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Improvement in Properties of Wool Fibers Pretreated with Chitosan and Nano- Chitosan and Dyed with Saffron Natural Dye

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WOOL fibers pretreated with chitosan and nano -chitosan and dyed with saffron red and yellow mixture as natural dye by using microwave heating method. The effect of chitosan and nano chitosan concentrations on color strength (K/S) was measured. The results indicated that, wool fibers pretreated with chitosan and nano chitosan recorded higher color strength than the untreated fibers. Fastness properties and the color yield of the dye on wool fibers were evaluated. The results indicated that color fastness to rubbing, washing and perspiration of all dyed wool fibers are excellent to good. The morphologies structure of the untreated and pretreated wool fibers were examined by scanning electron microscopy (SEM). The untreated wool fibers have a rough surface. The pretreated wool fibers were swelling compared to the untreated fibers. The diameter of the fibers increased and has smooth and even surfaces. The covering of the surface by bulk chitosan or nano-chitosan particles leads to the improvement in tensile strength and elongation of pretreated wool fibers. The antimicrobial activity with some species of bacteria and fungi were tested. The reduction percent for treated fibers were higher than the untreated fibers it reaches to 87% for *Aspergillus Niger*. The results obtained indicated that, the reduction percent of bacteria and fungi for fibers treated with nano chitosan was higher than chitosan it gave values from 75-87%

Keywords: Chitosan, Nano- chitosan, Saffron red and yellow mixture, Natural dye

Introduction

Wool fibers are considered one of the most natural fibers employed considerably in textile industry. It is composed of keratinous protein as a basic constituent and the minor component cell membrane complex [1].

Scaly structure determines performance and quality of the finished wool fabric such as handle, luster, pilling ,dyeability felting, and shrinkage. To overcome shrinkage and hydrophilicity disadvantages of wool fibers.Surface modification methods on fiber surface are necessary to proceed. In the past chemical methods were used for treatment to overcome these problems. Nowadays ecological processes are used due to the increasing of the environmental awareness in textile industry. Eco friendly treatments such as biopolymers, enzyme and plasma are used instead of chemical treatments [2-5]. To eliminate chemical pollutants and their effluents as a result of chemical processes. Natural polysaccharide was applied to pretreatment wool fibers to improve its properties.

Chitosan is a natural polysaccharide-based cationic biopolymer, is derived from the chitin component of the shells of crustaceans. The advantageous properties of chitosan are nontoxicity, biocompatibility, biodegradability, antimicrobial activity and chemical reactivity. It can be used mainly for the purpose of shrink resistance,dyeability treatments [6-9]. To obtain

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more advantages of chitosan, new studies have been focused on nano sized chitosan particles. In textile industry nanochitosan usage is relatively new material. Nano-particlespossess unique properties, such as large ratio of surface tovolume, surface-active multi centers and high surfacereactivity. The advantages of chitosan and nano-materials have emerged as nanochitosan with excellent physicochemical properties. It is bioactive and frequently used in many industrial areas including textiles [10-16].In present study, bulk chitosan and nanochitosan particles were used. All pretreated fibers were evaluated in terms of change in their color strength K/S values of dyed wool fibers by natural dye. Fastness properties, tensile strength, surface morphologies and antimicrobial activity also were evaluated.

Materials and Methods

Materials

Wool fibers

Mill scoured 100% wool fibers used for this study was supplied from Misr Co. (El Mehalla El-Kobra Egypt for spinning and weaving). The fibers was washed in a bath containing 2g/l non-ionic detergent (Nonidet) at 40°C to remove any impurities and then thoroughly washed with water and then dried by air at room temperature.

Dye:

Saffron red and yellow mixture as natural dye (1:1) Saffron is the dried stigma of flowers of Crocus sativus. It was supplied from commercial market.

Chemicals:

Chitosan (high molecular weight) (Aldrich),, nano- chitosan particles were supplied from (Aldrich) .

All chemicals used in this study were of laboratory grade.

Methods

Dye Extraction:

Microwave extraction:

Extraction was carried out to saffron red and yellow(20g/l) as natural dye by using microwave heating method. In 1000 ml distilled water using (20g) amounts of each dye materials at time (5 min/). After filtration saffron red and yellow were mixed as mixture of natural dyes.

