Enhancing Dye-ability and Antibacterial Features of Silk through Pre-treatment with Chitosan

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ABSTRACT

Biopolymers are suitable replacement materials for different chemical processes. In this work, silk yarns were treated with different chitosan concentration and then dyed with mono and bi-functional reactive dyes. The color yield, color difference and color fastness to light and washing of the dyed silk yarns were evaluated. Also, the effects of chitosan concentration, type of the reactive dyes on dye uptake of samples were studied. The bi-functional reactive dye has a high adsorption compared to mono-functional ones. The silk yarn treated with 3% chitosan had higher K/S values, washing and light fastness. The effects of chitosan on the antibacterial properties of silk yarns against two kinds of bacteria: *Staphylococcus aureus* and *Escherichia coli* were investigated. The treated silk samples were found to have antibacterial potential due to the antibacterial property of chitosan. Scanning electron microscopy (SEM) photographs reveal the deposition of chitosan on the treated yarns. Washing durability, handle properties, and yellowness of treated and dyed samples were also investigated.

Keywords: Chitosan, Silk, Dye-ability, Reactive Dyes, Fastness properties, Antibacterial.

INTRODUCTION

Silk worms produce a protein fiber discovered in 2,700 BC. Silk fibers consists of 97% protein - fibroin, a filamentous protein and sericin (gum), a non-filamentous protein- and also other impurities such as pigments, wax, carbohydrates, and inorganic salts. The proteins in silk fiber are approximately 75% fibroin and 25% sericin by weight. The sericin strengthens the silk fiber and makes it lack luster; therefore, it must be degummed before dyeing [1-3]. Silk fiber is well known for its water absorbency, dyeing affinity, thermal tolerances, insulation properties, and luster. Silk fiber can be used in many products such as precious fabrics, parachutes, tire lining materials, artificial blood vessels, and surgical sutures [3-5].

Today acid, metal complex and reactive dyes are widely used for silk dyeing. Reactive dyes have become very popular due to their brilliancy, variety of hues, high wet fastness, convenient usage, and high applicability despite having some problems, such as low dye-ability, requirements of large amount of auxiliary agents, and high volume of discharged wastewater, which always exist in the application of reactive dyes for silk fabrics [6-8]. Moreover, some properties of silk fiber such as crease recovery, wash and wear properties, photo-yellowing, water and oil staining resistance, dye-ability, and color fastness are weak and they should be improved. For this purpose, surface modification of silk by some physical and chemical techniques has been developed. Some techniques such as γ-Ray radiation grafting, plasma grafting, and ultraviolet ray initiated grafting are being explored as a physical method for improving silk fiber properties. These methods are some important alternative to wet treatments because they are considered as clean, dry, and environmental friendly physical techniques [9, 10]. In graft copolymerization- as a chemical technique-many monomers such as vinyl monomers (vinyl acetate, acrylonitrile, and phenylethylene), methacrylate monomers (methyl methacrylate, 2-hydroxyethyl methacrylate, ethyl methacrylate), acrylamide monomers (acrylamide, methacrylamide, hydroxy methacrylamide) and fluoroacrylate have been used. Graft copolymerization can improve the fluffiness and softness properties without any damages to the whiteness and handle of silk materials. In spite of these advantages, it is believed that chemical processes do not comply with environmental regulations, due to their generating of some toxic agents during processes [11-14].

Surface modification of textile fibers by using some natural polymers such as chitin or chitosan in the textile finishing processes is considered to be the best route to overcome these problems [15, 16].

Chitosan is the derivative of chitin, a major component in marine invertebrates such as crustacean shells (shrimps, crabs and lobsters), exoskeleton of insects and some fungi, and is prepared through the deacetylation of chitin [17, 18]. The unique properties of chitosan including availability, biodegradability, biocompatibility, bioactivity, cost-effectiveness, and non-toxicity, as well as bio-adhesion, sorption, and antimicrobial properties are the major reasons for its multiple applications [19, 20]. Chitosan has prospective applications in many fields, such as medicine, pharmaceuticals, textile, wastewater treatment, agriculture, food, the paper industry, cosmetics, and biotechnology [21-26].

The application of chitosan in textiles can be categorized into two main topics: the production of man-made fibers and textile wet processing, which include dyeing (improving the dye-ability), finishing (antimicrobial properties), and printing (as a print-paste thickener) [27-30].

Up to now, work was conducted to study chitosan applications in textile the industry as an antimicrobial agent, but there has been little work done on the application of chitosan to improve the dye-ability of textiles. The application of chitosan to silk could reduce the use of dyes due to increased dye exhaustion, which has positive effect on textile wastewater. On the other hand, studies claimed that the usage of chitosan could decrease the amount of salt required in the dyeing with direct and reactive dyes by about 50%, resulting in the production of a comparable shade compared to that of the untreated fabric [31-32].

Reactive dyes have been commonly used for silk dyeing, because of their wide color range and ease of application. However, these anionic dyes have a low affinity to the silk yarns. By adding an electrolyte like sodium chloride or sodium sulfate, which screens the surface charge of silk, this problem could be solved. Nevertheless, the large amount of salts required in dyeing has a destructive effect on the environment. As an attempt to reduce the use of salts, a number of researchers have cationized silk yarns through chemical modifications with compounds containing cationic groups. The majority of the chemicals used for the cationization of silk are not safe environmentally. Therefore, the use of chitosan, a polycationic biopolymer is more eco-friendly.

