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Dye-ability and antibacterial effect of dyed silk fabric with annatto in presence of inorganic salt and chitosan

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ABSTRACT

Natural colors are compatible with the environment than synthetic dyes. Including these natural colors can be noted annatto. Variety of hue of a natural dye depended on dyeing process and the types of mordant. In this work, silk fabrics were treated with different chitosan concentration as a bio mordant and mordant with inorganic salt such as ferric sulfate, aluminum sulfate, potassium dichromate and copper sulfate. The color yield, color difference and color fastness to rubbing and washing of the dyed silk fabrics were evaluated. Also the effects of chitosan concentration, type of mordents on dye uptake and antibacterial properties of samples were studied. All mordant fabrics have high adsorption compered to un-mordant ounces. The silk fabric treated with 0.6% chitosan had higher K/S values, washing and rubbing fastness. The antibacterial properties of treated silk fabrics against two kinds of bacteria: staphylococcus aurous and Escherichia coli were investigated. The treated silk samples were found to have antibacterial potential due to the antibacterial property of chitosan and annatto. Scanning electron microscopy (SEM) photographs reveal the deposition of chitosan and effect of mordents on the treated fabrics.

1. Introduction

Silk fabric can be used in many products such as precious fabrics, parachutes, tire lining materials, artificial blood vessels, and surgical sutures (Kumar et al., 2005). Some properties of silk fabric such as wash and wear properties, dye-ability, and color fastness are weak and they should be improved. For this purpose, Modification of silk by some physical and chemical techniques such as mordanting and surface modification have been developed (Kumar et al., 2005). Natural colors obtained from flowers, trees, shrubs, leaves, insects and minerals. The color was used in dyeing fabrics, yarn, leather, food, etc. for centuries (Sheikh et al., 2006). Natural colors can also be used for dyeing, food and drawing. However, natural colors on the fabric have a low fastness. Features including the ability to form complexes with metal ions in natural dyes such as chromium ions, iron, copper, aluminum co ordinance linkages. These metal ions are in the structures of materials which named as a mordant and using the mordant in the natural color dying bath cause increasing of washing and rubbing fastness. The metal ions have ability of linking with protein chain silk's fibers. The application of chitosan in textiles can be categorized into two main topics: The production man- made fibers and textile wet processing, which include dyeing (improving the dye –ability), finishing (antimicrobial properties), and printing (as print past thickener) (Sargunamani and Selvakumar 2007; Moazami et al., 2010). Chitosan as a non-toxic, biodegradable and biocompatible polymer, which linear polysaccharide units of N- acetyl glucosamine and

Glucosamine distributed randomly. In this paper it has been used as a biological mordant (Gulrajani, 1993). The chemical structure of chitosan is shown in Fig. 1.

Annatto natural carotenoid dye is obtained from shrub tree. This tree has a single or multiple branches that are light brown in color. Bixin and Noorbixin are the compounds which can be finding in these plants (Agarwal et al., 1997; Osman et al., 2010) that its chemical structure is shown in Fig. 2.

This paper focused on the dyeing and antibacterial properties and surface modification of the silk fabrics treated and mordant with chitosan and inorganic salt which dyed with annatto as a natural dye (Iriyama et al., 2002; Patel and Tandel, 2005).

2. Experimental materials

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The plain silk fabric used was scoured (Table 1) Produced by Yas sepid silk CO. in Tabriz. Iran. Chitosan was provided chitotec. (Degree of deacetylation (DD) =92.5% Molecular weight=1000Kpa, Iran).

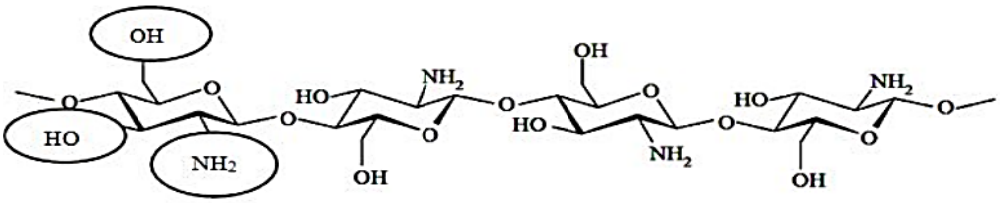


Fig. 1: Chemical structure of chitosan

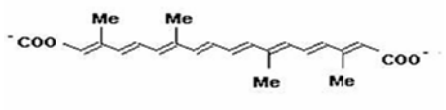


Fig. 2: Chemical structure of Bixin

Annatto dye obtained from M/S ALPS Industries Ltd., India, was used without any purification unless otherwise mentioned. Metal salts as mordents used for the present investigations are ferric sulfate, potassium dichromate, aluminum sulfate and copper sulfate- from Merck Company.