Pretreatment with chitosan and nano chitosan

Chitosan high molecular weight solutions were freshly prepared by dissolving (1-4 g/l) in distilled water containing acetic acid (1% v/v). Nano chitosan was obtaned in liquid form,we used conc.(1-3 ppm) were used for pretreatment. The wool fibers were immersed in these solutions at a 50:1 liquor ratio for 5 min using microwave, and then thoroughly washed, and air dried at room temperature.

Dyeing procedure:

Dyeing of wool fibers was carried out using microwave heating. Saffron yellow and red mixture (1:1) were applied at different pH (3,5,7,8.11)in dyeing bath, for periods of time (1-5 minutes).After dyeing, wool fibers were rinsed with water and then dried at room temperature. K/S values of dyed wool fibers were measured

Measurements

Measurements of Color strength (K/S value):

An Ultra Scan PRO spectrophotometer was used to measure the reflectance of the samples and hence, the K/S was measured spectrophotometrically at wave lengths: λmax 385nm). The K/S of untreated and pretreated wool fibers with chitosan and nano-materials dyed with saffron red and yellow mixture was evaluated.

K/S where K and S are the absorption and scattering coefficients, respectively

Fig.1. Saffron red and yellow dyes (Saffron is the dried stigma of flowers of Crocus sativus)

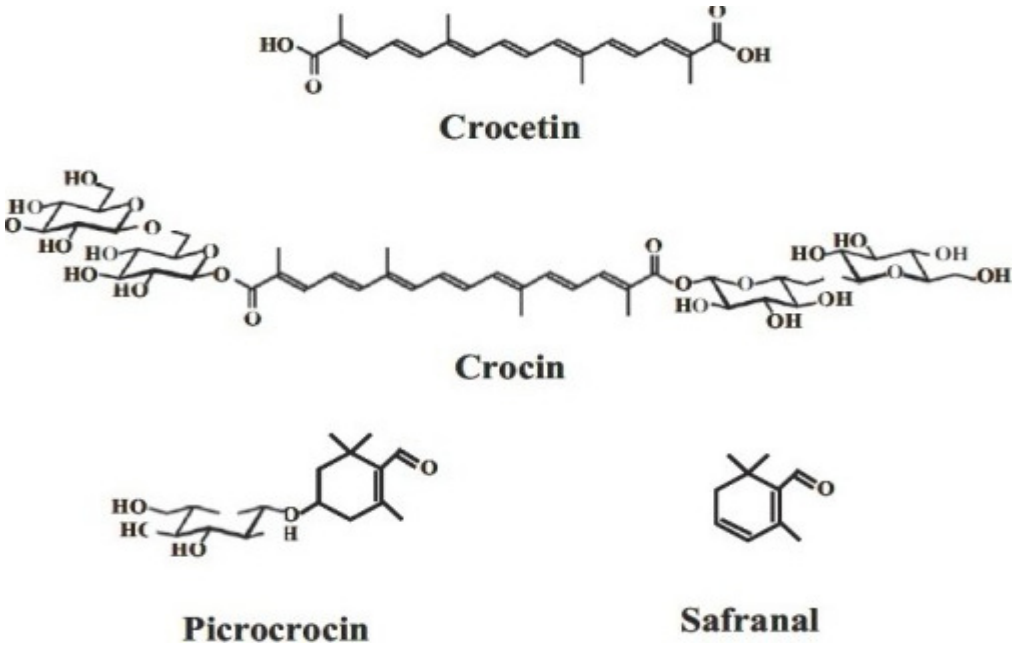

Fig.2: Structures of the chemical constituents of saffron

CIELAB coordinates (L* a* b*) of undyed and dyed wool fibers were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 108 standard observer.

Fastness properties:

The dyed samples were tested according to ISOstandard methods. The specific tests were: ISO 105-X12(1987), color fastness to rubbing; ISO 105-C02 (1989), color fastness to washing; ISO 105-E04 (1989), colorfastness to perspiration; and ISO 105-B02 (1988), colorfastness to light (carbon arc).

