

## Multi-functional Cotton Fabrics Using Nano-Technology and Environmentally Friendly Finishing Agents

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**T**<sub>io<sub>2</sub></sub> NANOPARTICLES were prepared using sol-gel technique. The prepared nanoparticles were analyzed using transmission electron microscope (TEM). Cotton fabrics were treated using prepared TiO<sub>2</sub> nanoparticles in presence of citric acid and commercially flame retarding agent named Flovan CWF to produce cotton fabrics having multi-functional properties (anti-crease, self cleaning, and flame retardant) using pad-dry-cure- method. The treated fabrics examined by several testing and analysis methods such as crease recovery angle (CRA), tensile strength (TS), elongation at break (El), whiteness index (WI), self cleaning through K/S measurement and flame retarding properties through thermogravimetric analysis (TGA). Results obtained reveal that the optimum condition for the preparation of multi-functional cotton fabric is by using the following formulation (6 % citric acid, 3 % TiO<sub>2</sub>, 300g/l Flovan CWF) padded for pick-up 100%, dried at 100°C for 5min and cured at 160°C for 3 min. The presence of TiO<sub>2</sub> nanoparticles on the surface of the fabrics was proofed using EDX and the fabrics were examined also using scanning electron microscope.

**Keywords:** Multifunctional, cotton fabrics, TiO<sub>2</sub>, self cleaning, anti-crease, finishing, nanoparticles.

### Introduction

Cotton fabrics are considered one of the most important textile fibres world wide, Cotton fabrics have many advantages over all other types of textile fibres. The serious defect of cotton fabrics is its ability to ignite easily. Many trials are conducted to impart flame retardant properties for cotton fabrics [1]. Halogens based organic compounds were used as a flame retarding agents for cotton fabrics, but due to the hazard effect of these compounds on health and environment, many countries restricted the use of these compounds [2]. Phosphorus based organic compounds were used as safe alternatives for halogen compounds. They are effective flame retardants for cotton fabrics [3]. Nowadays all flame retardant compounds are based on phosphorus organic compounds [4-8].

Nanotechnology was first used in textile industries in USA [9]. Nanoparticles can be applied on textile fabrics by coating on the

surface of fabrics using several techniques such as spraying, printing and padding [10-12]. Textile fabrics can acquire many properties using nanotechnology including water repellence, soil resistance, wrinkle resistance, flame retardant, .....etc. The commonly used nanoparticles in textile industry are Ag, ZnO, TiO<sub>2</sub>, CuO and Al<sub>2</sub>O<sub>3</sub> [13-15]. The aim of the present work is to impart multi-functional properties for cotton fabric such as flame retardance, self cleaning and anti-crease using environmentally friendly finishing agents including citric acid, TiO<sub>2</sub> nanoparticles and flame retarding agent based on phosphate salts.

### Experimental

#### Materials

Mill scoured and bleached plain weave cotton fabric (169 g/m<sup>2</sup>) was supplied by Misr Company for Spinning and Weaving, Mehalla Elkobra, Egypt. The fabric was further purified by treatment with a solution containing 2 g/l sodium carbonate and 5 g/l Egyptol for 2 h. at boiling.

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After that the fabric was washed thoroughly with distilled water and left to dry in open air. Citric acid, titanium tetraisopropoxide, HCl, ethyl alcohol were of laboratory grade chemicals. Flovan CWF (flame retarding agent) was kindly supplied by Huntsman, Germany.

#### *Treatment*

Cotton fabric samples were padded to about 100% wet pickup with a finishing formulation bath containing 4–8 % citric acid and 2–4% TiO<sub>2</sub> from mother sol solution. Padded fabrics were dried at 100°C for 5 min. and cured at a temperature of 120°C to 180°C for 60 to 180 seconds. Finally, the samples were washed thoroughly with tap water to remove the non-reacted materials.

#### *Preparation of titanium dioxide nanoparticles (TiO<sub>2</sub>-NPs)*

Titanium tetraisopropoxide 6 ml was mixed with 2 ml of 1% acetic acid with continuous stirring using magnetic stirrer [16]. After 5 min., 56 ml of ethanol was added drop wise with continuous stirring then pH of the solution was adjusted to 1–2 by adding 2 ml of concentrated HCl. The mixture was magnetically stirred well for 45 min., and then obtained the sol-gel TiO<sub>2</sub> while was characterized by TEM.

