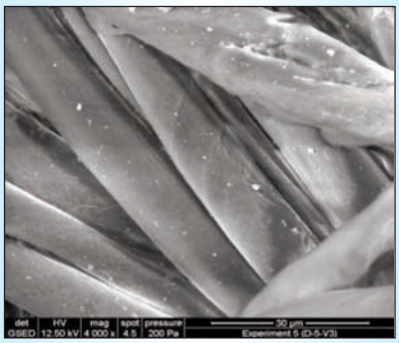
G5-V1

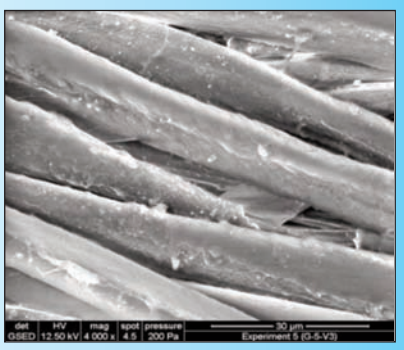

A4-V2

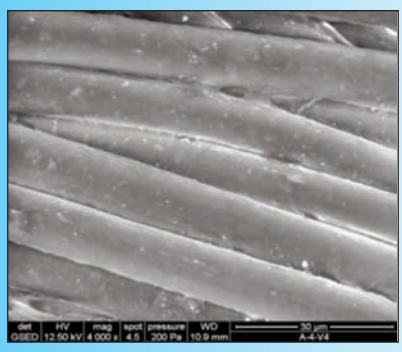

D4-V2

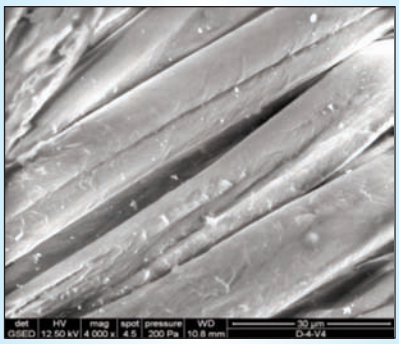

G4-V2


A5-V3


D5-V3


G5-V3


A4-V4


D4-V4


G4-V4

cotton/polyester fabric, followed by polyester and cotton. On 50/50% cotton/polyester materials treated by padding (V1, V2) a greater amount of photocatalysts, regardless of their composition, is deposited.

Due to the small particles size (less than 100nm), the amount of TiO_2 deposited on polyester and polyester/cotton is higher than that of TiO_2-Fe. Apparently, the material structure has a decisive influence on the amounts of deposited titanium dioxide. Thus, on cotton/polyester (G5-V1) fabric three times more TiO_2 is deposited than on polyester fabric (A5-V1) and five times more than on cotton fabric (D5-V1). This massive deposition is due both to the polyester fibers (less negatively charged) and to the nonplanar structure of the material, composed of yarns with different fineness

