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ORIGINAL RESEARCH

Denim Fabric with Flame retardant, hydrophilic and self-cleaning properties conferring by in-situ synthesis of silica nanoparticles

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Abstract In this study, Stöber method was utilized to synthesize silica NPs on the denim fabric via sodium silicate solution under alkali solution applying *Keliab* (*Seidlitzia rosmarinus*), as a natural alkali source, at pH 12 and also ethanol/*Keliab*. X-ray diffraction (XRD), Fourier transform infrared (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and ultraviolet–visible (UV–Vis) analysis verified the formation of silica NPs on the denim fabric. Further, self-cleaning features, air permeability, hydrophilicity, flame retardant, shrinkage, bending rigidity and tensile strength of the fabrics were studied. The final denim fabric indicated boosted features along with novel properties such as higher heat resistance, strength, water absorption rate, air permeability, and self-cleaning properties. These traits are making the fabric appropriate for application in diverse environmental conditions due to the silica NPs.

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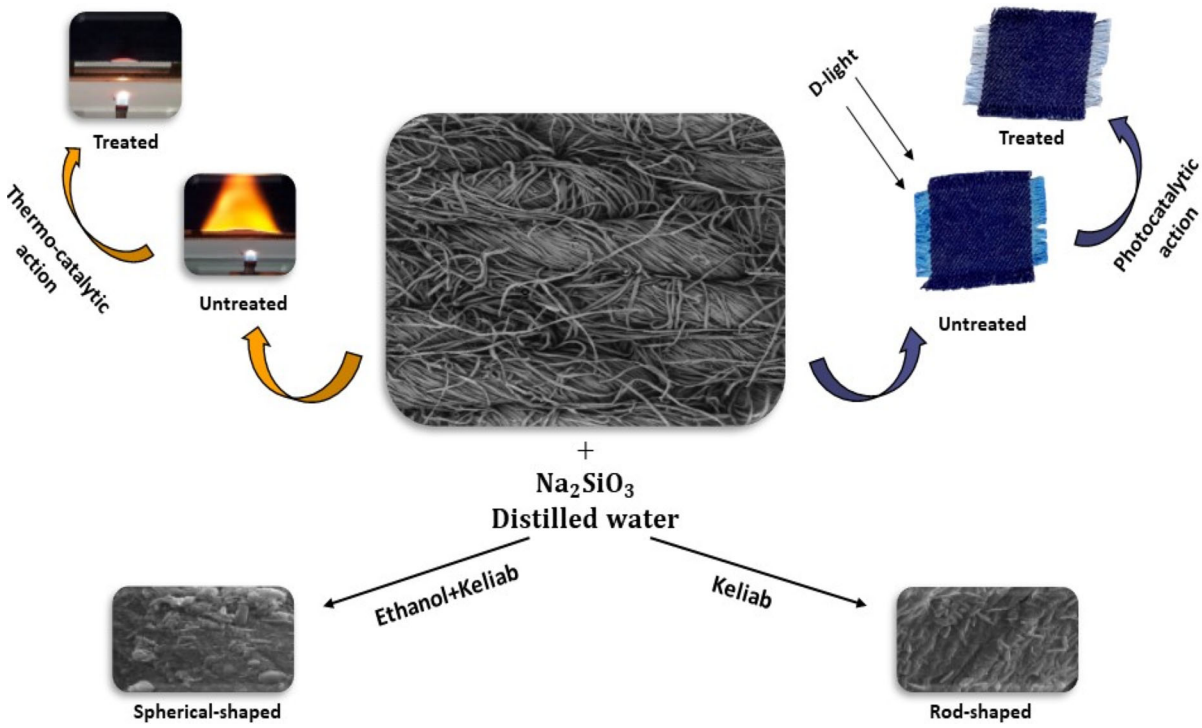
Graphic abstract



Keywords Silica NPs · Cotton denim fabric · *Keliab* · In situ synthesis · Flame retardant

Introduction

Human beings have always tried to increase safety of textiles such as fabric, furniture, carpet, curtain, and flooring in the fire accidents since they are recognized as one of the main combustion sources due to their high burning speed and the flame spread (Norouzi et al. 2015). Denim, among the fabrics used since 1800, has been popular due to characteristics such as perceived beauty, warmth, comfort, durability, biodegradation, coloring speed, and low-cost (El-Hady et al. 2013; Eryuruk 2019; Ghaani Farashahi et al. 2018; Haghighat et al. 2013; Kan and Wong 2010; Li et al. 2010; Marsh et al. 2005; Miller 2015; Miller and Woodward 2011; Morris and Prato 1981; Rahman 2012). Manufacturers have used a variety of finishes to enhance the efficiency, durability, color stability and quality of denim fabric, and also textile researchers have used nanofinishing on the denim fabrics (Kan et al. 2011; Nallathambi et al. 2011).

Cotton denim fabrics are flammable and burn quickly (Grancaric et al. 2016) and need to be fire retardant while still having suitable handle and drape (Nelson 2008). Horrocks et al. (1996) reported the flame retardant cotton fabric by using chemical softeners. Silica nanoparticles (NPs) have widespread applications in various industries with some known effects on textiles. Fanglong et al. (2016) caused enhanced flame retardance of cotton fabric by applying nano-silica. In fact, an optimal nano-silica amount increased the LOI and reduced the thermal decomposition of the cellulosic materials. Also, a mixture of nano-silica and traditional intumescent flame retardant showed synergistic effects on the flame resistance of cellulosic textiles (Fanglong et al. 2016). In addition, Carosio et al. (2011) applied silica NPs through the layer-by-layer coating as a flame-retardant and found impressive changes in the principle factors of flammability. Further, silica NP films reduced burning time, delayed rate of heat release ignition and eliminated melt dripping of polyester fabric.

The ignition of fabrics plays a key role at the start of the fire therefore, there are numerous reports on the combustion of textiles (Khattab et al. 1992). Early studies were accomplished by heating the fabrics to different temperatures using a hot plate (Brewster and Barker 1983; Nakagawa et al. 1989; Sayers 1965). Other investigators have tried to study the fabrics to ignite in the conventional thermo-gravimetric analyzers (Miller et al. 1983). Moreover, the ignition behavior of fabrics was studied by different methods such as placing the fabrics in hot air (Torvi et al. 1999; Vantelon and Breillat 1982), in different oxygen concentrations (Khattab et al. 1990), and in the furnace under defined time and temperature (Khattab et al. 1992).

The study of Norouzi et al. (2015) showed the effects of nanoparticles such as nano-clay, carbon nanotubes, and silica NPs on the flame retardant properties of various textile fibers. Silica NPs and cross-linking agents were applied to cotton to make a hydrophobic surface. The thermal properties and flame retardation of the coated fabrics increased due to the high heat resistance, heat protection effect, and mass transport limitation of the silica NPs in the coating. In addition, they confirmed the flame retardant effect of silica NPs on PET by reducing the heat release rate. Moreover, they compared thermal stability and flame retardation of the treated cotton fabrics with diverse metal alkoxide coatings showed the protective efficiency arrangement of: $TiO_2 > SiO_2 > Al_2O_3 > ZrO_2$.

Recently, the nanoparticles were applied on the cellulosic fabrics in many studies. For instance, Xu and Cai (2008) reported formation of the chemical bonds between hydroxyl groups of cellulose and silica NPs through heat treatment. Moreover, cellulosic fabrics were treated through an eco-friendly synthesis with nano cupric oxide by *Seidlitzia Rosmarinus* ashes as a natural and non-toxic source of alkali (Rezaie et al. 2017b). Furthermore, silica NPs were synthesized on cellulosic fabric by treating with tetraethylorthosilicate (TEOS) under alkaline conditions (ethanol and 3-aminopropyl) to achieve flame retardant (Aksit et al. 2016). In addition, silica nanoparticles and polydimethylsiloxane were applied on cotton fabric to produce a cloth with multifunctional features (Liu et al. 2018).