#### *Testing and Analysis*

##### *Self-cleaning finishes and testing*

The untreated and TiO<sub>2</sub>-loaded fabric samples were dipped in a basic blue dye solution (1% owf) for 15min. for staining, then dried and conditioned. The samples were exposed to day light irradiation for 12 hr. The color strength, expressed as K/S value, of untreated and TiO<sub>2</sub>-loaded fabric samples was measured. The decrease in K/S values is a direct consequence of the degradation of the dye stains [17,18]. It is determined according to the following relation:

Extent of discoloration (%) =  $(K/S)_a \times 100 \setminus (K/S)_b$   
where (K/S)<sub>a</sub> is the color strength after exposing to daylight and (K/S)<sub>b</sub> is the color strength before exposing to daylight .

$K/S = (1-R)^2/2R$ , where K/S is the ratio of absorption and scattering coefficient and R is the reflectance at the wave length of maximum absorbance of the used basic dye.

##### *Crease recovery angle (CRA)*

CRA was measured according to the AATCC standard test method “wrinkle recovery of fabrics” (recovery angle method 66-1990).

##### *Tensile strength (TS) and elongation at break (El)*

TS and El were measured using the textile tensile Egypt. J. Chem. Special Issue (2017)

strength tester (Asano) No. 6202 machine (Japan).

##### *Thermal gravimetric analysis (TGA)*

TGA was carried out using Perkin Elmer 7DX Thermo Gravimetric Analyzer, USA.

##### *Scanning electron microscope (SEM)*

The samples were examined by a JEOL–840X scanning electron microscope, from Japan, magnification range 35–10,000, resolution 200Å°, acceleration voltage 19 kV. All the samples were coated with gold before SEM testing.

##### *Transmission electron microscope (TEM)*

TEM was measured using Zeiss-EM10-Germany.

##### *UV-vis spectrum:*

UV-vis spectrum was recorded on Perkin Elmer Lambda 3B UV-Vis spectrometer.

##### *Energy dispersive X-ray (EDX),*

The elemental ratio of prepared cotton fabric was characterized by SEM-EDS (electron dispersive spectroscopy) (JXA-840 an Electron Probe Microanalyzer-JOEL).

## **Results and discussion**

### *Effect of citric acid concentration*

This work is conducted to impart to cotton fabrics multi-functional properties including (flame retardant, self cleaning and anti-crease). To fulfill this target TiO<sub>2</sub> nanoparticles, citric acid and Flovan CWF (flame retarding agent) were used. Citric acid was used in the range 0-6 % (owf), TiO<sub>2</sub> nanoparticles were used in the range of 2- 4 % (owf) and Flovan CWF was used in the range of 100- 400 g/l. The curing temperature was in the range of 120°C to 180°C for time ranging from 60 second to 180 second. To reveal the effect of the amount of citric acid on the properties of the treated fabrics the fabrics were treated by formulation consists of 3 % TiO<sub>2</sub> nanoparticles with different amount of citric acid ranging from 0- 6 % padded to 100 % wet pick-up, the samples were dried at 100°C for 5 minute and cured at 160°C for 3 minute. It is worthy mentioning that sodium hypophosphite was not used as catalyst for crosslinking of cellulosic fabrics with citric acid, aiming to replace it by TiO<sub>2</sub> nanoparticles due to the adverse effect of sodium hypophosphite on properties of treated fabrics and environment.

Table 1 shows the results of the effect of citric acid concentration on the CRA, TS, El at break, WI and self cleaning expressed as the extent of discoloration (%). Table 1 indicates that CRA is elevated by increasing the concentration of citric acid

from 0 to 6 %. The elevation of CRA is expected as the amount of citric acid increases the ability of crosslinking cellulosic chains increases which is true only in case of using a catalyst has the ability to initiate crosslinking through an anhydride formation. In this case the catalyst is TiO<sub>2</sub> nanoparticles; this is a quite good proof that TiO<sub>2</sub> nanoparticles have the ability to initiate the crosslinking of cellulose by citric acid, so it can be used as a catalyst for crosslinking with citric acid [19].