Tensile strength and elongation

The tensile strength was measured according to ASTMD 2256 standard by using Lloyd LLOYDX-LR5K device.

Scanning Electron Microscopy (SEM)

The surface morphology of untreated and pretreated wool fibers were investigated by using scanning electron microscopy (SEM), with a JSMT-20, JEOL-Japan. Before examination, wool fibers surface was prepared on an appropriate disk and randomly coated with a spray of gold. SEM was carried out at the National Research Centre (Egypt).

Antimicrobial measurement:

The antimicrobial activity with some species of bacteria and fungi of the pretreated wool fibers and untreated fibers were tested by reduction percent method. The antibacterial and antifungal studies of dyed pretreated and untreated wool fibers were accomplished using standard methods (AATCC TM 100 and AATCC TM 30). The dyed pretreated wool fibers fabric was introduced into 20 ml nutrient broth and inoculated with the respective bacterial strains followed by overnight (24 h) incubation at 37°C. Growth of the bacterial strains were determined by a spectrophotometer at optical density 660 nm (OD660) in presence of the dyed untreated wool fibers against a blank of un-inoculated sterile medium. Similarly, the fungal strains inoculated into potato dextrose broth and incubated for 48 h at 28°C in a shaker incubator followed by measurement at optical density 450 nm (OD450) against a blank of un-inoculated sterile medium. Before recording the optical density of the respective media after incubation, the culture tubes were shaken thoroughly in order to bring micro-organisms into suspension. Optical density is directly proportional to the number of micro-organisms (bacteria or fungi) in the medium. The percentage of reduction of the micro-organisms was expressed as follows:

$$R=(B - A)/Bx100$$

Where; R: Percentage of reduction of microbial population; B:Absorbance of the media inoculated with microbes and A: Absorbance of the media inoculated with microbes and dyed pretreated and untreated wool fibers.

Results and Discussion

Effect of conc. of pretreatment on wool fibers

The color strength of pretreated wool fibers with chitosan and nano chitosan dyed with saffron red and yellow mixture affected by conc. . of pretreatment**.** Chitosan and nano-chitosan have high affinity for dye under investigation. Fig.3,4 showed that the color strength of pretreated wool fibers with nanochitosan and chitosan and dyed with saffron red and yellow mixture has high value of color strength than untreated wool fibers. It is also observed that pretreatment with nano chitosan exhibited higher values of color strength than pretreatment with chitosan.

Effect of the dye bath pH:

The color strength of pretreated wool fibers with chitosan , nano chitosan and untreated dyed fibers affected by dye bath pH. Chitosan and nano chitosan has high affinity for dye under investigation. In acidic medium, the cationized amino groups can adsorb anionic dye molecules by the electrostatic attraction. It is also known that the binding of chitosan to wool fibers is occurred by ionic interactions [17]. Figure 5, showed that the color strength of pretreated wool fibers with nanochitosan , chitosan , and untreated dyed fibers has high value in acidic medium at pH:5 of dyeing bath .It is also observed that pretreatment with nano chitosan exhibited higher values of color strength than pretreatment with chitosan.

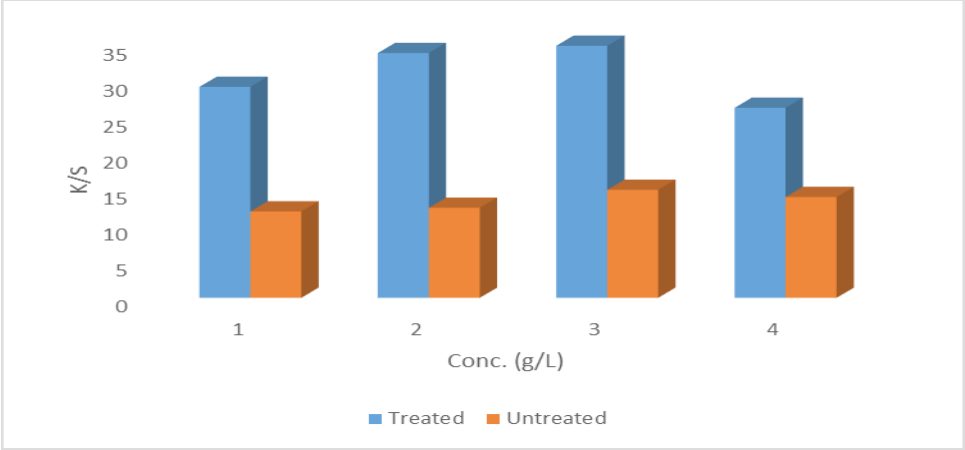

Fig. 3. Effect of conc. of pretreated wool fibers with chitosan on the color strength and untreated dyed wool fibers with saffron yellow and red mixture dye.