The woody plant of *S. Rosmarinus*, a species of *Chenopodiaceae* from *Salsoleaes* tribe, is growing in Middle East and Central Asia that can be used as an alkaline source (Aladpoosh et al. 2014). This was previously used for laundry and feeding of animals however it is using for soap, pottery, glasswork, degumming of silk yarns and pharmaceutical industry (Aladpoosh et al. 2014; Rezaie et al. 2017a). The plant was burnt in the special ponds cooled the melt and collected the final solids. The solid material is called *Keliab* as an alkaline source that is rich in sodium carbonate (Aladpoosh et al. 2014; Rezaie et al. 2017a). Lately, it has been used for biosynthesis of Ag (Aladpoosh et al. 2014), ZnO (Aladpoosh et al. 2014), and CuO nanoparticles on various textile substrates (Rezaie et al. 2017b).

Multifunctional fabrics with self-cleaning (photocatalytic), flame retardant, hydrophilic, and air permeability properties, have attracted more attention. The photocatalytic properties of fabrics were broadly studied in recent years since some users may give up from washing their clothes for months due to the negative effects of the household laundering on the shade and mechanical properties. Many researchers coated titanium dioxide (TiO_2) on textiles to chemically break down the color stains through exposing to the sunlight (Uğur et al. 2017; Onar et al. 2011; Sobczyk-Guzenda et al. 2013). Similarly, Guan (2005) reported the self-cleaning and hydrophilic properties of TiO_2/SiO_2 composite films.

Recently most published papers were concentrated on various finishing on textiles such as synthesis of nanoparticles on cotton fabric (Aladpoosh et al. 2014), industrial washing of denim garment (Jucienė et al. 2006) and changing the color of fabrics (Ding et al. 2010; Jucienė et al. 2006). The color psychology is a critical issue for the consumers because of the importance of the color in choosing of a product by the costumers (Dobilaitė and Jucienė 2005; Fan et al. 2009; Militky and Bajzik 1997; Thompson et al. 1992). Therefore color change can be a useful way to attract the costumers for buying a cloth.

The hydrophilic or hydrophobic nature of fabric can be strongly affected on the textile finishing, dyeing and printing. Hence, most researchers worked on various methods to enhance the hydrophilicity of fabrics. Nithya et al. (2011) treated the cotton fabrics by DC air plasma and cellulase to improve the hydrophilicity, wettability, and dye-ability without substantial fiber deterioration.

In this study, sodium silicate solution was used in an alkaline solution of *Keliab* as a friendly compound to synthesize silica NPs on the denim fabric. Also, the synthesis was performed in two different alkaline solutions and the results compared. The better thermal

behavior of denim fabrics with minimum effect on the handle and low color difference were explored. Besides, the hydrophilic, photocatalytic, and mechanical properties of the treated samples were investigated.

Materials and methods

Materials

A 100% cellulose with 1/3 twill indigo-dyed denim fabric, weight of 411 g/m^2, yarn count of 54/54 (warp/filling), thickness of 0.8 mm, warp density of 38/cm and weft density of 22/cm was used. A commercial nonionic detergent was purchased from a local market and *Keliab* obtained from Urmia, Iran. Sodium silicate solution [NaO_2 (7.5–8.5%), SiO_2 (25.5–28.5%)], having a pH 11.0–11.5, was provided from Merck Co., Germany. Ethanol (C_2H_5OH, 96%) was bought from Golriz Co., Iran. Methylene blue was obtained from Uhao Co., China.

Preparation of *Keliab* solution

In order to prepare an alkali solution, 5 g *Keliab* powder was mixed with 100 mL distilled water to obtain a heterogeneous mixture. After 24 h, some components of *Keliab* powder were dissolved in water and the rest precipitate at the bottom of the solution. The top transparent liquid having the pH of 13 was used.

In situ synthesis of silica NPs on denim fabric

First, denim fabric was washed with 1 g/L nonionic detergent at 60 °C for 30 min in liquor-to-goods ratio (L:G) of 40:1. Two different mixtures, a mixture of 20 mL distilled water and 10 mL *Keliab* solution (M1) and another mixture of 20 mL ethanol and 10 mL *Keliab* solution (M2) were made. Two denim samples (3 cm × 3 cm) were immersed in the each mixture. A 10 mL sodium silicate solution was added to 7 mL distilled water at room temperature. The diluted sodium silicate solution was added dropwise to M1 and M2 solutions, separately. Magnetic stirrer was used to stir. After 1 h, samples were washed with distilled water then dried at 100 °C for 1 h. A solution containing 10 mL *Keliab* and 20 mL distilled water (M3) without sodium silicate solution was made and the two samples were placed in the solution remained for 1 h and then washed with distilled water followed by drying at 100 °C for 1 h.

Methods

FESEM images and EDS patterns

Field emission scanning electron microscopy (FESEM, MIRA#TESCAN-XMU) pictures were used to observe the surface morphology and synthesized particle size. The weight percentage of the elements on the samples was obtained using energy dispersive spectroscopy (EDS) and the loading of the elements showed in the maps.

TEM analysis

Transmission electron microscopy was accomplished according to standard 3001-1503-7 by using Zeiss EM900. To prepare samples for TEM analysis, the synthesized effluents of M1 and M2 were placed on a copper grid coated with carbon. The solution was evaporated at room temperature left the nanosized silica particles on the grid.

X-ray diffractometer

An X-ray diffractometer (XRD, EQuniox 3000, INEL, France) was used to investigate the crystalline structure of synthesized silica nanoparticles on the treated fabrics. The wavelength of the Cu Kα radiation used in this study was 1.54190 Å.

FT-IR analysis

Fourier transform infrared spectrometry (FT-IR, NEXUS 670, Nicolet) was applied to recognize and analyze the new bonding of the treated fabrics from 500 to 4000 cm^{-1} at 4 cm^{-1} with 40 scans.

UV–Vis spectrophotometer

The UV–Vis absorbance (model 2100, Unico, China) was used in various wavelengths (200 to 800 nm) for the synthesized effluents according to Table 1.

Photocatalytic actions and color changes

The raw and treated samples were placed in a methylene blue solution (0.001%) for 10 min and then exposed to the sunlight for 48 h. The color

difference of the stained fabrics before and after the experiment was determined using a spectrophotometer (Varian Carry 5000) based on CIELAB color coordinates. The total color difference, ΔE, was calculated via Eq. 1:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}, \quad (1)$$

where L* stands for lightness and darkness, a* shows redness and greenness, and b* indicates yellowness and blueness.

The percentage of self-cleaning was determined by Eq. 2:

$$\text{Self - cleaningenhancement}(\%) = \left(\frac{\Delta E_C - \Delta E_T}{\Delta E_C}\right) \times 100. \quad (2)$$

ΔE_C and ΔE_T are the color difference of the stained untreated and treated samples after sunlight irradiation (Rezaie et al. 2017a). Also, the color change of treated fabric was measured in CIELab color space comparing with untreated fabric using Eq. 2.

Strength and bending

The strength of the treated denim fabrics was investigated using an Iranian CRE instrument named *Kardo Tec*. The test speed was 75 mm/min and the relative ambient humidity was 32% and the ambient temperature was about 28 °C. The test was repeated in warp direction three times for each sample.

To assess the bending resistance, Shirley instrument was used according to ASTM D 1388. The bending rigidity is affected by fabric drape that can be measured by Eq. 3:

$$B = 9.8 \times 10^{-6} \times WC^3\ (\mu\text{N.m}), \quad (3)$$

where B stands for bending rigidity, W is the fabric mass per unit area (g/m^2) and C is half of the bending length (mm).