Table 1 shows also that TS and WI decrease with increasing citric acid concentration; this adverse effect of citric acid on the TS and WI can be attributed to the increasing of the acidity of the medium with increasing citric acid concentration especially at high curing temperature. Self cleaning is the property of the ability of the fabrics to clean itself. This phenomenon is the most characteristic of TiO<sub>2</sub>, the results of extent of discoloration were found to be about 50 %. As mentioned before the self cleaning property is attributed to the presence of TiO<sub>2</sub>, so as the concentration of TiO<sub>2</sub> is fixed the ability of the samples of self cleaning was fixed to about 50 %.

#### *Effect of TiO<sub>2</sub> nanoparticles concentration*

**TABLE.1. Effect of citric acid concentration.**

Citric acid %	CRA (W+F) °	TS (w.kg)	EL (%)	WI	Extent of discoloration (%)
Blank	161	67	18	75	0
0	168	58	17.5	71.95	49
1	171	56	16	72.77	50
2	173	58	16.5	72.67	48
4	177	56	15.5	70.22	49
6	176	52.5	16.5	66.29	51

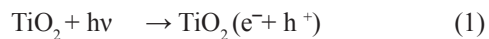
Finishing formulation: Flavon CWF (400 g/L); TiO<sub>2</sub> NPs 3 % ; Wet-pickup (100%); drying at 100 °C/5 min, curing at 160 °C/180 sec.

**TABLE . 2. Effect of TiO<sub>2</sub> nanoparticles concentration.**

TiO <sub>2</sub> %From mother sol-gel	CRA (W+F)°	TS (w.kg)	EI %	WI	Extent of discoloration (%)
2	174	59	18.5	72	49
3	177	59	15.5	70.2	50
4	167	56.5	15.5	70	49

Finishing formulation: Flavon CWF (400 g/L); Citric acid 6 % ; Wet-pickup (100%); drying at 100 °C/5 min, curing at 160 °C/180 sec.

To optimize the quantity of TiO<sub>2</sub> nanoparticles needed to impart self cleaning property to cotton fabrics, the concentration of TiO<sub>2</sub> nanoparticles must be changed. So the concentration of TiO<sub>2</sub> nanoparticles will be used in this section in the range of 2- 4 % in presence of 6 % citric acid. The samples will be dried at 100°C for 5 min and cured at 160°C for 3 min.



Mechanism of self cleaning of TiO<sub>2</sub>

It is obvious that increasing the concentration of TiO<sub>2</sub> nanoparticles from 2 to 4 % (Table 2) has almost no effect on the self cleaning properties of cotton fabrics expressed as the extent of discoloration of the dyed fabrics. According to the results obtained there is no need to use TiO<sub>2</sub> nanoparticles with concentration higher than 2 %. Meanwhile using a higher amount of TiO<sub>2</sub> nanoparticles leads almost to the same results with respect to TS, CRA, EI and WI. This means that 2 % of TiO<sub>2</sub> nanoparticles is almost sufficient to give enough self cleaning and also does not affect

adversely the physical and mechanical properties of treated fabrics.

#### *Effect of curing temperature*

Table 3 discloses the effect of curing temperature in the range studied (120°C to 180°C) on the physical and mechanical properties of treated cotton fabrics with 6 % citric acid, 3 % TiO<sub>2</sub> nanoparticles, wet pick up 100 % dried at 100°C for 5 minute and curried at different curing temperatures. It is shown from the results of Table 3 that crosslinking of cellulosic fabrics is temperature dependent. Increasing curing temperature leads to clear enhancement in the CRA. Higher curing temperatures would act in favors of segmental movement in cotton substrate as well as more ability of the reagents under investigation. This is expected to create accessible environment which help establish interaction of these reagents with the cotton hydroxyls.

This means that increasing curing temperature has an incremental effect on the crosslinking of cellulosic fabrics with citric acid.