Table 1: Characterize of silk fabric

Fabric	Material	Weaving	Made	Company	Warp and weft density	
					Weft	wrap
Silk	100% Silk	Plane	Iran	Yas Sepied	67	71

3. Methods

3.1. Finishing and dyeing

Silk fabrics were treated with 5 gr/L of aqueous solution of inorganic salt for 45 min in presence chitosan (0.1, 0.6 conce) by the exhaustion method in an acetic acid solution at 30`C for 30-40 min. The treated Fabrics were dyed with annatto. The silk fabrics were dyed keeping material-to- liquor ratio at 1:50. The dye bath temperature was kept at 90 c for 1 h.

3.2. Assessment of color strength

In order to determine dye receptivity, reflectance value of the treated and dyed fabrics was measured using spectrophotometer (X. rite color- Eye 7000 A, Minolta). At their λ_{max} of reflectance, and color strength was calculated in terms of K/S values by kuble-Munk (Eq. 1):

$$K/S = \frac{(1-R_{Max})^2}{2R_{Max}} \quad (1)$$

Where k is the coefficient of absorption; S is the coefficient of scattering; R is the reflectance value of the fabric at λ_{max}. K/s values were calculated at 480 nm as the measured λ_{max}.

3.3. Assessment of color fastness properties

Rubbing and washing fastness of treated and dyed fabrics were measured by using ISO 105-X12: 1993 and 105 C. 1998 to determine the change and stain in fabrics after tests.

3.4. Assessment of antibacterial properties

AATCC Test Method 100-1999 was used to determine the antibacterial activity of the treated and dyed fabrics. The organisms taken for this study were staphylococcus aurous (s. aurous), a gram-positive bacterium and Escherichia coli (E.coli), and a gram negative bacterium. To evaluate the antibacterial activities of the treated fabrics, the reduction in colony number between the pre and post treated. An untreated fabric after incubation was determined. The percentage reduction was calculated using the Eq. 2:

$$R\ (\%) = \frac{A-B}{A} \times 100 \quad (2)$$

Where A is the number of bacteria on the un-treated fabrics after 24 hours and B is the number of bacteria on the pre and post treated fabrics with chitosan after 24 hours.

3.5. Morphology observation

Treated and dyed fabrics were observed the surface Morphology by (KyKy-EM-3200) Phillips scanning electron microscope (Holland) with an accelerating voltage of 24 KV.

3.6. Samples coding

To make it easier to work out the samples code is given in Table 2 were used.

4. Result and discussion

4.1. Effect of chitosan and mordant on color strength and color change

Silk is a natural protein fabric, which is composed of 18 amino acids with various reactive functional groups including hydroxyl and Amin groups.

Chitosan has three reactive groups. They are the primary and secondary hydroxyl groups on each

repeat unit and the amino group on each repeat unit and the amino group on each deacetylated unit.

Table 2: coding of sample

Code	Name of samples
A_1	Sample without finishing
A_2	Sample only finishing with chitosan
A_3	Sample only finishing with mordant
A_4	Sample first mordant and then finished by 0.1 chitosan and finally dyed.
A_5	Sample first mordant then finished by 0.6 chitosan and finally dyed.
$A_2^{0.1}$	Samples only finishing with chitosan 0.1
$A_2^{0.6}$	Samples only finishing with chitosan 0.6
A'	Samples only finishing with chitosan 0.1 and then dyeing
A''	Samples only finishing with chitosan 0.6 and then dyeing
A'''	Samples of just dyeing
A^0	Samples of without finishing

As a kind of protein fabrics, silk was believed to be bonded to chitosan mainly due to ionic interactions between free amino groups of chitosan and the carboxyl groups of silk. The mechanism of dye adsorption of fabric is shown Fig. 3 and the possible mechanism of the adsorption process of chitosan and annatto dye is electrostic attraction between protonated-NH_2 of chitosan and anion of dye (coo^-) in Fig. 4.

Natural dyes are commonly applied with mordant, as they are known to promote the binding of the dyes to fabrics by forming a chemical bridge between dye and fiber, improving the staining ability of the dye along with increasing fastness property. The possible mechanism of the adsorption process of annatto dye with presence of mordant and chitosan is shown in Fig. 5.