Table 2

EDX SPECTRUM OF THE MATERIALS COATED WITH TiO_2 AND TiO_2-Fe BY PADDING

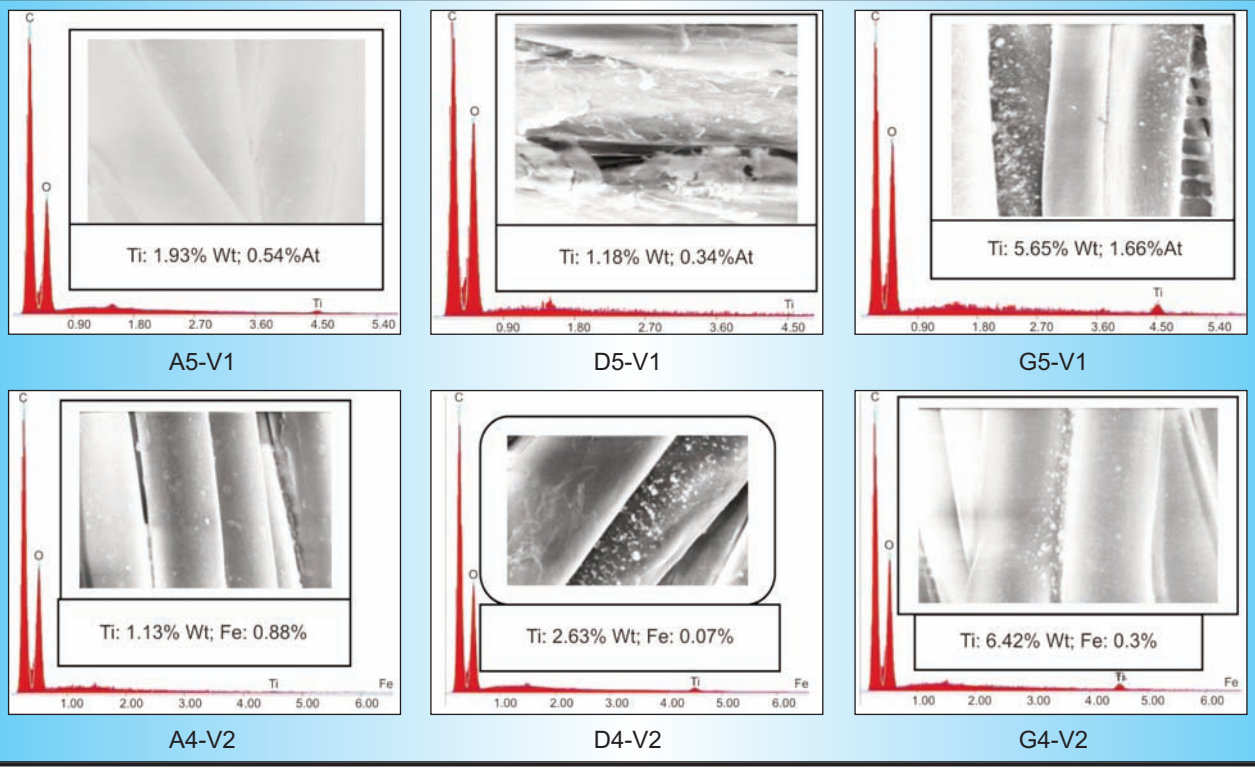


Table 3

EDX ANALYSIS OF THE MATERIALS TREATED WITH SOLUTIONS 4 OR 5 BY PADDING (V1, V2) AND CATIONIZATION-PADDING (V3, V4)

	TiO_2		TiO_2- Fe		TiO_2		TiO_2- Fe		TiO_2		TiO_2- Fe	
Element, %Wt	A5-V1	**A5-V3**	A4-V2	**A4-V4**	D5-V1	**D5-V3**	D4-V2	**D4-V4**	G5-V1	**G5-V3**	G4-V2	**G4-V4**
TiK	**1.93**	**8.10**	**1.13**	**2.55**	**1.18**	**3.30**	**2.63**	**1.40**	**5.65**	**7.54**	**4.07**	**2.81**
FeK	0	0	**0.88**	**0.81**	0	0	**0.07**	**0.88**	0	0	**0.30**	1.16

creating trenches favourable to physical deposition of particles.

The evaluation of the photocatalytic efficiency of the treated materials under visible light

The effect of the visible light on the materials treated with photocatalysts is shown in the tables 4 and 5.

As demonstrated by the dL* and dE* values, the highest discoloration at visible light is produced by the treatment with TiO_2-Fe without pre-cationization on polyester (A4 V2) and cotton/polyester (G4 V2). In the case of cotton treated with TiO_2-Fe (D4 V4), the cationization pre-treatment brings a small enhancement of discoloration degree, the dL* values being in this case bigger than the one obtained for the process without cationization (D4 V2). The samples treated with TiO_2 have a lower grade of discoloration, presenting smaller values of dL* and dE* compared to those treated with TiO_2-Fe. Nevertheless, the best results from discoloration point of view are obtained on polyester (A5 V1) followed by cotton/polyester (G5 V1) treated by padding without pre-cationization. Also, the color is more shifted to long wavelength for the materials coated with TiO_2-Fe than for TiO_2.