Table 3 shows also the effect of curing

temperature on the TS and WI which is an adverse effect to the effect on the CRA. A curing temperature of 160°C optimum curing temperature which gives an optimal crease recovery angle without adversely affecting the TS and WI. With respect to self cleaning, Table 3 shows the effect of curing temperature on the self cleaning properties of the treated cotton fabrics. Almost curing temperature has no effect on the self cleaning properties since the only source for self cleaning is TiO<sub>2</sub> nanoparticles and the concentration of TiO<sub>2</sub> is fixed regardless to curing temperature.

#### *Effect of curing time*

As mentioned before curing temperature has the ability to facilitate the movement of the reagents to vicinity of the cellulose functional groups.

Curing time will give these reagents the chance to react with the cellulose molecules, curing time increases the opportunity of increasing the efficiency of reaction increases.

Table 4 depicts that 1.5 minute is enough time to give a valuable CRA without negatively affecting the physical and mechanical properties

**TABLE. 3. Effect of curing temperature.**

Curing temperature (°C)	CRA (W+F)°	TS (w.kg)	EI %	WI	Extent of discoloration(%)
blank	161	67	18	75	0
120	159.5	52	15	69.58	50
140	159.5	54	12	69.32	50
160	174	56	18.5	70	49
180	175	20.5	12	50.75	50

Finishing formulation: Flavon CWF (400 g/L); Citric acid 6 % ; 3 % of TiO<sub>2</sub>, Wet-pickup (100%); drying at 100 °C/5 min.

**TABLE. 4. Effect of curing time.**

Curing Time (min.)	CRA (W+F)°	TS (w.kg)	EI %	WI	Extent of discoloration
1	178	46.5	11	69.58	48
1.5	179	47.5	12	69	48
2	174.5	44	10	70	49
3	182	42	13	63	49

Finishing formulation: Flavon CWF (400 g/L); Citric acid 6 % ; 3 % of TiO<sub>2</sub>, Wet-pickup (100%); drying at 100 °C/5 min., curing at 160°C.

of treated fabrics (TS, El and WI). Here too, the results of self cleaning did not change as the amount of  $\text{TiO}_2$  remained constant regardless of the curing time within the range studied.

*Effect of the concentration of Flovan CWF on the properties of cotton fabrics*

Table 5 reveals the effect of flame retarding agent on the properties of treated fabrics. It is seen that as the concentration of Flovan CWF increases from 100 to 400 g/l at fixed amount of citric acid and  $\text{TiO}_2$  nanoparticles there is no effect on the physical and mechanical properties of cotton fabrics. Presence of Flovan CWF in the treatment formulations leads to an important effect on the thermal stability of cotton fabric as shown in Fig. 1 (a, b and c). Figure 1 shows the TGA spectra of untreated cotton fabrics, cotton fabrics treated with citric acid and  $\text{TiO}_2$  nanoparticles and cotton fabrics treated with citric acid and  $\text{TiO}_2$  in presence of Flovan CWF (flame retarding agent) respectively.

It is clear from Fig. 1 that the maximum decomposition temperature of the cotton fabrics in question are  $358^\circ\text{C}$ ,  $260^\circ\text{C}$  and  $260^\circ\text{C}$  for untreated fabric, treated fabrics with citric acid and  $\text{TiO}_2$  nanoparticles and cotton fabrics treated with citric acid and  $\text{TiO}_2$  nanoparticles in presence of Flovan CWF respectively. Figure 1 shows also that the weight loss as are 78 %, 57 % and 33 % for untreated fabrics, treated fabrics with citric acid and  $\text{TiO}_2$  nanoparticles and treated fabrics with citric acid and  $\text{TiO}_2$  nanoparticles in presence of Flovan CWF respectively, which means that presence of Flovan CWF enhances the thermal stability of cotton fabrics.

*TEM of  $\text{TiO}_2$  nanoparticles*

Figure 2 shows TEM of the prepared  $\text{TiO}_2$  nanoparticles. It is clear that the size and shape of the prepared  $\text{TiO}_2$  nanoparticles are homogeneous and the nanoparticles size displays a range of 3-7 nm.