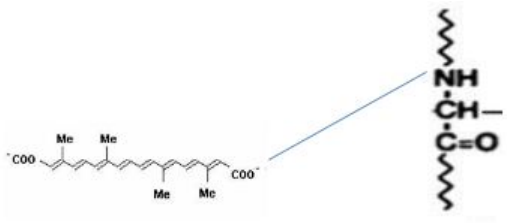


Fig. 3: Dyeing silk fabric with annatto

K/S value and color change of dyed fabrics have a close relationship to the amount of dye absorbed by the fabrics. K/S values, color change and the relative color strength of silk dyed samples with annatto in separate presence of chitosan and mordant in Table 3 and 4 and simultaneous effect of chitosan and mordents in the table 5 and 6 are shown.

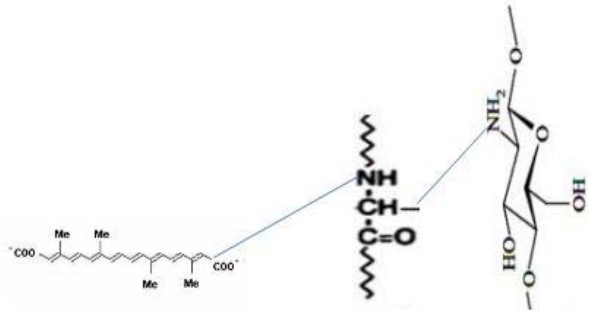


Fig. 4: Dyeing silk fabric with annatto in presence chitosan

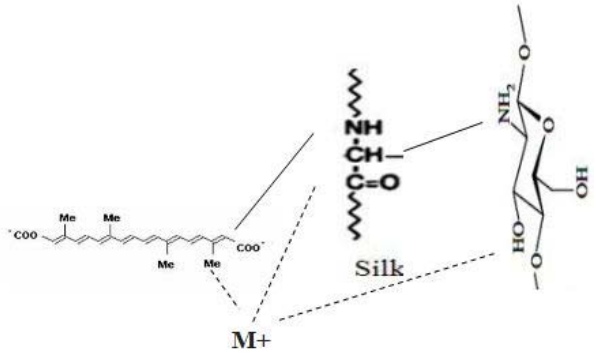


Fig. 5: Dyeing silk fabric with annatto, in presence chitosan and mordant

Table 3: The values of L *, a *, b * and K / S at chitosan concentrations of 0.1 and 0.6 silk fabric finished

Chitosan concentration (%)	Finished silk fabric with chitosan				Finished silk fabric with chitosan and dyed with annato			
	L*	a*	b*	K/S	L*	a*	b*	K/S
A^0	92.84	-0.04	4.54	0	65	29.52	50.04	6.1
$A_2^{0.1}$	92.62	-0.17	4.97	0.0125	62	29.68	50.1	8.22
$A_2^{0.6}$	92.55	-0.14	5.50	0.03	61	29.99	50.25	8.31

Regarding Table 3 and Table 4 they can be concluded that the K/S values of chitosan and mordant treated dyed fabrics are higher than that of untreated dyed samples. Regarding Table 5 and 6 they can be conciliated that as the chitosan concentration increases, the dye uptake also increases. This enhancement in (K/S) values of chitosan treated silk fabrics shows the chitosan has an incremental effect in dying process. This result further affirms that chitosan increase the amount of dye uptake in the treated silk fabrics. From the Table 5 and 6 they are observed that the depth of color increased with all combinations of mordents as it

can be seen in tables, a* and b* of silk fabrics which are treated with chitosan and mordant increased.

Table 4: a*, b*, L* of mordant samples

Samples	CIE L* a* b*			K/S Value
	L*	a*	b*	
A"'	65	29.52	50.04	6.1
A_3^{Al}	63	29.6	50.09	6.199
A_3^{Cu}	62.5	29.65	50.21	6.49
A_3^{Cr}	61.9	29.75	50.42	6.85
A_3^{Fe}	59	30.08	50.7	6.9

Table 5: a*, b* and K/S value of Mordents and finished with chitosan 0.1%

Samples	CIE L* a* b*			K/S value
	L*	a*	b*	
A_4	62.043	29.678	50.123	8.224
A_4^{Al}	59.96	29.987	50.17	8.332
A_4^{cu}	59.095	30.056	50.538	8.423
A_4^{cr}	57.087	30.143	50.543	8.525
A_4^{Fe}	54.921	30.25	50.78	8.847
A_5^{Fe}	56.043	30.143	50.768	8.8
A_5^{cu}	59.145	30.06	50.24	8.35
A_5^{Al}	61.078	29.72	50.148	8.3
A_5^{cr}	57.065	30.07	50.53	8.5