The evaluation of the photocatalytic efficiency of the treated materials under UV light

The effect of the UV light on the materials treated with photocatalysts is shown in the tables 6 and 7.

In the case of the materials treated with TiO_2 by padding without pre-cationization (V1) and exposed to UV light, the most intense discoloration (the highest dL* and dE* values and the smallest note on gray scale) is observed for 100% cotton fabric (D5-V1), followed by 100% polyester fabric (A5-V1) and that of 50/50% polyester/cotton (G5-V1). The cationization pre-treatment (V3) has no positive effect on MB photodegradation, the difference in lightness values being smaller (very close to one) in comparison with the variants treated without cationization. There cannot

Table 4

TREATED MATERIALS STAINED WITH 2x10^{-5}mol/L MB EXPOSED TO VISIBLE LIGHT 4 HOURS

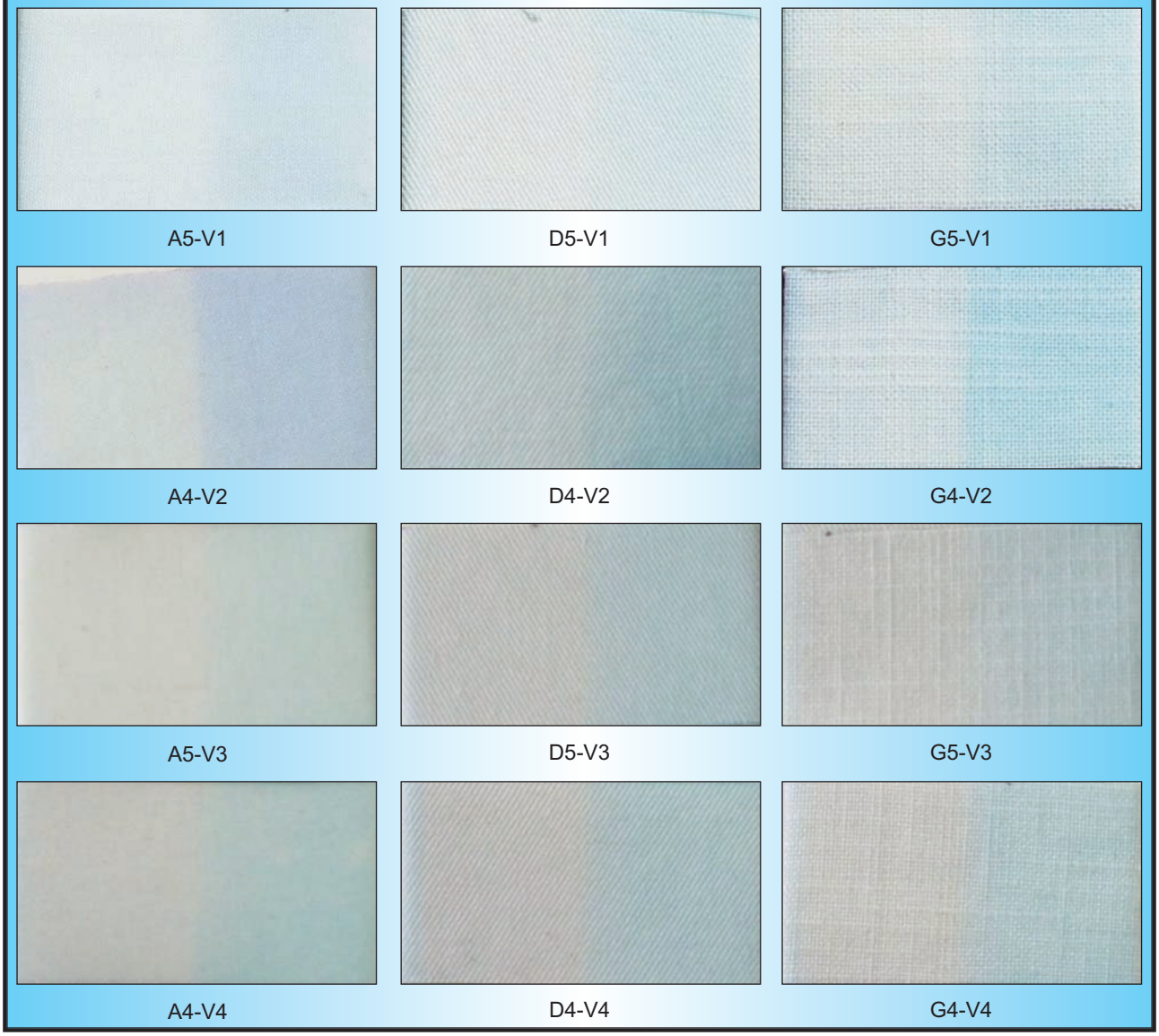


Table 5