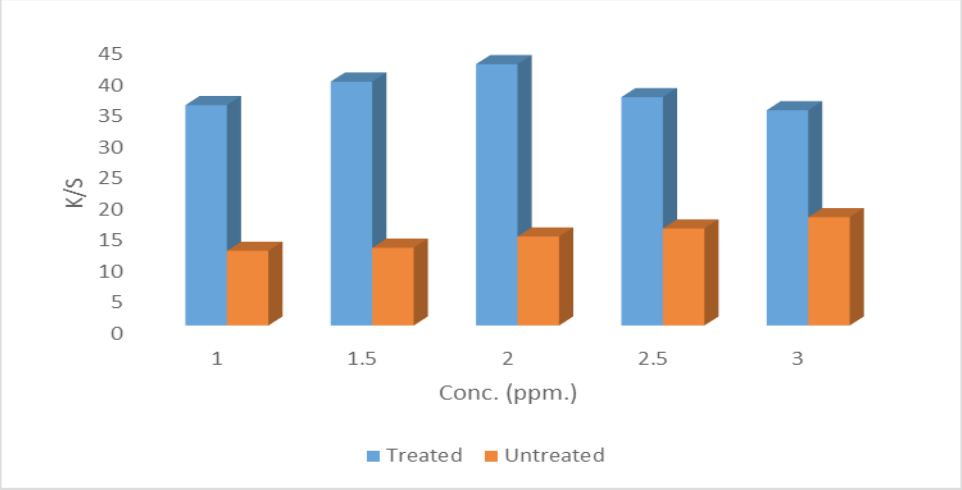

Fig. 4. Effect of conc. of pretreated wool fibers with nano chitosan on the color strength and untreated dyed wool fibers with saffron yellow and red mixture dye.

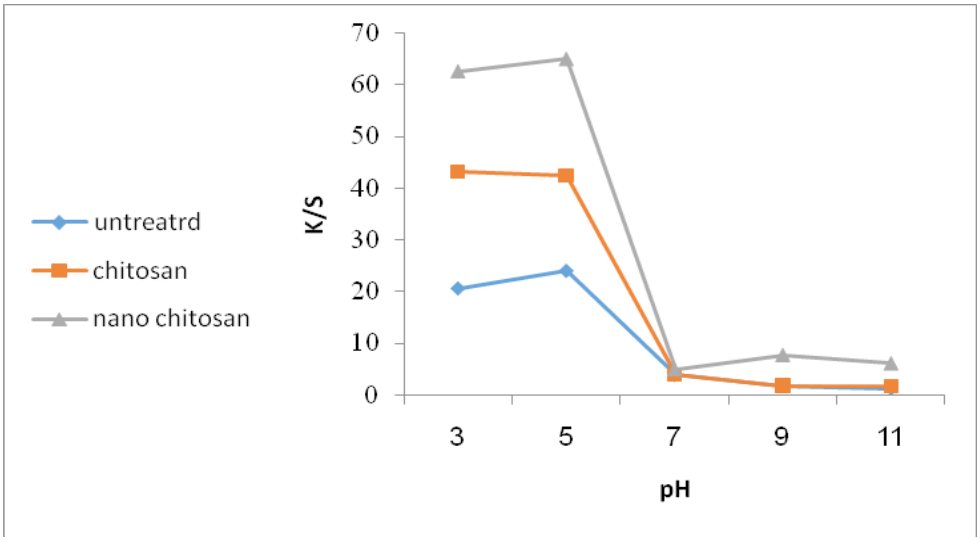

Fig. 5. Effect of the dye bath pH on the color strength for pretreated wool fibers with chitosan, nano chitosan and untreated dyed fibers using microwave.