Table 6: a*, b* and K/S value of mordant and finished with chitosan 0.6%

Samples	CIE L* a* b*			K/S Value
	L*	a*	b*	
A_5	61.039	29.986	50.243	8.31
A_4^{Al}	58.029	30.054	50.332	8.465
A_4^{cu}	57.064	30.19	50.578	8.52
A_4^{cr}	56.653	30.282	50.696	8.623
A_4^{Fe}	53.0241	30.404	50.85	8.93
A_5^{Fe}	54.02	30.335	50.834	9
A_5^{cu}	58.946	30.14	50.435	8.532
A_5^{Al}	58.87	29.99	50.243	8.435
A_5^{Cr}	56.087	30.147	50.627	8.9

The L* value decreased with increasing concentrations of chitosan. From b* values it is found that by increasing the chitosan concentrations and using mordents, there is slight increase in yellowness values of silk fabrics compared to the untreated one and the reverse of these results holds true for whiteness trend. Also, the L* results indicate that there is a very slight gradual decrease in lightness values with increasing chitosan concentrations and using mordant.

In all samples, ferric sulfate has the lowest L* and the highest, a*, b* and K/S. the ferric sulfate, potassium dichromate, copper sulfate and aluminum sulfate have the highest to lowest a* , b* and k/s and L* are the lowest to the highest, respectively.

4.2. Color fastness properties

Fabrics are subjected to frequent treatments such as washing and rubbing during their usage. As the durability of the finish applied on the fabric material is extremely important these conditions, it has been assessed and is given in Table 7.

Results of washing and rubbing fastness of treated and untreated fabrics shown that samples which are treated with chitosan and mordents have high washing and rubbing fastness, because these mordents able to link to fabric and dye by carboxyl groups from both sides. Between mordant, ferric sulfate has highest washing and rubbing fastness. Also, increasing of chitosan concentration n reduced washing and rubbing fastness. Respectably samples of $A_3^{Al} < A_3^{Cu} < A_3^{Cr} < A_3^{Fe}$ and then $A_4^{Al} < A_4^{Cu} < A_4^{Cr} < A_4^{Fe}$ and then $A_5^{Al} < A_5^{Cu} < A_5^{Cr} < A_5^{Fe}$ have low to high washing and rubbing fastness effect.

Table 7: Determination of rubbing and washing fastness

Samples	Washing fastness	Rubbing Dry	Fastness Wet
A"'	2	3-4	3
A_3^{Fe}.	5	5	4-5
A_3^{Cr}	4	4-5	4
A_3^{cu}.	4	4	3-4
A_3^{Al}	4	3-4	3
A'	2-3	4	3-4
A_4^{Fe}	4	4-5	3-4
A_4^{Cr}	4	4	3
A_4^{Cu}	4	3-4	3
A_4^{Al}	3	3	2-3
A"	3	3-4	3
A_5^{Fe}	4	4	3
A_5^{Cr}	3	3-4	2-3
A_5^{Cu}	4	3	2-3
A_5^{Al}	3-4	2-3	2

4.3. Antibacterial activity

The antibacterial activities of dyed silk fabrics have been tested for the various possible treatment combinations, treatment with chitosan alone and treatment with simultaneous chitosan and mordents. Table 8, 9 present the reduction values for treated fabrics (with chitosan 0.1, 0.6 and various mordents) against both E.coli and S.aureus.

Results show that in case of E.coli for treated fabrics the bacterial reduction is better against s.aureus. The antibacterial activity of the silk treat with chitosan was considerably decreased after mordanting due to the blocking of cationic groups of the chitosan and fabrics by mordant molecules.

In general, for treated samples with chitosan 0.6 a highest reduction was observed. For all samples a higher reduction was observed for E.coli as compared to S.aureus. S.aureus is a gram positive bacterium and has thicker cell wall hence is more resistant to chitosan than E.coli.

Table 8 shows that samples of $A^{Cu}{}_5 > A^{Fe}{}_5 > A^{Al}{}_5 > A^{Cr}{}_5$, $A^{Cu}{}_4 > A^{Fe}{}_4 > A^{Al}{}_4 > A^{Cr}{}_4$ have the maximum and the minimum antimicrobial effects. Table 9 shows that samples of $A^{Cu}{}_5 > A^{Fe}{}_5 > A^{Al}{}_5 > A^{Cr}{}_5$ $A^{Cu}{}_4 > A^{Fe}{}_4 > A^{Al}{}_4 > A^{Cr}{}_4$ have the maximum and the minimum antimicrobial effects.

4.4. Morphologies of silk fabrics

The SEM micrographs of untreated, chitosan (0.1, 0.6 conce) treated and simultaneous chitosan (0.1, 0.6 conce) with mordant treated fabrics followed by a dyeing process using annatto dye are shown in Figs. 6 to 18.