CHROMATICITY COODINATES OF THE TREATED MATERIALS BY PADDING (V1, V2) AND CATIONIZATION-PADDING (V3, V4) STAINED WITH 2x10^{-5}mol/L MB EXPOSED TO VISIBLE LIGHT 4 HOURS

	L*	a*	b*	dL*	da*	db*	dE*	dC*	dH*	Note
A5 V1	92.29	–3.84	–1.14	5.37	4.99	7.47	10.47	–8.33	–3.37	1.5
A4 V2	91.85	–4.09	–0.96	8.9	8.27	13.71	18.32	–15.03	–5.86	**1**
A5 V3	96.26	–0.9	3.05	2.61	6.24	3.09	7.44	–3.96	–5.73	2
A4 V4	88.61	–3.77	–0.87	5.92	10.21	8.5	14.55	–12.97	–2.91	**1**
D5 V1	91.11	–2.22	–0.16	2.55	4.95	3.77	**6.72**	**–5.95**	–1.82	2
D4 V2	88.08	–3.21	–0.6	2.21	6.41	4.44	**8.11**	**–8.52**	–1.53	**2**
D5 V3	89.58	–3.1	–1.34	2.51	7.42	4.2	8.89	–8.51	–0.48	1.5
D4 V4	88.5	–2.54	–0.12	3.07	8.29	5.43	10.38	–9.63	–2.36	**1.5**
G5 V1	91.87	–2.62	0.6	3.29	6.09	5.31	8.72	–7.21	–3.65	1.5
G4 V2	88.67	–4.13	–1.03	6.86	10.53	9.58	15.81	–13.1	–2.31	**1**
G5 V3	90.47	–2.95	–0.51	2.69	5.86	4.09	7.64	–3.31	–1.69	2
G4 V4	88.85	–2.56	0.52	2.88	8.51	5.19	10.38	–9.4	–3.31	**1.5**