*Scanning electron microscope (SEM)*

Figure 3 (a, b, c) reveals the SEM images of untreated fabric, treated fabrics with citric acid in presence of  $\text{TiO}_2$  nanoparticles and treated samples with citric acid in presence of  $\text{TiO}_2$  nanoparticles and flame retarding agent (Flovan CWF) respectively. As is evident the Figure exhibits the presence of  $\text{TiO}_2$  nanoparticles citric acid and Flovan CWF on the surface of treated cotton fabrics.

*Energy dispersive X-ray (EDX)*

Figure 4 proofs the presence of  $\text{TiO}_2$  nanoparticles on the surface of cotton fabrics and the % of  $\text{TiO}_2$  on the surface amounts to 0.25 % on the weight of the fabric.

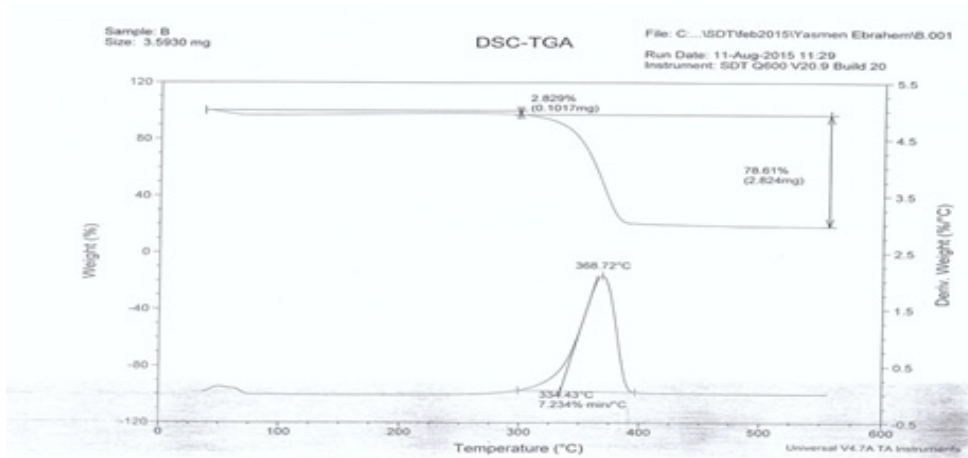
**Conclusion**

Cotton fabrics were treated using prepared  $\text{TiO}_2$  nanoparticles in presence of citric acid and commercially flame retarding agent named Flovan CWF. This was done to produce cotton fabrics having multi-functional properties (anti-crease, self cleaning, and flame retardant) through employment of the pad-dry-cure- method. The treated fabrics were submitted to several testing and methods such as creases recovery angle (CRA), Tensile strength (TS), Elongation at break (El), whiteness index (WI), self cleaning and flame retarding properties expressed as thermal gravimetric analysis (TGA). Results obtained make it possible to conclude that  $\text{TiO}_2$  nanoparticles has a dual effect 1) it is catalyst for crosslinking of cotton fabrics with citric acid 2) it is a finishing agent to impart self cleaning properties for cotton fabrics. on the other hand Flovan CWF induces give the ability to cotton fabrics to be flame retardant property to be fabric when used at a concentration of more than 200 g/l without seriously affecting the physical and mechanical properties of the cotton fabric.

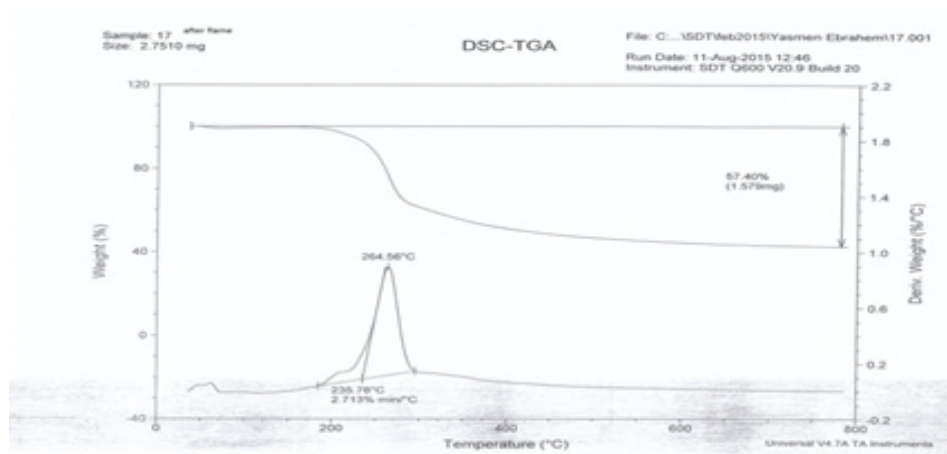
**TABLE 5. Effect of the concentration of Flovan CWF on the properties of cotton fabrics.**