All of the treated SEM micrographs showed the presence of foreign materials attached to the surface of the silk fabrics. Control sample Fig. 6 (a-c) showed a clean and smooth surface, while slight longitudinal flutes and pits were appeared on the surface of treated silk fabrics Figs. 6-18 (a-c).

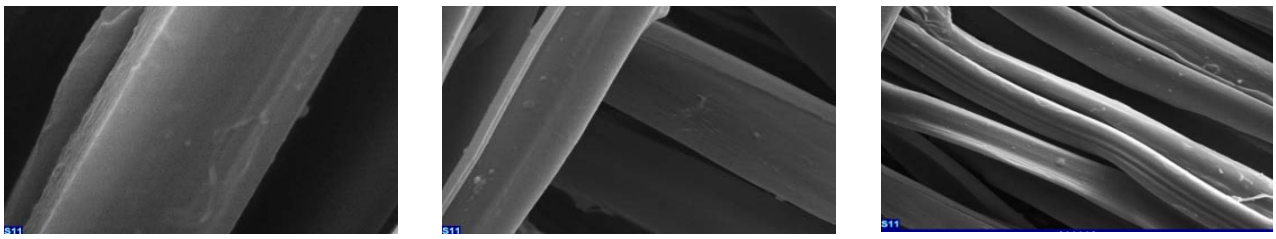
Fig. 10 showed , the 0.6 concentration of chitosan treatment on fabrics made more flutes and pits and Figure 11 through 18 showed that samples $A^{Cu}{}_5 > A^{Fe}{}_5 > A^{Al}{}_5 > A^{Cr}{}_5$ $A^{Cu}{}_4 > A^{Fe}{}_4 > A^{Al}{}_4 > A^{Cr}{}_4$ respectively have created the maximum flutes and pits on surface through accompanying with chitosan know low to high.

Table 8: Bacteria reduction percentage for $A_5{}^{(Fe,Cu,Al,Cr)}$, $A_4{}^{(Fe,Cu,Al,Cr)}$ for Escherichia Coli before laundering and after laundering

Sample	Antimicrobial effect percent before laundering	Antimicrobial effect percent after laundering
$A_5{}^{Cu}$	100	99.9
$A_5{}^{Fe}$	100	99
$A_5{}^{AL}$	100	99.3
$A_5{}^{Cr}$	99.8	98.4
$A_4{}^{Cu}$	97.7	81.8
$A_4{}^{Fe}$	93.9	70
$A_4{}^{Al}$	92.3	69.8
$A_4{}^{cr}$	91.2	69.6
D	0	0

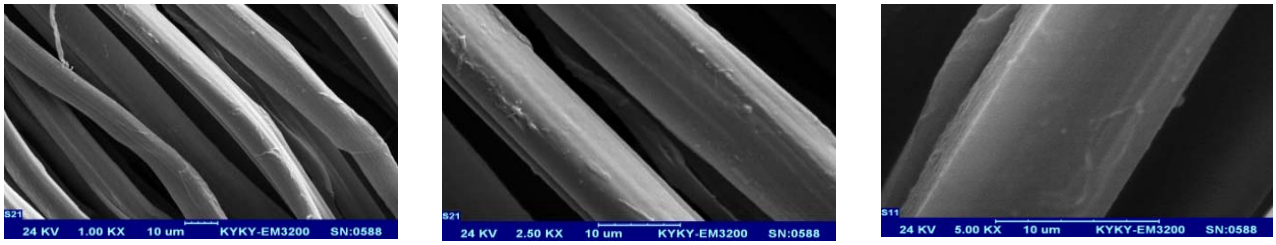
Table 9: Bacteria reduction percentage for $A_5{}^{(Fe,Cu,Al,Cr)}$, $A_4{}^{(Fe,Cu,Al,Cr)}$ *Staphylococcus aureus* before laundering and after laundering

Name of sample	Antimicrobial effect percent before laundering	Antimicrobial effect percent after laundering
$A_5{}^{Cu}$	99.9	98.8
$A_5{}^{Fe}$	99.9	89.9
$A_5{}^{AL}$	99	86
$A_5{}^{Cr}$	98.9	80.9
$A_4{}^{Cu}$	61.6	0
$A_4{}^{Fe}$	59.2	0
$A_4{}^{Al}$	56.8	0
$A_4{}^{cr}$	55.3	0
U	0	0