Air permeability and handle

Air permeability of the fabric was measured using the Shirley instrument according to ISO 9237 method, 1995 with constant pressure (100 Pa) at relative ambient humidity of 40% and the ambient temperature of 26 °C.

In this study, the hand-feel of treated fabrics was compared to the raw via expert panel and qualitatively reported.

The equipment can determine no feelings when someone touches a fabric (handle), therefore, a group of 50 people were used in this experiment for evaluating the handle property.

For the handle of fabrics, a 5-point scale was used. The meanings and the frequency of the rating numbers are shown in Table 3. Before the evaluation, the group members were asked to wash their hands with the non-moisturizing soap and dry by the paper towel.

In the evaluation process, the team members held the untreated sample in their most-used hand and tried to grade the fabric according to the designed 5-point scale. Then, they appraised the treated samples by their most-used hand. The data was statistically analyzed.

Water droplet absorption and fabric shrinkage

The time for the water absorbed was used to measure the fabric hydrophilicity after the treatment. For this purpose, a drop of water was trickled down on the surface of the samples from 2 cm using a dropping-tube. The time of the full absorption of the water droplet was measured for 10 times and the average value was reported.

The shrinkage percentage (S%) was also measured by Eq. 4:

$$S\% = \frac{A - B}{A} \times 100. \quad (4)$$

Table 1 Preparation of the synthesized baths for UV–Vis absorbance investigation

Bath	Sodium silicate solution (mL)	*Keliab* solution (mL)	Ethanol (mL)	Diluted water (mL)
M1	10	10		20
M2	10	10	20	
M3		10		20

A is the initial size and B is the secondary size.

Flame testing

The samples were placed at the distance of 4 cm from the 2 cm long flame for 12 s according to AATCC 6941 and the burning speed was measured using Eq. 5:

$$x = vt, \tag{5}$$

where x is burning length (cm), t is time, and v is burning speed.

Another important method to study the thermal properties of textiles is thermo-gravimetric analysis (TGA) that was conducted by using a SDT Q600 V20.9 Build 20. TGA showed weight losses of fabrics under different temperatures from 25 to 800 °C at a heating rate of 10 °C/min under N_2 using derivative TGA (dTGA) plots, also the temperature of maximum weight loss was acquired. The amount of samples was about 4 mg. Also, the loss in mass of the samples was determined by using a furnace in 300 °C for 3 h.

Results and discussion

Mechanism of in-situ synthesis of silica NPs

The mechanism of synthesis and deposition of silica NPs on cotton denim fabric by using *Keliab* solution was considered as follows:

When sodium silicate solution was diluted in distilled water, SiO_2 is formed (Reaction 1) (Nozari et al. 2018).

$$Na_2SiO_3 \xrightarrow{H_2O} SiO_2 + NaOH. \tag{1}$$

The *Keliab* solution contains sodium alkali-metals prepares alkali media through hydroxyl ions (OH^-) in the synthesis bath (Reactions 2–4) (Aladpoosh et al. 2014; Rezaie et al. 2017a).

$$Na_2CO_3 + H_2O \rightarrow 2Na^+ + CO_3^{2-} + H_2O, \tag{2}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-, \tag{3}$$

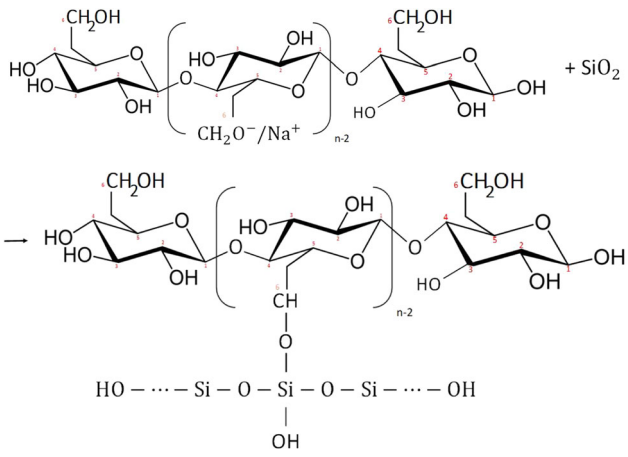
$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-. \tag{4}$$

Also, cellulosate anion was produced due to alkali medium (Reaction 5) (Aladpoosh et al. 2014; Nozari et al. 2018; Rezaie et al. 2017a). This was then reacted with sodium cation created the sodium salt of cellulose (Reaction 6) (Aladpoosh et al. 2014; Rezaie et al. 2017a).

$$\text{Cellulose}-OH \xrightarrow{OH^-} \text{Cellulose}-O^- + H_2O, \tag{5}$$

$$\text{Cellulose}-O^- \xrightarrow{Keliab} \text{Cellulose}-O^-/Na^+. \tag{6}$$

By adding diluted sodium silicate solution to the synthesis bath, SiO_2 was replaced with Na^+ owing to the higher electronegativity of SiO_2 (1.90) comparing with sodium (0.93) (Reaction 7) (Aladpoosh et al. 2014).



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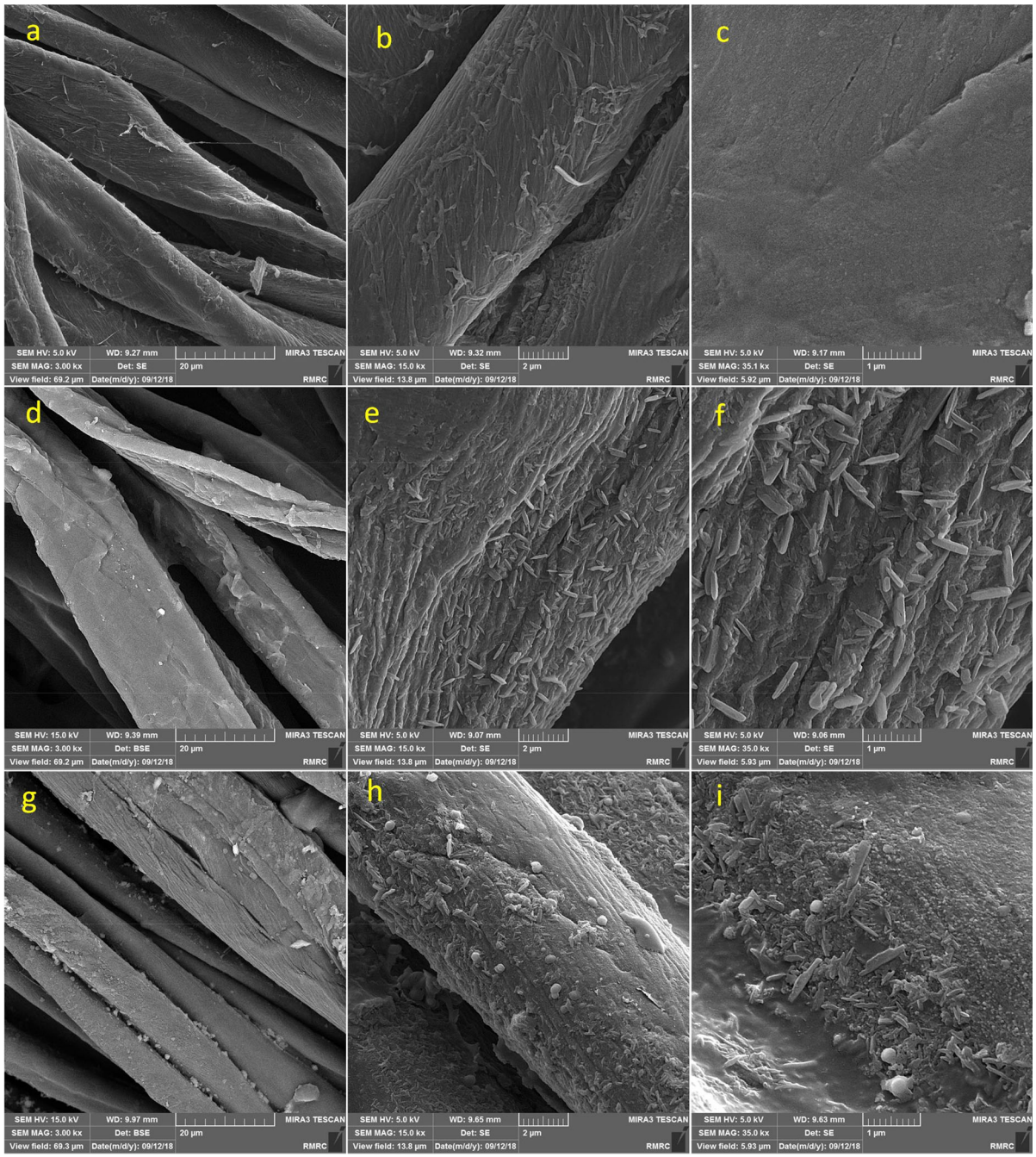