Table 6

EDX SPECTRUM OF THE MATERIALS COATED WITH TiO_2 AND TiO_2-Fe BY PADDING

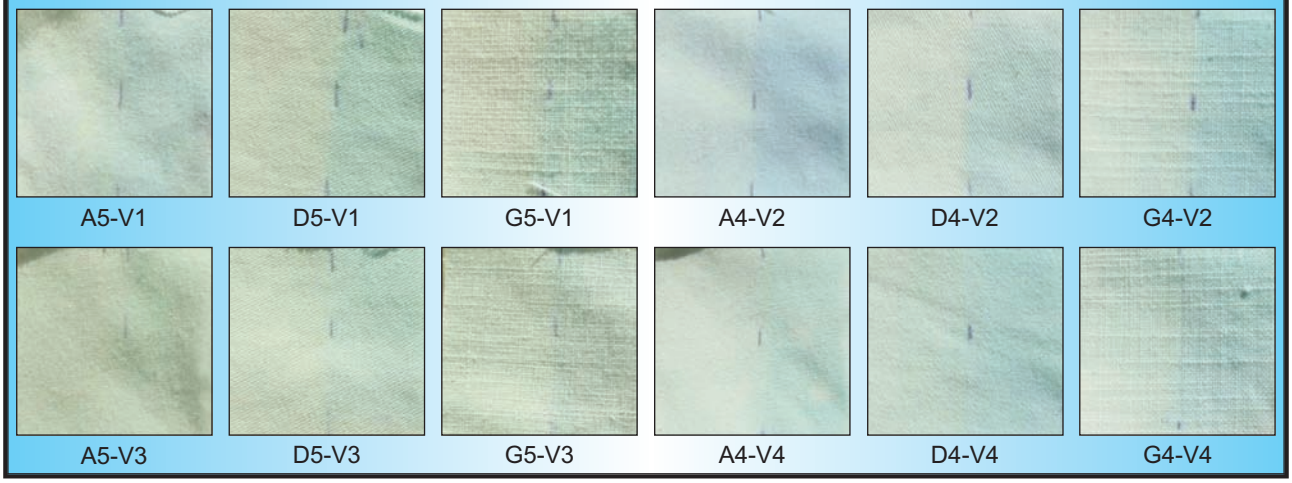


Table 7

CHROMATICITY COORDINATES OF THE TREATED MATERIALS BY PADDING (V1, V2) AND CATIONIZATION-PADDING (V3, V4) STAINED WITH $2x10^{-5}$ mol/L) MB EXPOSED 23 HOURS TO UV (254 nm) LIGHT

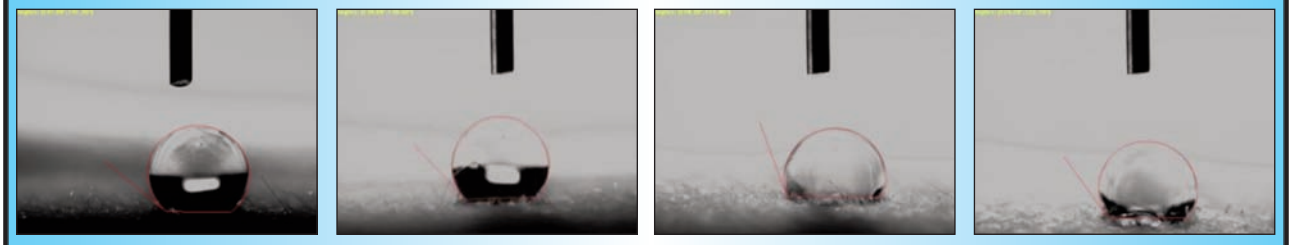
	L*	a*	b*	dL*	da*	db*	dE*	dC*	dH*	Note
A5 V1	85.52	–6.81	–7.06	1.8	2.41	5.86	6.59	–6.06	–1.84	2
A4 V2	86.45	–4.28	–6.20	**0.74**	**1.99**	**-0.20**	**2.13**	–1.14	–1.64	3.5
A5 V3	93.01	–1.71	0.38	0.74	1.67	2.28	2.92	–2.12	–1.86	3.5
A4 V4	92.21	–1.79	1.02	1.41	5.15	3.04	6.14	–5.17	–3.01	2
D5 V1	88.94	–4.02	–0.64	3.15	6.71	5.89	**9.47**	–8.49	–2.76	**1.5**
D4 V2	90.43	–1.91	1.63	**4.49**	**5.03**	**6.17**	**9.14**	–5.78	–5.48	**1.5**
D5 V3	87.15	–6.31	–2.28	1.75	3.73	3.97	5.72	3.42	3.88	2.5
D4 V4	88.25	–4.32	0.37	2.97	4.92	5.74	8	–6.18	–4.13	2
G5 V1	86.52	–7.71	–3.63	0.79	2.8	3.39	4.47	–1.42	2.58	2.5
G4 V2	86.65	–4.12	–6.03	**2.38**	**6.18**	**1.55**	**6.80**	–5.48	3.24	**2**
G5 V3	86.54	–5.67	–3.12	0.89	1.09	2.13	2.25	1	2.08	3.5
G4 V4	85.95	–7.4	–2.33	2.57	5.25	4.59	7.43	–2.11	0.17	1