Effect of time on the color strength:

The dyed wool fibers pretreated with chitosan ,nano chitosan and untreated dyed fibers using microwave affected by time. From Figure 6, it can be seen that the K/S values of chitosan and nano chitosan pretreated fibers are higher than that of untreated fibers and exhibited the highest value of K/S at 5min..

Pretreated wool fibers with chitosan and nano chitosan gave higher K/S values than that of untreated fibers as showen in Fig. 7,8. This improvement in color strength (K/S)values of chitosan and nano chitosan of pretreated wool fibers is associated with the introduction of primary amino groups to the fiber structure .The color strength can be significantly increased after pretreated by nanochitosan in comparison to the bulk chitosan pretreated wool fibers. Chitosan particle sizes were taken into consideration, it was found that nanochitosan had greater capillarity on account of its large surface area and smaller size when compared with chitosan .

Table 1 showed that the effect of dye amount on K/S and CIELAB value of saffron yellow and red mixture for 5 min .using microwave on untreated, pretreated wool fibers with chitosan and nano chitosan. The dye amount increase as the K/S increases We can notice also that the K/S of treated wool fibers is much higher than untreated one.Table 1 shows the colorimetric data (L*, a* and b*) of different fiber samples dyed with different dye concentration. From data listed in the Table 1 we can be concluded that increasing of the extracted dye concentration, accompanied by decreasing of L* values and thus color of samples got darker.By growing the dye concentration, a* and b* values increased in the positive direction. The color of dyed wool turned to more reddish color and became darker with increasing the dye concentration therefore a* values and b* values slightly decreased.

Fastness Properties

The color fastness to light, washing and rubbing was studied in dyed samples. All samples showed staining onto multi fiber and color change values of between four and five. When the color fastness to dry and wet rubbing wasexamined, similar values (ranging between 3-4 and 4) wereobserved among the treated fibers .for both dry and in wet states. Since dye molecules were adsorbed on the surfaceand could not penetrate into the fiber as easily as treatedsamples, all treated fibers show better values than untreated fibers The values of fastness to light of the pretreated samples gave values changing between 6 and 7 as shown in Table 2.

Tensile Strength

The effect of chitosan and nano chitosan were evaluated in terms of tensile strength changes of the wool fibers Effect of applied pretreatments on tensile strength and elongation values of the wool fibers weregiven in Table 3.

The covering of the surface by bulk chitosan or nanochitosan particles leads to the improvement in tensile strength and elongation of pretreatment

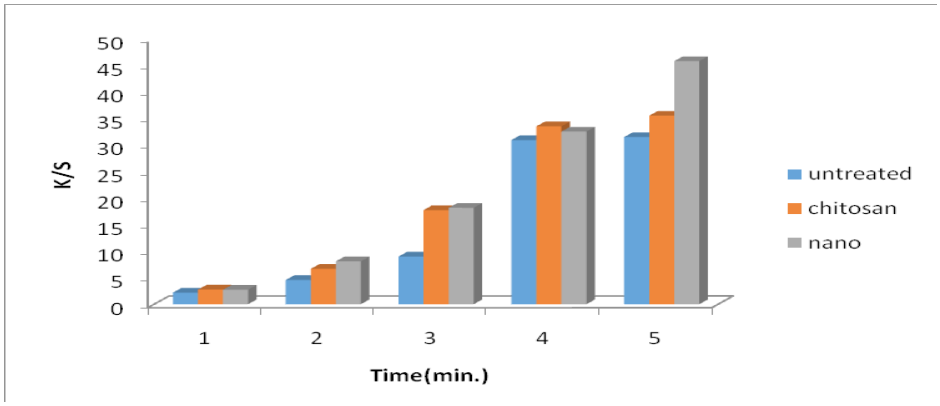

Fig.6. Effect of time of dyeing on the color strength for pretreated wool fibers with chitosan,nano chitosan and untreated dyed fibers.