Fig. 1 FESEM images of untreated fabrics with magnifications of **a** ×3000, **b** ×15000, **c** ×35100, and treated fabrics by M1 with magnifications of **d** ×3000, **e** ×15000, **f** ×35000, and M2 with magnifications of **g** ×3000, **h** ×15000, **i** ×35000

Morphology and structure

Figure 1a–c indicates the surface of the untreated samples. Figure 1a clearly demonstrates the ribbon-shaped and size distribution of the cotton fibers in denim fabrics. Fibers are regular with a relatively smooth surface at low magnification. Figure 1b shows the fibrils in the individual cotton fiber at large magnification. This indicates the pure cotton surface without any additives (Fig. 1).

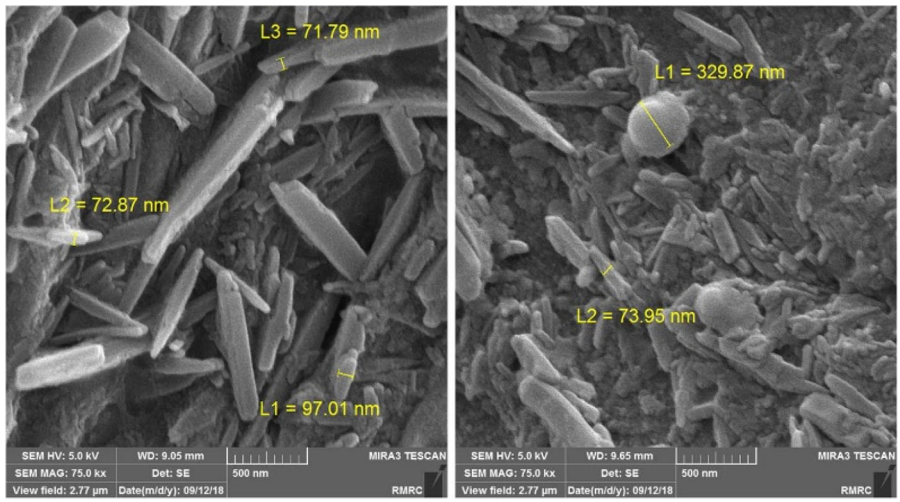
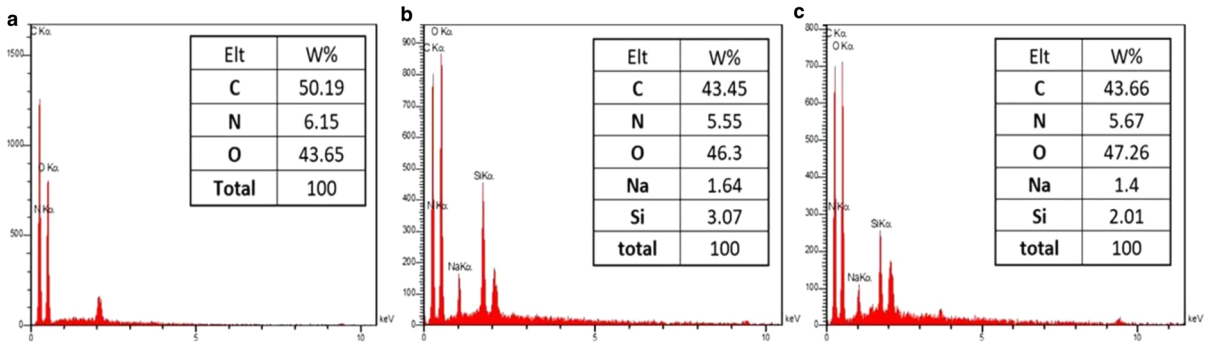


Fig. 2 FESEM images of rod and spherical-shaped synthesized silica NPs



Elt	W%
C	50.19
N	6.15
O	43.65
Total	100

Elt	W%
C	43.45
N	5.55
O	46.3
Na	1.64
Si	3.07
total	100

Elt	W%
C	43.66
N	5.67
O	47.26
Na	1.4
Si	2.01
total	100

Fig. 3 EDX analysis of the **a** untreated fabric, **b** treated fabric with M1, and **c** M2

The rod-shaped silica NPs were synthesized using M1. Figure 1d–f illustrates the synthesized silica NPs on the cotton surface covered fibrils. The ethanol in M2 leads to the synthesis of spherical-shaped NPs. Figure 1g–i displays both the rod and spherical-shaped silica NPs wrapped on fibrils. Nozari et al. (2018) reported regular hexagonal silica NPs on PET fabric synthesized under alkali conditions with ammonia and ethanol. The average sizes of the rod and spherical-shaped silica NPs were 78.9 and 311.43 nm, respectively (Fig. 2).

Ethanol leads to the increase in the number of synthesized nanoparticles (Zulfiqar et al. 2016). EDS was employed to recognize C, N, O elements on the raw fabric and C, N, O, Na, Si on the treated samples along with the weight percentages. Figure 3 illustrated that the weight percentages of Si and Na increased for the treated samples due to synthesis in alkaline condition. The percentage of O increased for the treated samples, because of the formation of hydroxyl groups also C and N decreased by addition of Si and Na. Further, Fig. 4 shows the uniform distribution of Si on the specific area of the fabric.

Figure 5 shows the TEM micrographs of the various shapes of silica NPs. Figure 5a, b, is related to the rod-shaped silica NPs synthesized by *Keliab* solution (M1). The ethanol in M2 leads to the synthesis of spherical-shaped silica NPs however in Fig. 5c, d, both the rod and spherical-shaped NPs can be observed.

The XRD patterns of different samples are revealed in Fig. 6. The peaks at $2\theta = 14.9°$, 16.8°, 22.8°, and 34.7° are related to the crystalline structure of cellulose Iβ (French 2014). Silica NPs are synthesized in amorphous and crystalline forms (Nozari et al.