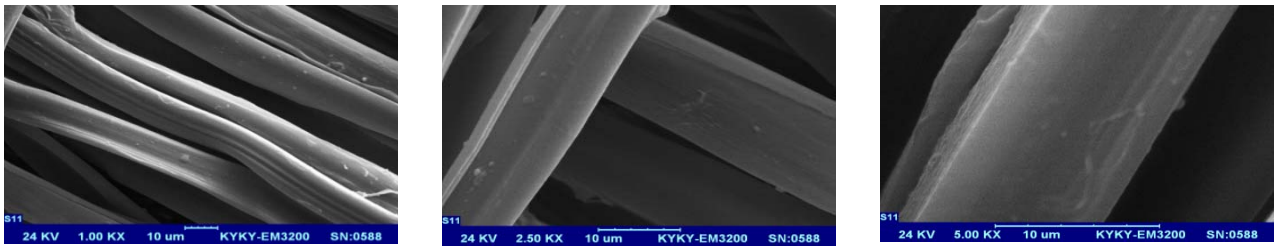
(a) **(b)** **(c)**

Fig. 6: SEM image of A_1 (a) 1000X (b) 2500X (c) 5000X



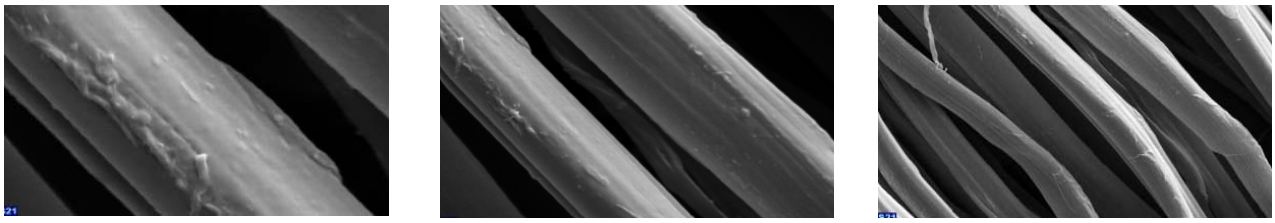
(a) **(b)** **(c)**

Fig. 7: SEM images of $A_{2\ samples}$ (a) 1000X (b) 2500X (c) 5000X



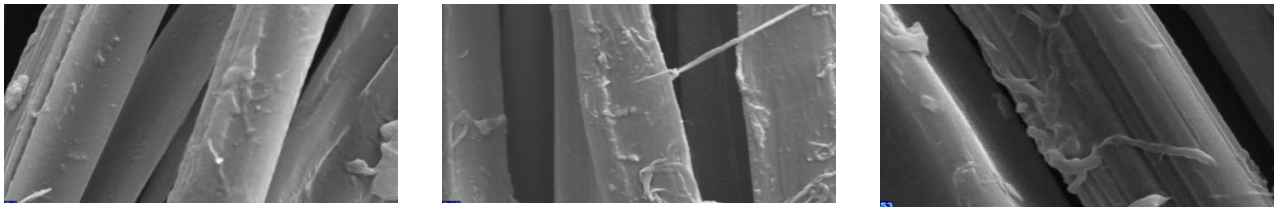
(a) **(b)** **(c)**

Fig. 8: SEM images of $A_{3\ samples}$ (a) 1000X (b) 2500X (c) 5000X



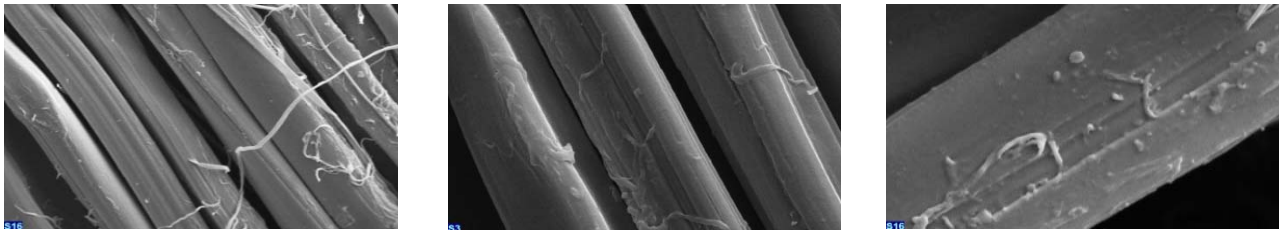
(a) **(b)** **(c)**

Fig. 9: SEM images of $A_{4\ samples}$ (a) 1000X (b) 2500X (c) 5000X



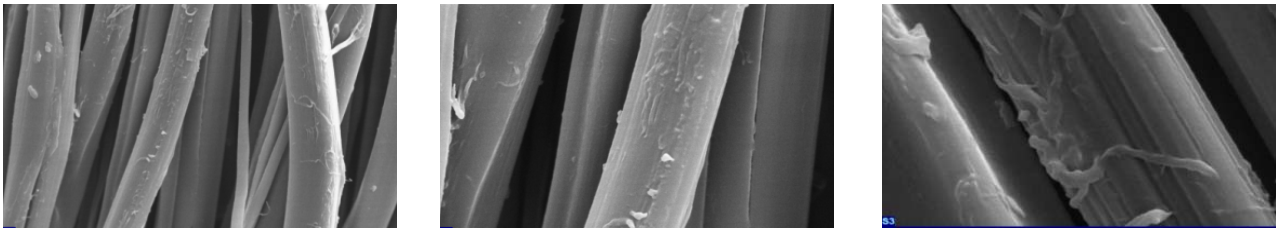
(a) **(b)** **(c)**

Fig. 10: SEM images of A_5 samples (a) 1000X (b) 2500x (c) 5000X



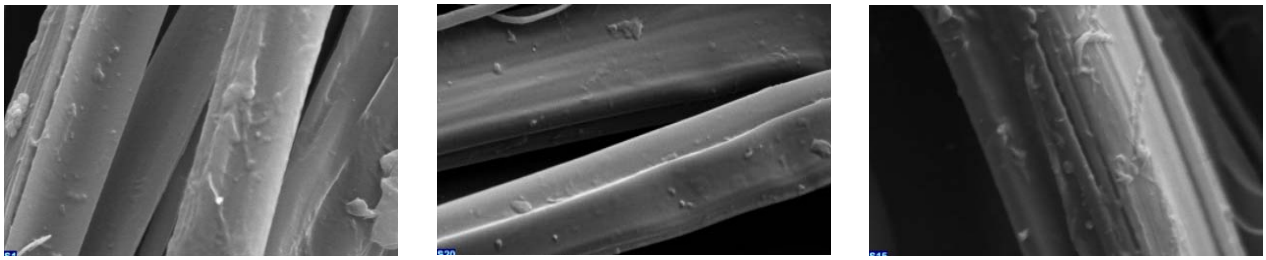
(a) **(b)** **(c)**

Fig. 11: SEM images of samples A_4^{Fe} (a) 1000X (b) 2500X (c) 5000X



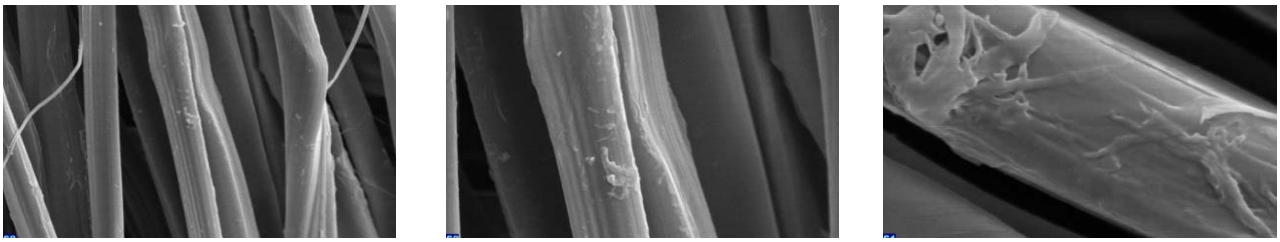
(a) **(b)** **(c)**

Fig. 12: SEM images of A_5^{Cr} samples (a) 1000X (b) 2500x (c) 5000X