be made a correlation between the amount of TiO_2 founded on the materials and the degree of discoloration. Even if the amount of TiO_2 found on the materials are bigger in the case of cationization pretreatment, the obtained discoloration degree is smaller. In the case of the materials treated with TiO_2-Fe by padding without pre-cationization (V2) and exposed to UV light, according to difference in lightness (dL*) and total color difference (dE*), the most intense discoloration is obtained on cotton fabric (D4 V2), being followed by blended cotton/polyester (G4 V2), and, finally by the polyester fabric (A4 V2), who presents the lowest degree of discoloration. The cationization-padding treatment with TiO_2-Fe (V4) does not lead to improved discoloration degree, the dL* values being similar or smaller than those obtained in the case of padding treatment without cationization. Under the UV light, a better discoloration degree is noticed on 100% cotton and 50/50% polyester/cotton treated by padding with TiO_2-Fe than with TiO_2. In the case of 100% polyester the discoloration has low level being similar for both formulations. Overall, the degree of discoloration of the polyester and polyester/cotton fabrics stained with MB is higher under visible light as compared to the exposure to UV light. In the case of cotton, however, it can be seen a slightly higher discoloration when using the UV light spectrum.

From the point of view of efficiency of the tested fotocatalysts, TiO_2-Fe applied by pad-dry-cure without cationization, provides the most advanced photodegradation of MB dye under the visible light, especially when is applied on 100% polyester fabrics. Even under UV light, TiO_2-Fe based photocatalyst induces an intense discoloration though it is deposited in much smaller amounts on the materials than TiO_2. The better efficient photocatalytic effects of TiO_2-Fe than TiO_2 are determined by a more efficient separation of photogenerated electrons and holes, Fe^{3+} acting as collector of holes and/or electrons [14]:

Table 8

CONTACT ANGLES IMAGE ON THE MATERIALS TREATED WITH TiO_2-Fe (V4)



100% polyester (A) initial: 136.20; 136.90	A4-V4: 123.6; 122.88	D4-V4: 105.82; 106.2	G4-V4: 111.28; 110.42

$$Fe(III) + h^+_{VB} \rightarrow Fe(IV) \quad (1)$$

$$Fe(IV) + OH^- \rightarrow Fe(III) + {}^{\bullet}OH \quad (2)$$

$$Fe(III) + e^-_{CB} \rightarrow Fe(II) \quad (3)$$

$$Fe(II) + Ti(IV) \rightarrow Fe(III) + Ti(III) \quad (4)$$

Fe^{2+} ions being relatively unstable due to loss of energy by transition from d5 (half filled with electrons) to d6 orbital, tend to return to the valence 3+ (d5) by releasing the trapped electron. Since the energy level of Fe (II)/Fe (III) is very close to that of Ti (III) / Ti (IV) level, the electrons trapped by the Fe (II) can be easily transferred to the neighbouring surficial Ti (IV) [15], where they can combine with oxygen molecules generating reactive species, O°_2 and $^{\circ}OH$:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O^{\circ-}_2 \quad (5)$$

Consequently, due to promotion of the electrons and holes separation under the influence of light, Fe (III) improves the photocatalytic efficiency of TiO_2.

In addition, in such photocatalytic systems, may generate H_2O_2 on the surface of TiO_2 [16]. Simultaneous presence of Fe^{2+} and H_2O_2 in an acidic environment can produce $^{\circ}OH$ which act as oxidizing agents:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\circ}OH + OH^- \quad (6)$$

The effect of the photocatalytic treatment on the materials hydrophilic properties

The initial cotton and cotton/polyester fabrics are hydrophilic, while polyester fabric is hydrophobic. After padding, all the materials become hydrophilic.

By cationization-padding, the materials treated with TiO_2-Fe (V4) become hydrophobic (table 8).