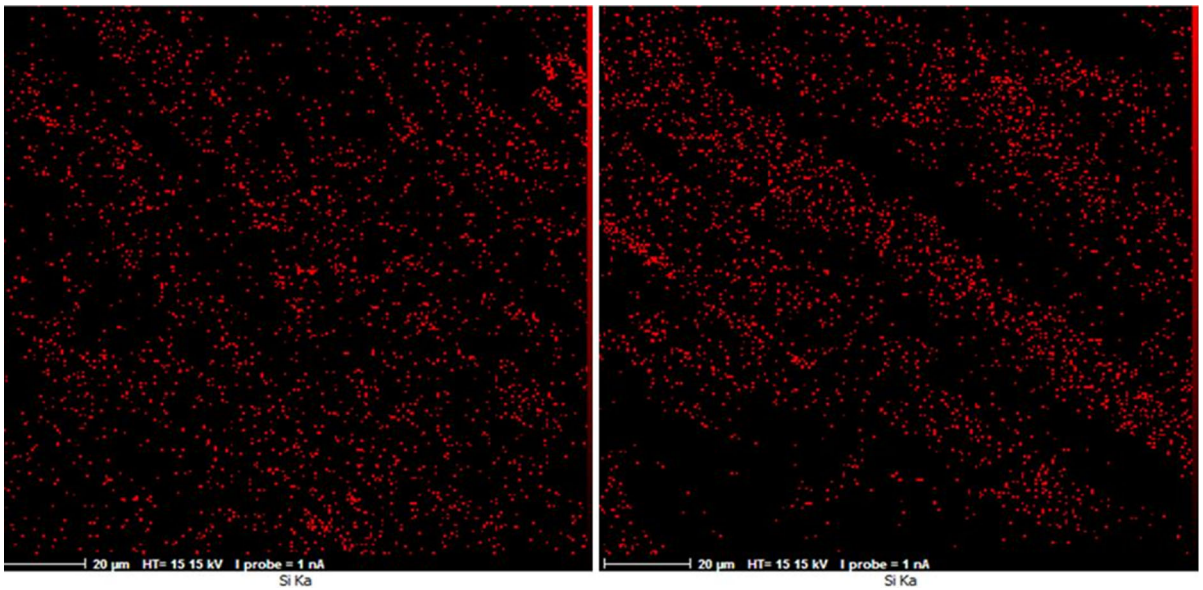


Fig. 4 Mapping of Si on treated samples with (right) M1 and (left) M2

2018). By stimulating the synthesis condition on the fabric, the silica nanoparticles are synthesized and the powder of SiO_2 obtained. The XRD pattern of SiO_2 powder shows the amorphous peak in the range of 10°–30° (Nozari et al. 2018) and the strongest peak at $2\theta = 22.5°$ can be matched with SiO_2 JCPDS Card No. 39-1425. However here, X-ray diffraction data cannot clearly prove the synthesis of silica NPs on the samples due to the overlapping of SiO_2 and cellulose peaks in the treated samples.

Figure 7a illustrated the FT-IR spectrum of the untreated sample indicated the characteristic peaks of denim fabric due to the cellulose macromolecule and indigo dye at 3267 cm^{-1} (O–H and N–H stretching), 2915 cm^{-1} (C–H aromatics), 1560 cm^{-1} (N–H stretching), 1313 cm^{-1} (C–N stretching), and 1026 cm^{-1} (C–O stretching) (El-Shishtawy et al. 2011).

According to Fig. 7b, c, the stretching of Si–O–Si appears at 1000 cm^{-1} (Al-Oweini and El-Rassy 2009; Bertoluzza et al. 1986). Mendoza-Castillo et al. (2016) claimed that the intense stretching vibrations of Si–O–Si groups locate at 1040 cm^{-1}. Moreover, the stretching of O–H and N–H is positioned at 3264 and 3271 cm^{-1} for treated sample with M1 and M2, respectively. El Nahrawy et al. (2018) showed a very weak peak at 3103 and 3473 $cm^{-1}$for stretching of N–H and OH respectively. The peaks at 1629 and 1312 cm^{-1} are corresponded to the absorbance of N–H and C–N stretching in treated sample with M1. The peaks at 1606 and 1313 cm^{-1} are related to N–H and C–N stretching in the treated sample with M2.

Keliab solution, rich in sodium carbonate, has the peak around 250 cm^{-1} for M3 (Fig. 8) effluent corresponds to Na_2CO_3 (Jin et al. 2013). The peaks related to the M1 and M2 effluents (Fig. 8) are shifted toward 300 cm^{-1} with the intense absorbance due to the SiO_2 in mixtures (Kukovecz et al. 2001). Moreover, the width of the peaks demonstrates the aggregation of NPs which is higher for M2 due to the ethanol as similarly reported by Aladpoosh et al. (2014).

Photocatalytic properties

The fabrics treated with SiO_2 semiconductor NPs have self-cleaning properties decomposing the color stain of methylene blue (Nozari et al. 2018; Rezaie et al. 2017a).

The valence electrons of SiO_2 available on the treated fabrics are affected by ultraviolet radiation lead to positive holes. Further, the electrons react with oxygen and water molecules produced superoxide ions (O_2^-) and hydrogen peroxide (H_2O_2). Moreover, hydroxyl radicals are formed as a result of a reaction

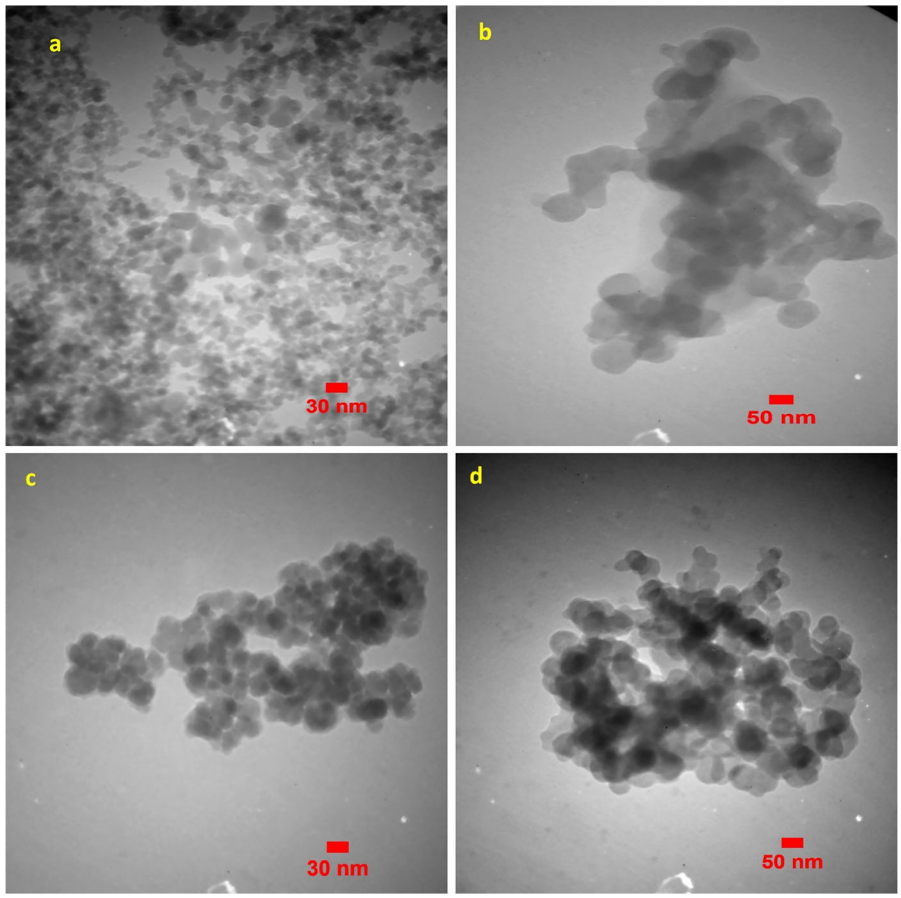


Fig. 5 TEM images of silica NPs synthesized through **a**, **b** M1 and **c**, **d** M2