TABLE 1 :CIELAB coordinates (L* a* b*) for Wool fibers dyed by saffron yellow and red mixture

Sample	K/S	L*	a*	b*	C	H	ΔE
untreated	30	56.86	43.75	24.28	49.88	29.13	-26.92
Chitosan	40	32.29	85.18	41.87	86.42	35.74	-39.92
Nano chitosan	45.93	59.28	35.55	41.85	43.84	33.52	-41.01

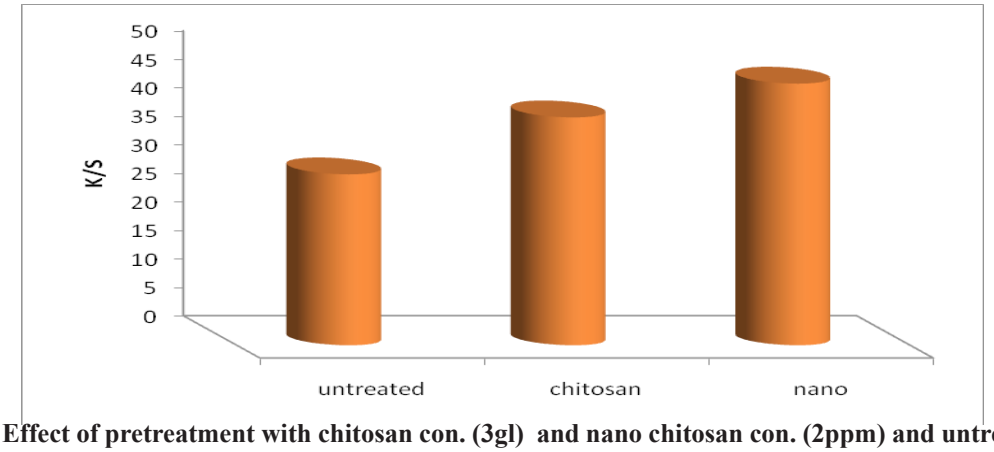

Fig. 7: Effect of pretreatment with chitosan con. (3gl) and nano chitosan con. (2ppm) and untreated of wool fibers dyed with saffron yellow and red mixture dye for 5 min. on the color strength

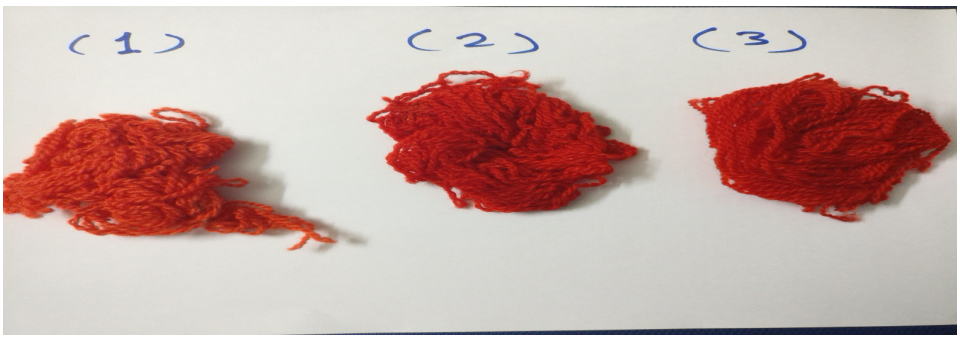

Fig. 8: Wool fiber samples dyed by saffron yellow and red mixture using microwave for 5 min. : 1 (untreated), 2 (chitosan treated), 3 (nano chitosan treated).

TABLE 2: Fastness properties of dyed wool fibers pretreated with chitosan and nano chitosan and dyed with saffron red and yellow mixture dye.

Sample	Fastness to rubbing		Wash fastness			Fastness to Perspiration						Light
						Alkaline			Acidic			
	Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
Untreated	3-4	3-4	4	4	4	4	3-4	3-4	4	3-4	3-4	5
Chitosan	4-5	4-5	5	5	4-5	5	4-5	4-5	5	4-5	4-5	7
Nano chitusan	4-5	5	5	5	4-5	5	4-5	4-5	5	4-5	4-5	7

TABLE 3.The effect of different pretreatments on tensile strength and elongation values

Treatment	Elongation %	Tensile strength (gm/Tex)
Untreated	27.8	10.3
Chitosan	29	11.8
Nanochitosan	34.4	11.8

wool fibers. The protective effect on tensile strength and elongation by biopolymer treatment is more dominant by nanochitosan pretreatment due to its larger surface area.