In the variant V4, it is found that the value of the contact angle decreases for 100% polyester fabric from (138.2, 138.93) to (123.6, 122.88) showing a slight hydrophilization of the material. Instead, the material of cotton and polyester/cotton become more hydrophobic because cotton being negatively charged has a higher affinity to quaternary compounds than polyester. Consequently, on the cotton surface a larger amount of polyethylene polyamine resin is deposited whose hydrophobic alkyl chains are oriented toward the exterior of the fabric. What must be emphasized is that the same cationized materials under the same conditions but using TiO_2 instead of iron doped TiO_2 (V3) do not change their hydrophilic nature, contrary the polyester fabric becomes more hydrophilic after treatment with TiO_2. A hypothesis on this behaviour would be the lower acidity (pH = 5) of the TiO_2-Fe solution due to which secondary and tertiary amino groups of polyamine resin used are protonated and attract more hydrophilic carboxyl group of used polyacrylic binder. Consequently, due to electrostatic repulsion between the carboxyl groups of the acrylic binder coating the cotton surface and those found on the surface of TiO_2, the photocatalyst amount deposited on the material is lower. In addition, free quaternary groups involved in ionic bonds with the hydroxyl groups of cellulose can form ionic bonds with acrylic polymer (Itobinder AG), increasing the hydrophobicity of cotton fabric.

Antifungal activity of the materials treated with TiO_2-Fe

The treated textile materials and controls were tested in duplicate against 2 pathogenic strains, *Candida albicans and Epidermophyton floccosum* by using modified **ISO 20743:2007** standard, absorption method, an evaluation method where the inoculum is inoculated directly onto the samples. Colony plate count method was used after 24 h incubation for quantification of Colony Forming Units (UFC), and percentage and logarithmic reduction rates were calculated against control sample for each material.

When tested against *Candida a.*, all samples yielded very good reduction rates, with reduction rates of over 90%, with maximum percent of 100% for samples A4-V2, D4-V2 and G4-V2. Highest inoculum concentration was of 24400 CFU/mL for control sample C (Aster).

When tested against *Epidermophyton f.,* the reduction rates of tested materials varied between 46.87% (D4-V2) and highest reduction rate of 90.58% for A4-V2. Highest inoculum concentration was of 15360 CFU/mL for control sample A (Dockers). It is important to notice that, due to the irregularity of textile materials surface, an uniform and homogeneous dispersion of photocatalytic particles on theirs surface is practically not possible to be achieved. More than that, the tested samples were taken randomly, so the antibacterial activity is difficult to be related to

Table 9

ANTIMICROBIAL ACTIVITY AGAINST *CANDIDA ALBICANS*

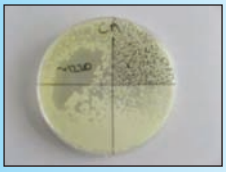
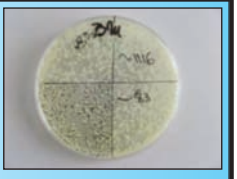
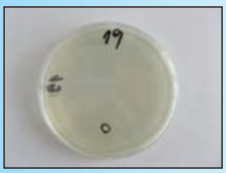
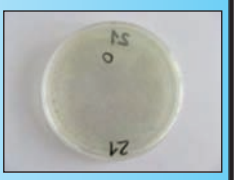
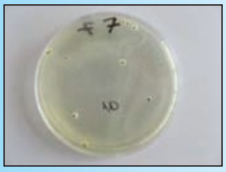
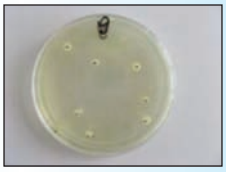
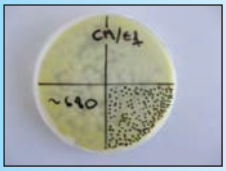
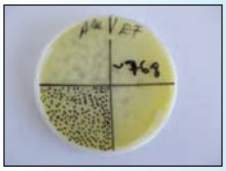
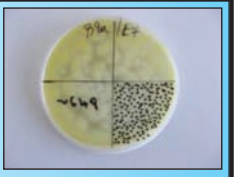
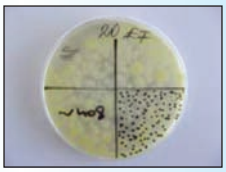
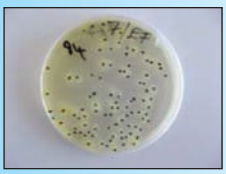
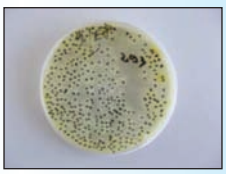
Sample/Results	Picture	Sample/Results	Picture	Sample/Results	Picture
(**CM**) ASTER C_i=2.440x10^4 UFC/mL Control		(**AM**) DOCKERS C_i= 2.312x10^4 UFC/mL Control		(**BM**) GOLF C_i=2.232x10^4 UFC/mL Control	
(**19**) A4-V2 C_i=2.440x10^4 CFU/mL C_{24h}=0 CFU/mL R%=100 Log_{10} red.=4.38		(**20**) D4-V2 C_i=2.312x10^4 CFU/mL C_{24h}=0 CFU/mL R%=100 Log_{10} red.=4.36		(**21**) G4-V2 C_i=2.232x10^4 CFU/mL C_{24h}=0 CFU/mL R%=100 Log_{10} red.=4.34	
(**7**) A4- V4 C_i=2.440x10^4 CFU/mL C_{24h}=2x10^2 CFU/mL R%=99.18		(**9**) D4-V4 C_i=2.312x10^4 CFU/mL C_{24h}=2x10^2 CFU/mL R%=99.13		(**8**) G4-V4 C_i=2.232x10^4 CFU/mL C_{24h}=6x10^1 CFU/mL R%=99.73	