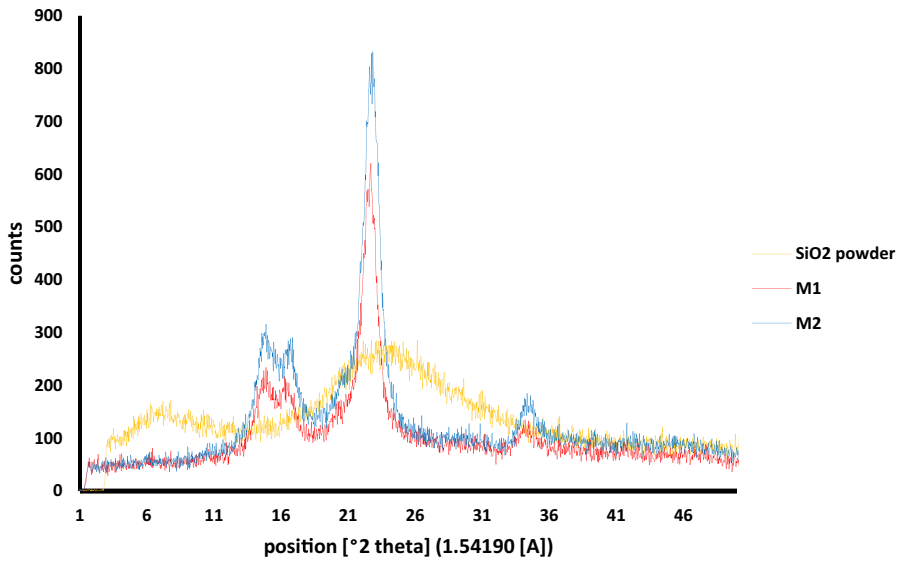


Fig. 6 XRD spectrum of the treated and untreated fabrics

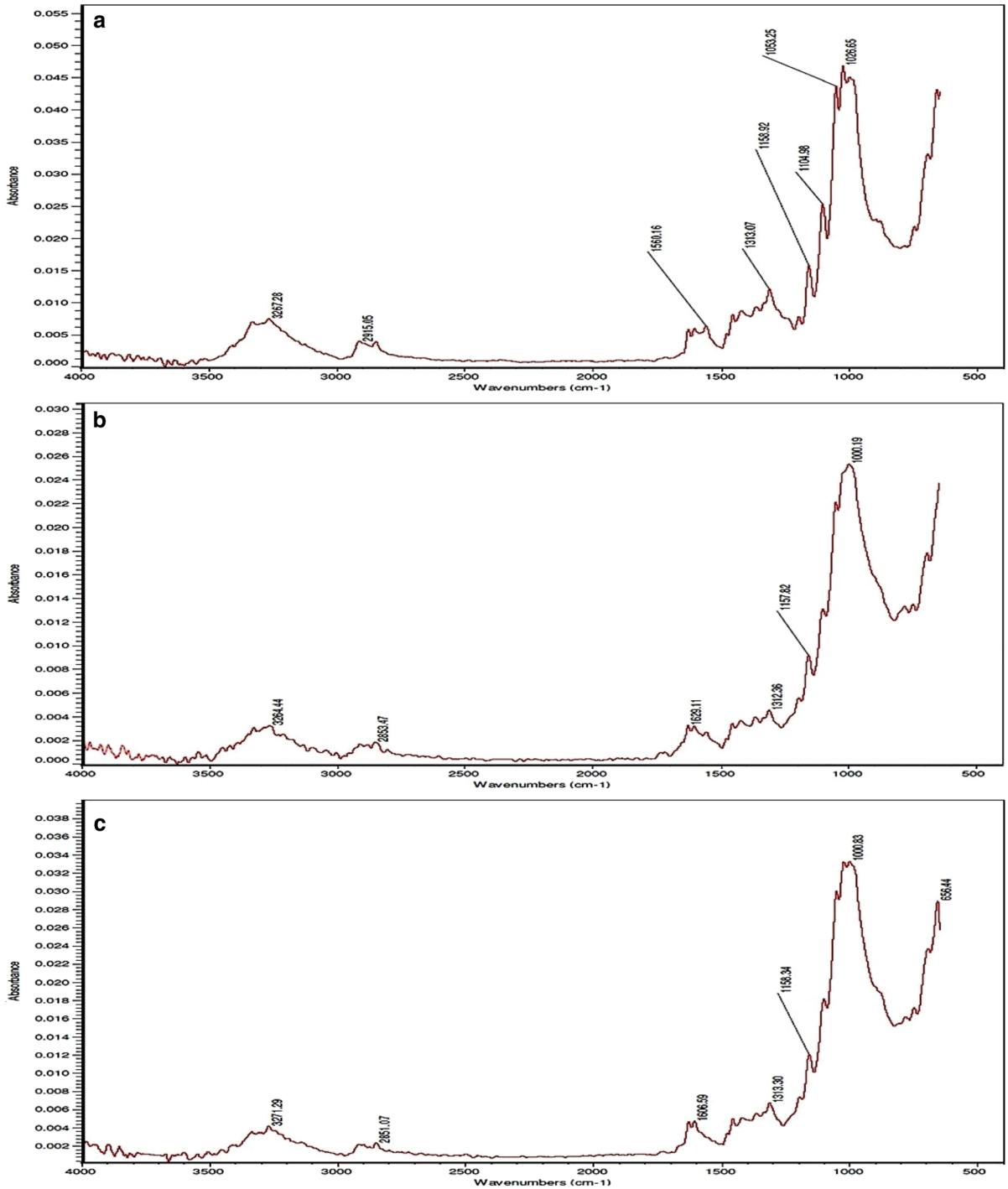


Fig. 7 FT-IR spectra of untreated (**a**) and treated fabrics with M1 (**b**) and M2 (**c**)

between positive holes with water molecules. The hydroxyl radicals are known as the main factor in the decomposition of the harmful compounds. Hence, the blue stain of the methylene can be decomposed to non-toxic products such as CO_2, H_2O, and minerals (Nozari et al. 2018; Rezaie et al. 2017a).

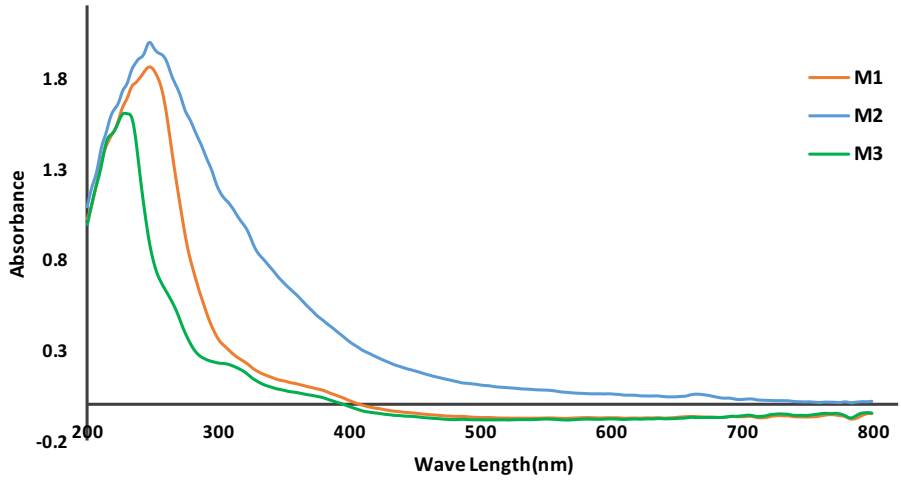


Fig. 8 UV–Vis spectra of the various synthesized effluents

Table 2 Different properties of the untreated and treated samples with M1, M2 and, M3

	Untreated	M1	M2	M3
Bending rigidity (μN.m)	27.32	43.76	41.88	27.52
Air permeability ($cm^3/s/cm^2$)	5.00	5.47	5.33	5.20
Photocatalytic performance (ΔE)	4.1	6.9	9.9	
Self-cleaning enhancement (%)		12	153	
Color change (ΔE)		3.2	2.3	1.3
Young's modulus (gf)	18.69	21.79	24.68	23.32
Shrinkage (%)	0	0	0	0
Weight lost (%)	74.45	72.46	70.25	74.38