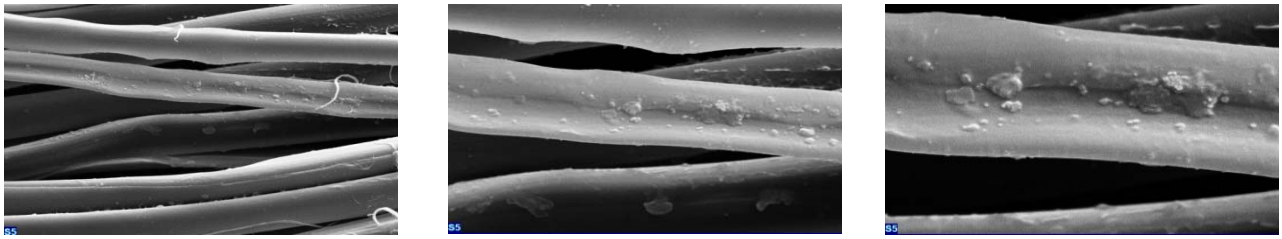
(a) **(b)** **(c)**

Fig. 13: SEM images of A_4^{Al} samples (a) 1000X (b) 2500X (c) 5000X



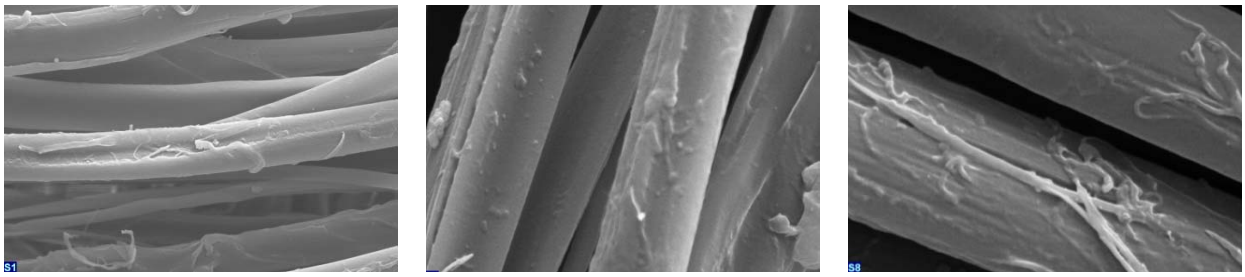
(a) (b) (c)

Fig. 14: SEM images of A_5^{Al} samples (d) 1000X (e) 2500x (f) 5000X



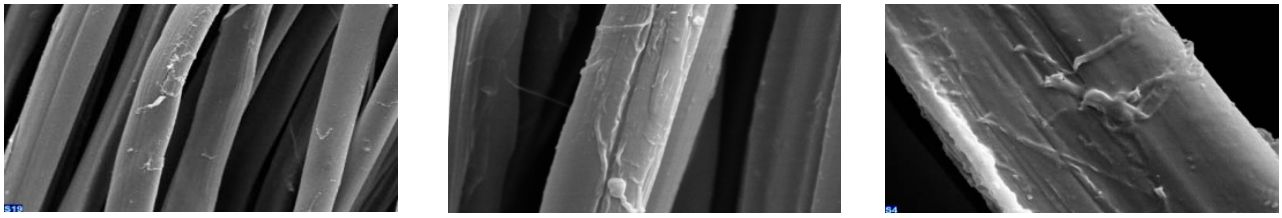
(a) (b) (c)

Fig. 15: SEM images of samples A_4^{Fe} (a) 1000X (b)2500X (c) 5000X



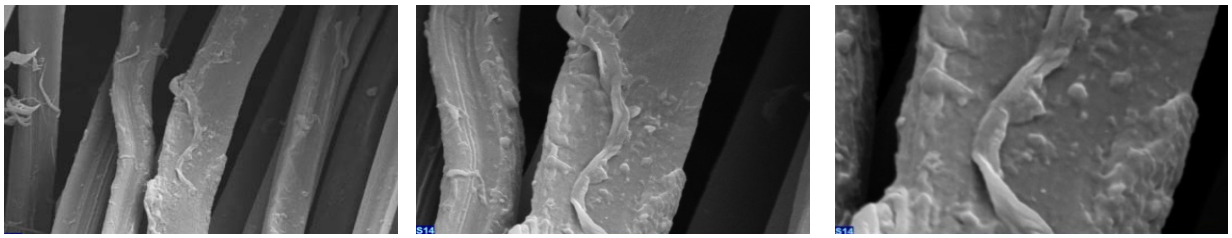
(a) (b) (c)

Fig. 16: SEM images of A_5^{Fe} samples (a) 1000X (b) 2500x (c) 5000X



(a) (b) (c)

Fig. 17: SEM images of samples A_4^{Cu} (a) 1000X (b) 2500X (c) 5000X



(a) (b) (c)

Fig. 18: SEM images of A_5^{Cu} samples (a) 1000X (b) 2500x (c) 5000X

5. Conclusion

The purpose of this study was to investigation the effect of chitosan and mordant on dyeing properties, washing and rubbing fastness and antibacterial effect of silk treated fabrics. Results showed that annatto as a natural dye can be successfully applied on silk fabric. Silk samples treated with chitosan and mordant with different composition of mordents gave better results. It was found that the treated fabric with chitosan enhanced the dye uptake and also increased the antibacterial activity of silk fabric compared with untreated silk fabric. Moreover, color fastness properties of the treated and mordant silk fabrics were improved. There is a very slight gradual increase in yellowness of silk samples with increasing chitosan concentration and using mordant. Ferric sulfate sample showed the highest color strength, yellowish – blueness, reddish – greenness and lowest lighting also by increasing of chitosan concentration from %0.1 to 0.6 rubbing and washing fastness decreased. Mordant of cu has been more antimicrobial more than all of the samples.

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