Flovan CWF (g/l)	CRA (W+F) <sup>o</sup>	TS (w.kg)	El %	WI
100	171	53	14	71.73
200	173	56	12	71.65
300	180	56	12.5	68.85
400	174	53	13	66.21

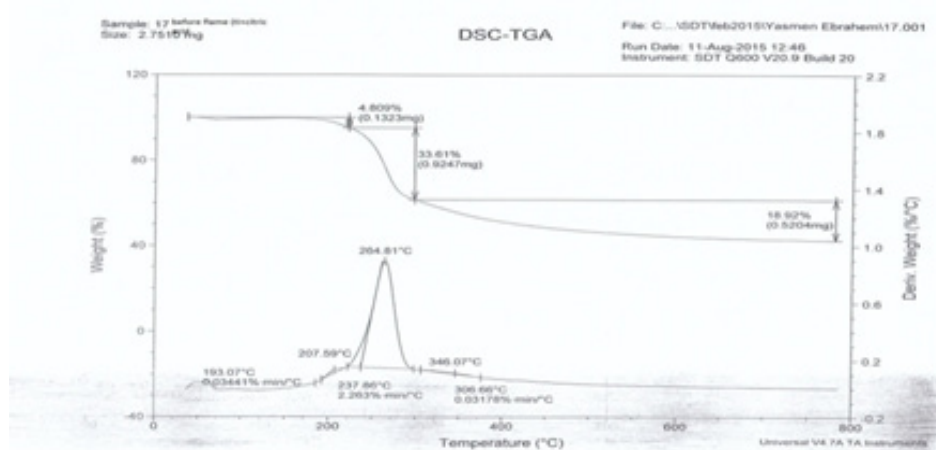
Finishing formulation: Citric acid 6 % ; 3 % of  $\text{TiO}_2$ , Wet-pickup (100%); drying at  $100^\circ\text{C}/5$  min., curing at  $160^\circ\text{C}$  .



(a)



(b)



(c)

Fig. 1. TGA of cotton fabrics.

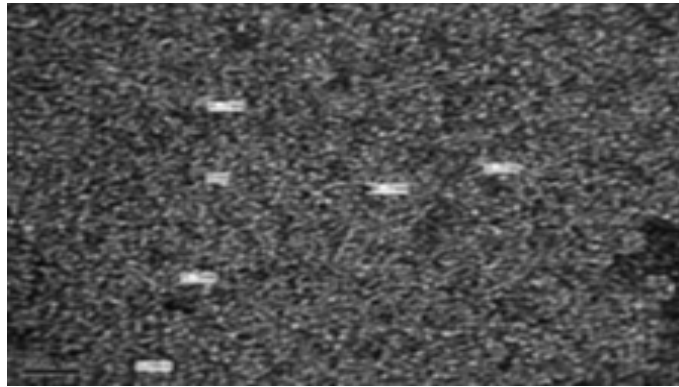
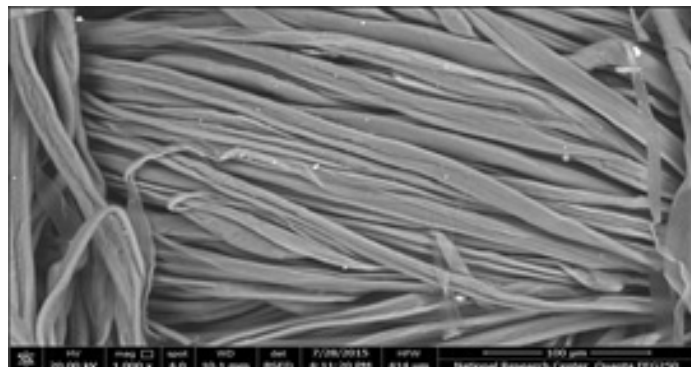
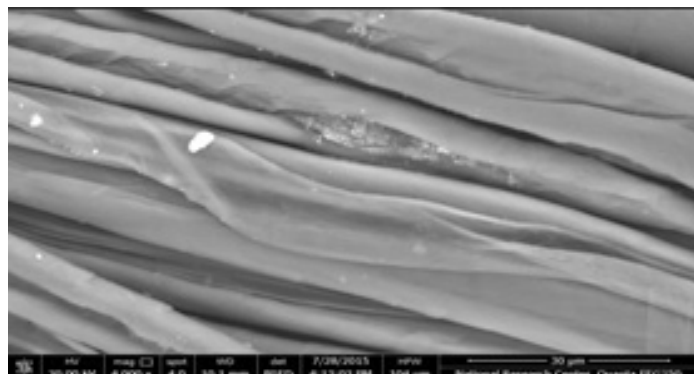