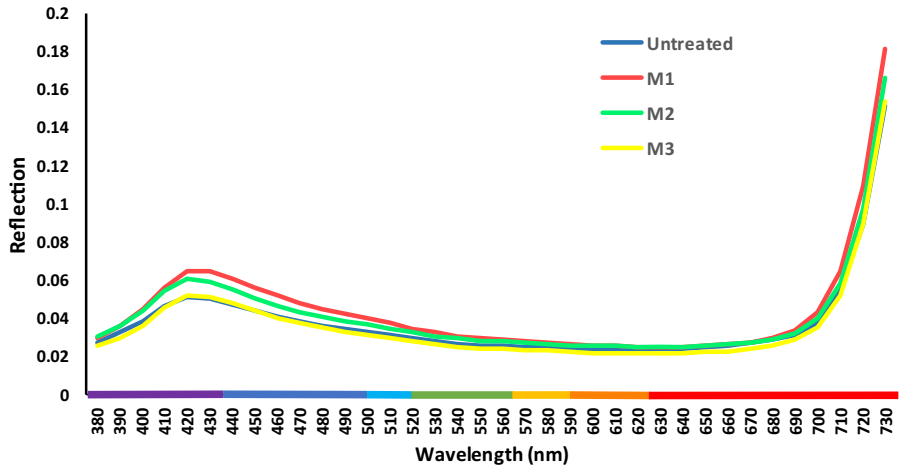


Fig. 9 The reflection of various samples in the visible wavelength

The color differences and self-cleaning enhancement of different samples are reported in Table 2 indicating a higher level of self-cleaning property for the treated fabrics with M2 comparing with M1. As a result, the treated fabrics designated the higher color differences than raw due to silica NPs (Nozari et al. 2018). The self-cleaning enhancement was measured nearby 12 and 153% for the treated samples with M1 and M2 comparing with the untreated.

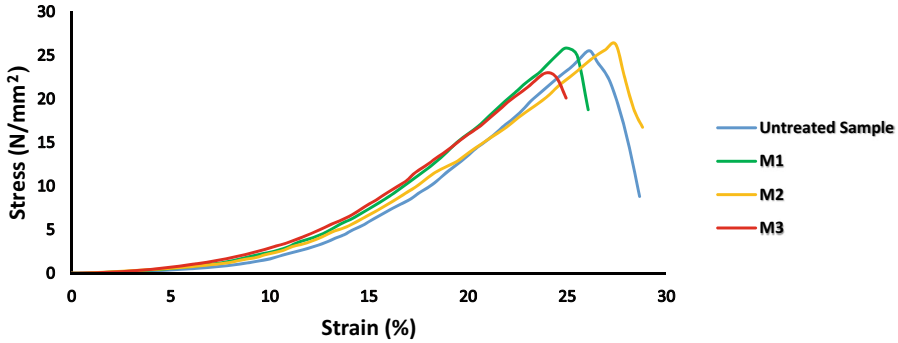


Fig. 10 Stress–strain curves of the various treated and untreated fabrics

Color change measurement

The lower ΔE indicates the less color difference (Zhang et al. 2003). Table 2 shows the color difference (ΔE) of treated samples as M3 with no silica NPs displays less color change and M1 confirms a higher color difference. However, the results confirm no significant changes after synthesis in alkaline condition. Hence, this method is very efficient for in-situ silica NPs synthesis without striking color changes.

Moreover, the reflections of the samples were investigated in the visible wavelength since more reflection confirms less absorption (Montazer et al. 2012). Figure 9 provides the closest reflection curve for sample M3 to untreated because of the less color change (ΔE = 1.3). Sample M1 has the highest reflection and the greatest difference was recorded at 380 to 520 nm related to the violet, blue, and cyan colors corresponded to the blue jeans dyed with indigo.

Physico-mechanical properties

The bending properties of fabrics determine different characteristics such as handle, softness, drape, thickness and crease recovery of cloth (Lee et al. 2015). The bending length and stiffness of the treated samples increased (Table 2). In addition, the shrinkage in Table 2 exhibited no-shrinkage since the broken cellulose bonds under alkaline conditions reacted with SiO_2 and the newly formed bonds left no space for the fabric to shrink.

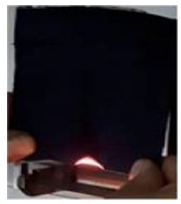
The alkaline condition of synthesis possibly leads to the scission of cellulosic chains reduces the tensile strength of the fabric (Aladpoosh et al. 2014; Maryan et al. 2013a; Rezaie et al. 2017a). Moreover, the sample treated with M3 (*Keliab* without sodium silicate solution) has the lowest tensile strength (Fig. 10).

The bonds formation between SiO_2 and cellulose compensate the decrease in the tensile strength to some extent. As a result, the samples treated with silica NPs are stronger than the untreated (Fig. 10). The treated sample with M2 has the highest tensile strength among the others (Fig. 10) due to the more synthesis in ethanol and formation of more bonds between SiO_2 and cellulosic chains. The Young's modulus of various samples is also reported in Table 2. It was shown that he synthesis of silver NPs on the cotton fabric under alkaline conditions reduced the tensile strength (Aladpoosh et al. 2014; Maryan et al. 2013a). In addition, (Rezaie et al. 2017a) similar results reported with the biosynthesis of cupric oxide on cotton fabric under alkaline conditions. However,

Table 3 5-Point scale for the fabric handles of different samples with the average rate

	Frequency					
	Smooth (1)	Fine (2)	Medium (3)	Rough (4)	Harsh (5)	Average
Untreated		14	28	8		2.88
M1			3	32	10	4.04
M2				10	39	4.8
M3		3	39	8		3.1

Table 4 Flame retardant of the untreated and treated fabrics with M1, M2 and M3

Samples	Burning length (cm)	Burning speed (cm/s)	Fabric burning picture	Time after burning (s)
Untreated	10.0	2.5		4
M1	1.900	0.160		8
M2	1.200	0.100		8
M3	0.900	0.075		8

other researchers reported the increase in tensile strength after synthesis of silica NPs on PET in alkali media (Nozari et al. 2018).

Air permeability is an important comfort factor of garments (Maryan et al. 2013b; Yuen 2009). According to Table 2, the fabric air permeability increases for M1 higher than M2 and M3. The alkaline condition can be a reason for the higher air permeability of treated samples. In addition, the loose fibers can be removed from the surface of the fabric during the synthesis of silica NPs causing the air easily pass through the pores of the fabric.

The finishing can affect the fabric handle that is influencing on the product and the application (Ünal 2010). Here, the synthesis of silica NPs on denim fabric negatively influenced on the handle though improved other properties. The participants were evaluated the untreated fabric with an average scale of 2.88 arranging the untreated fabric handle as medium (Table 3). They also rated the treated samples as M3 with a medium rate (3.1) showed the closest handle to the untreated fabric. The silica NPs on surface of treated samples led to the rough (4.04) and harsh (4.8) handle for M1 and M2, respectively. Moreover, according to the bending rigidity results, it is obvious that the handle of the treated samples with M1 and M2 is harsh, hard, and rough hence the samples treated with M3 are not different from the raw.