Table 10

ANTIMICROBIAL ACTIVITY AGAINST *EPIDERMOPHYTON FLOCCOSUM*

Sample/Results	Picture	Sample/Results	Picture	Sample/Results	Picture
(**CM**) ASTER C_i=1.36x10^4 UFC/mL		(**AM**) DOCKERS C_i=1.536x10^4 UFC/mL		(**BM**) GOLF C_i=1.296x10^4 UFC/mL	
(**19**) A4-V2 C_i=1.36x10^4 CFU/mL C_{24h}=1.28x10^3 CFU/mL **R%=90.58** Log_{10} red.=1.03		(**20**) D4-V2 C_i=1.536x10^4 CFU/mL C_{24h}=8.16x10^3 CFU/mL **R%=46.87** Log_{10} red.=0.27		(**21**) G4-V2 C_i=1.296x10^4 CFU/mL C_{24h}=4.8x10^3 CFU/mL **R%=62.96** Log_{10} red.=0.43	
(**7**) A4- V4 C_i=1.36x10^4 CFU/mL C_{24h}=1.68x10^3 CFU/mL **R%=87.64** Log_{10} red.=0.91		(**9**) D4-V4 C_i=1.536x10^4 CFU/mL C_{24h}=5.86x10^3 CFU/mL **R%=61.84** Log_{10} red.=0.42		(**8**) G4-V4 C_i=1.296x10^4 CFU/mL C_{24h}=2.26x10^3 CFU/mL **R%=82.56** Log_{10} red.=0.76	

the content of TiO_2-Fe particles. As for example, even A4-V2 sample contains 1.13% TiO_2-Fe, the antibacterial reduction rate for *Epidermophyton floccosum* is higher than that of A4-V4 fabric which contains 2.55% TiO_2-Fe.

CONCLUSIONS

As results demonstrate, the largest amount of **TiO_2** is deposited on **cationised** materials, regardless the fabric composition while the largest amount of **TiO_2-Fe** is deposited by **pad-dry-cure** method except polyester fabric. By both methods, the greatest amount of photocatalyst is found on **pes/cotton** fabric.

The **highest discoloration under visible light** is produced by treatment with **TiO_2-Fe**, by both methods, especially on polyester and cotton/polyester. The **discoloration is stronger** on materials treated

by **pad-dry-cure** than by cationization-padding. Under the **UV light**, the most intense discoloration is noticed on the materials treated by **cationisation-padding** with **TiO_2-Fe** than with TiO_2.

All samples yielded very good reduction rates of *Candida a.*, with 100% reduction for samples treated by pad-dry-cure method. The reduction rates of *Epidermophyton f.* varies between 46.87% (D-V1-Fe) and to 99.18 % for A-V2-Fe, the best antibacterial activity being for the cationised materials.

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