Surface Morphology

The morphologies of the untreated and pretreated wool fibers were examined by scanning electron microscopy (SEM). Effect of pretreatment with chitosan and nano chitosan using scanning electron microscope (SEM) for wool fibers. Figs 9 a, b,c represent the SEM images of untreated , pretreated wool fibers with chitosan and nano chitosan respectively. The untreated samples have a rough surface as shown in Fig. 8a, the treated samples as shown in Fig 9 b and c indicate that the pretreated wool fibers were swelling compared to the untreated fibers , the diameter of the fibers increase and have smooth and even surfaces. The changes in the surface morphology due to the effect of pretreatment with chitosan and nano chitosan. As can be seen from the images, chitosan and nano chitosan treatments covers wool surface. Chitosan and nano chitosan created a smooth surface which is a significant improvement for wool fibers in terms of their hydrophilicity and dyeability propert

Antimicrobial Activity:

Table 4 showed that the antimicrobial activities of chitosan and nano chitosan may be attributed to the chelation of metals, suppression of spore elements and binding to essential nutrientsto microbial growth. Chitosan oligomers diffuse inside hyphae interfering on the enzymes activity responsible for the fungus growth. Chitosan molecules in bacteria surrounds might complex metals and blockage some essential nutrients to flow, contributing to cell death [18-20]. The positive charge on the N atom of, chitosan below pH 5.0 is more soluble and has a better antimicrobial activity by interfering with the negatively charged residues of macromolecules exposed on the fungal cell surface, and thereby changes the permeability of the plasma membrane.. It is found that the pretreatment with nanochitosan, effectively enhanced the antimicrobial activity due to large effective surface area **[21-24].**

Conclusion

The applications of chitosan in textiles have received great attention in numerous studies due to its several uniqueproperties. The huge molecular size and high viscosity of chitosan polymer limit its penetration into the fiber. Reducing the particle size of chitosan to nano level increases theextent of penetration into fiber structure and maintainsinherent properties of wool fibers.

Comparison of chitosan and nanochitosan in dyeing, fastness properties, tensile strength ,elongation and surface morphology were investigated The results showed improvements in properties of wool fibers.