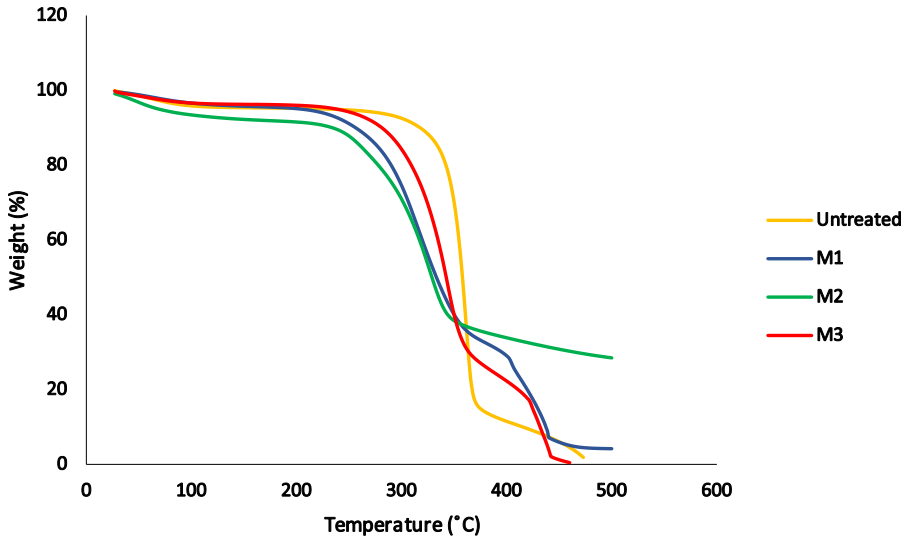


Fig. 11 TGA curves of the untreated and various treated fabrics

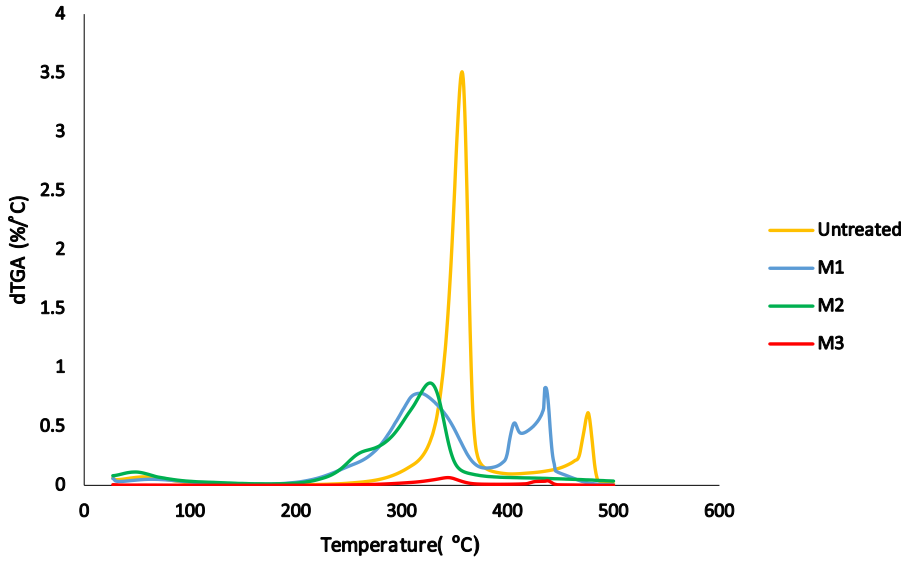


Fig. 12 dTGA curves of the untreated and various treated samples

Table 5 dTGA data for untreated and diverse treated samples

Samples	Weight loss at 500 °C (%)	T_{max1} (°C)	Derivative weight at T_{max1}	T_{max2} (°C)	Derivative weight at T_{max2}	T_{max3} (°C)	Derivative weight at T_{max3}	T_{max4} (°C)	Derivative weight at T_{max4}
Untreated	100	57	0.072	357	3.51	476	0.62		
M1	95.8	64	0.052	317	0.78	407	0.53	435	0.83
M2	71.53	49	0.113	327	0.868				
M3	100	334	0.63	423	0.11	437	0.13		

Hydrophilic properties

The time needed for the entire spreading of water drop on the sample is a way to evaluate hydrophilic properties. The full absorption on untreated fabric required 10.36 s whereas M3 showed an inconsiderable longer time of 13.16 s. The treated samples are more hydrophilic than the raw. The silica NPs synthesized on the fabric led to the higher surface roughness (Zhu et al. 2011) however, the alkaline conditions of synthesis caused to the formation of the hydroxyl groups. Furthermore, SiO_2 NPs under the light and humidity hydroxylated forming silanol groups (Si–OH) initiated the higher hydrophilicity (Nozari et al. 2018). Therefore, the required time for the full absorption of water drop on the treated sample with M1 and M2 was 1 and 6.6 s, respectively.

Thermal behavior

One of the important factors of the silica NPs is the heat resistance which leads to slow burning and shorter burning length (Alongi and Malucelli 2012). A special high level of silica is the main factor in increasing fabric stability at high temperature hence the silica NPs on treated fabrics decreases the burning speed (Rezaei et al. 2013). Burning length and speed of treated samples are lower than raw. Moreover, the size of SiO_2 NPs on the treated samples with M2 is bigger with more agglomeration thus its burn length and speed was lower compared to M1. Table 4 indicates the lowest burning length and speed for the sample treated with M3.

Figures 11 and 12 show the TGA thermograms of untreated and treated samples, derivative TGA (dTGA) plots and temperatures of maximum weight loss (T_{max}). The three main stages of weight loss can be observed for both untreated and treated samples with M2. The first stage for the both samples displays the loss of water near 100 °C (Nam et al. 2014). The second stage occurs between 300–380 °C and 250–350 °C for untreated and treated with M2 verifying a higher rate of weight loss due to the decomposition of cellulose (Gaan and Sun 2007). A lower rate of weight loss happens at 380 to 500 °C for the decomposition of residue or char with no residue or char for the untreated at 500 °C. Moreover, the amount of residue was about 28% at the highest temperature (500 °C) for the treated sample with M2. In fact, the silica enhances the heat resistance and ethanol expands the NPs' aggregation and size.

The treated samples with M1 and M3 demonstrate four main stages. The first stage is similar to the untreated however the treated samples confirm two stages of decomposition for cellulose due to the silica NPs and *Keliab*. The first stage happens around 250–350 °C and the second between 400 and 450 °C. The stage of decomposition of residue occurs between 450 and 500 °C however there is no residue for sample M3 at 500 °C. A 4.2% weight of sample treated with M1 was remained as a result of silica NPs. Hence, the silica NPs synthesis under the alkaline condition improved the heat resistance caused to the good thermal stability of the treated denim fabrics.

The derivative TGA curves in Fig. 12 and the temperature of the maximum weight loss in Table 5 related to the untreated and treated samples confirm the TGA curve findings.

Conclusions

In summary, *S. Rosmarinus* (*Keliab*) ash, as a source of alkali, can be used for in situ synthesis of silica NPs on denim fabric. This can be achieved by means of diluted sodium silicate solution under alkaline conditions. The FESEM images revealed the rod-shaped silica NPs by *Keliab* solution and spherical-shaped NPs by ethanol in alkaline conditions with the average size of 78.9 and 311.43 nm, respectively. FTIR spectra confirmed formation of the Si–O stretching at 1000 cm^{-1} on the treated fabric. The breakages in cellulosic chains due to alkaline treatment at high temperature along with ionic linkages of cellulose with SiO_2 caused to the higher tensile strength and bending rigidity. The silica NPs on the fabrics made absorption of water faster and improved the hydrophilic properties. Besides, the silica NPs on the fabric surface significantly decreased the burning length and increased the residue of fabric at 500 °C providing the consumer protection. The handle of the fabrics turn to rigid, harsh, and hard, nevertheless the fabric air permeability improved. Overall, the applied synthesis method is environmentally friendly and low cost that can be applied on cellulose fabric to produce multifunctional properties such as flame retardant and self-

cleaning. The final denim fabric can be used in various situations such as apparel manufacturing, protective clothing for humans and pets, mobile cases, insulation textiles, and bags and shoes industry. It can also be exploited in home textiles including curtains, furniture, seat covers, mattresses, and sleepwear.

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