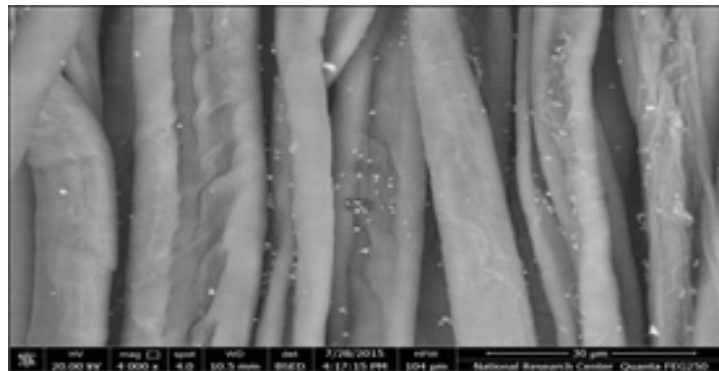
Fig. 2. TEM of TiO<sub>2</sub> nanoparticles



(a)



(b)



(c)

Fig. 3. SEM Images.

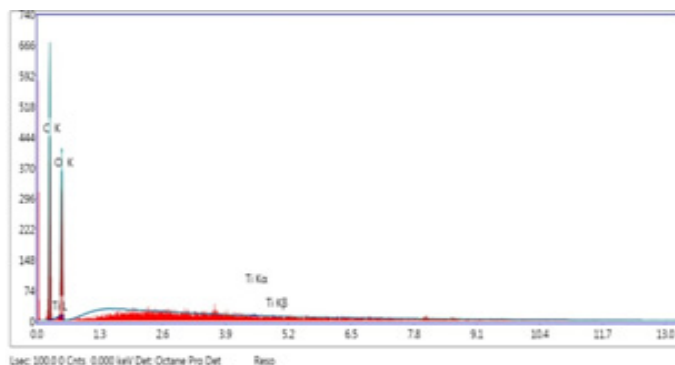


Fig. 4. EDX of treated cotton fabrics.

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## التجهيز الوظيفي للاقمشة القطنية باستخدام تكنولوجيا النانو ومواد تجهيز صديقة للبيئة

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تم تحضير جزيئات ثاني اكسيد التيتانيوم في حجم النانو باستخدام طريقة السول جيل ثم تم قياس حجم هذه الجزيئات باستخدام الميكروسكوب الالكتروني النافذ. تم بعد ذلك معالجة الاقمشة القطنية باستخدام جزيئات ثاني اكسيد التيتانيوم في حجم النانو في وجود حمض السيتريك ومادة الفلافون بغرض اكساب الاقمشة خواص مقاومة التجعد و مقاومة الاحتراق بالاضافة الي التنظيف الذاتي. تم توصيف الاقمشة المعالجة بقياس العودة من زاوية التجعد - التنظيف الذاتي - معدل البياض - قوة الشد - الثبات الحراري و ايضا XDE.

اثبتت النتائج ان افضل نتائج تم الحصول عليها باستخدام ٦٪ حمض السيتريك، ٣٪ ثاني اكسيد التيتانيوم، ٠.٣ جم/ل من مادة الفلافون.