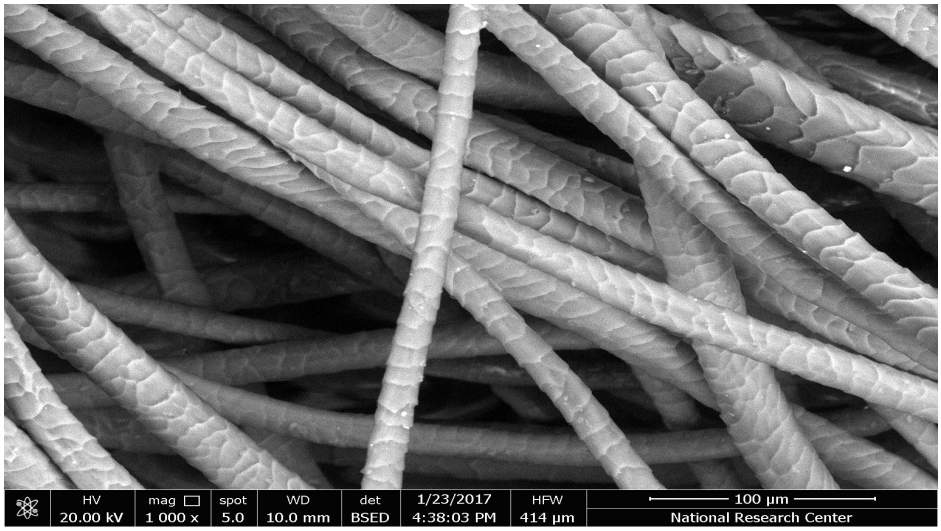

Fig.9 a: SEM for untreated wool fibers

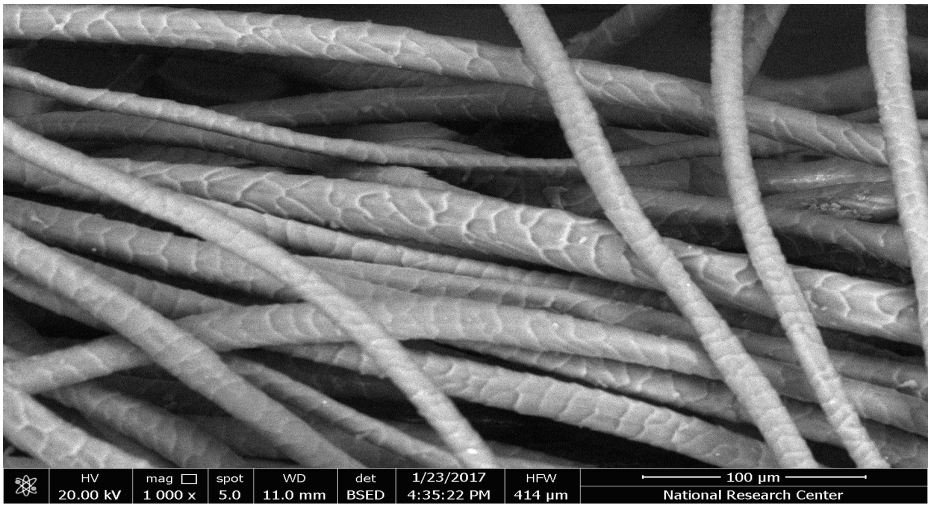

Fig.9 b: SEM for pretreated wool fibers with chitosan

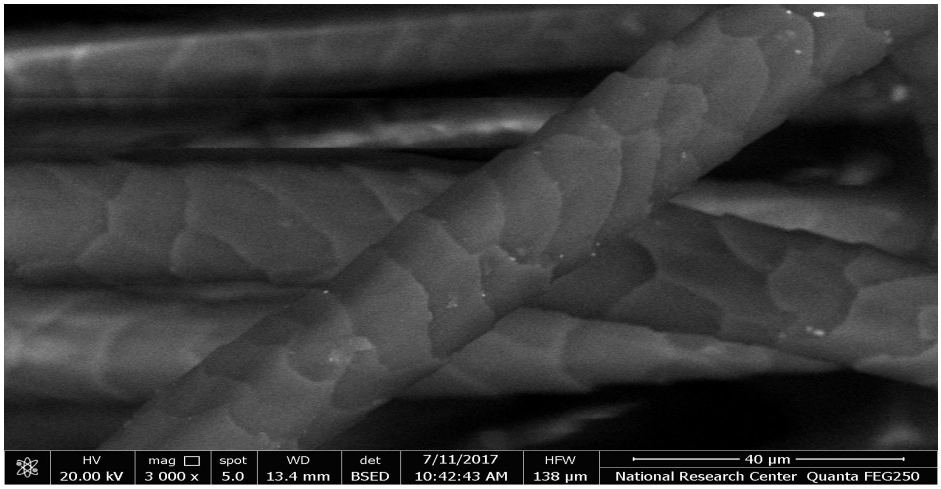

Fig.9c: SEM for pretreated wool fibers with nano chitosan.

TABLE 4 : Antimicrobial activity of dyed wool fibers pretreated with chitosan con. (3gl) and nano chitosan con. (2ppm) and untreated of wool fibers.

Microbes		Growth reduction (%)	
		untreated	treated
Stophyloccus aureus	Chitosan	12	65
	Nano chitosan	12	70
Pseudomonas Aeruginosa	Chitosan	15	70
	Nano chitosan	20	80
Asperigullas niger	Chitosan	15	75
	Nano chitosan	20	87

Chitosan pretreatment of the wool fibers generates additivefunctional groups on surface which cause increase in hydrophilicity. K/Svalues of treated fibers in comparison to untreated one gave higher values and good fastnessproperties.

Nanochitosan showed better properties due to its large surface area and smaller size when compared with bulkchitosan.. However, pretreatment with chitosan and nanochitosan showed protective effect and improved tensile strength..Pretreatmentof wool fibers with chitosan and nano-sized chitosan has ecologically acceptable. It's more applicable and promising for sustainable textile industry.

Conflicts of interest

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