This paper focused on the antibacterial and dyeing (dye uptake, color measurement and color fastness) properties of the silk yarns treated with chitosan which dyed with reactive dyes. Furthermore, other textile properties such as physical and antibacterial activity of the chitosan-grafted silk yarns were investigated.

EXPERIMENTAL

Materials

The silk yarn used was degummed silk (yarn count=82 Tex) produced by Khorasan silk Co. in Sabzevar, Iran. Chitosan was provided by Chitotec. (Degree of deacetylation (DD) = 92.5%, Molecular Weight=1000kDa, Iran). Samples were dyed with C.I. (Color Index) Reactive Red 66 (BITCROL) as a mono-functional reactive dye and C.I. Reactive Red 195 (ME 4 BL) as a bi-functional reactive dye both, purchased from Color and Chemical Co. The structural formulas of dyes are shown in *Figure 1*.

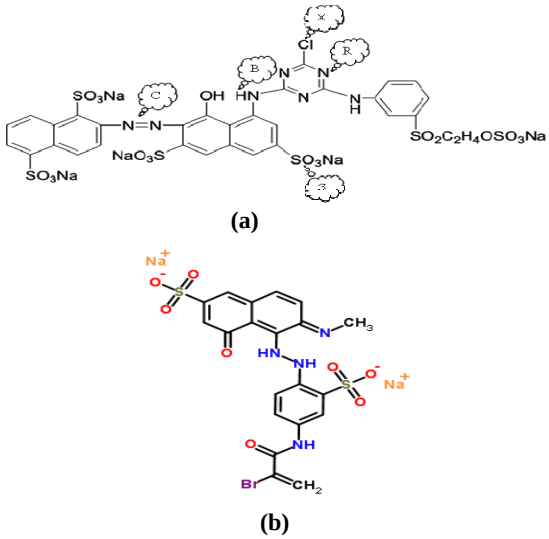


FIGURE 1. Chemical structural of a) C.I. Reactive Red 195 and b) C.I. Reactive Red 66.

Acetic acid, sodium carbonate (both from Merck), ammonium acetate (Ghatran Shimi Co., Iran), leveling agent (Bayer Levegal RDL-Germany) and non-ionic surfactant (Nassaj Rang Tehran Co) were used in the dyeing and scouring processes. Modified nutrient agar medium composed of the following ingredients (g/L) was used as the culture medium: tryptone (15.0g/L), soytone (5.0g/L), sodium chloride (5.0g/L) and agar (15.0g/L).The pH was set to 7.3±2 at 25°C. The medium was sterilized for 15 min at 121°C under 15 pound pressure. Antibacterial tests were performed with two types of bacteria: A gram-positive bacterium (*Staphylococcus aureus*, ATCC 1112) and gram-negative bacterium (*Escherichia coli*, ATCC 11303).

Methods

Scouring of Silk

Silk yarns (1g) were washed with a solution containing 1 g/L of a non-ionic detergent at 60˚C for 5 min, keeping the liquor to a good ratio at 40:1. The scoured material was thoroughly washed with water and dried at room temperature.

Finishing

All samples were treated with chitosan by the exhaustion method. For this purpose, a 2% (w/v) stock solution of chitosan was prepared by dissolving the required amount of chitosan in an aqueous acetic acid solution at 30˚C for 30-40 min. The silk yarn (1g), prepared as noted in previous section, was then immersed directly in aqueous solutions of chitosan (prepared from the stock solution) at room temperature, keeping the material to liquor ratio at 1:40 and the temperature was raised to 70˚C with constant rate of 1.5 ˚C/min and then the yarn was kept for 10 min at 70˚C. The silk yarn, after pretreatment with chitosan, was rinsed with water and allowed to dry in the open air in the laboratory.

Dyeing

The treated and untreated samples were dyed with reactive dyes by a common process. The silk yarns were dyed, keeping material-to-liquor ratio at 1:40 while the pH was maintained at 4 by adding acetic acid gradually. The dye bath was prepared by adding dye (1g), ammonium acetate (2g/L), and leveling agent (1mL) to distilled water (100ml) at room temperature. Wet yarn was added to dye-bath then the dyeing process was commenced after 5 minutes and continued for 20 minutes at 40˚C. The temperature was raised to boiling temperature at 1.5˚C /min. and dyeing was continued at boiling temperature for 10 minutes. The dyed material was then rinsed in warm (50˚C) water followed by cold water to remove the unfixed dye and dried at room temperature.

Weight add-on was determined after treating the samples with chitosan and dyed with reactive dyes and comparing the initial weight (before treatment with chitosan) and final weight (after treatment with chitosan and dyed) which reported as add-on percentage Eq. (1).

$$\text{Weight add-on (\%)} = ((W_2-W_1)/W_1)*100 \quad (1)$$

Where W_1 is the weight of yarn before treatment with chitosan and W_2 is the weight of yarn after treatment with chitosan and dyed.

Characterization

Determination of Color Strength

Reflectance values of the treated and dyed samples were measured using UV–Vis spectrophotometer (X.rite Color-Eye7000 A, Minolta) at their λ_{max} of reflectance, and color strength was calculated in terms of K/S values (calculated by Kubelka-Munk equation):

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

Where K is the coefficient of absorption; S is the coefficient of scattering; R is the reflectance value of the yarn at λ_{max}. K/S values were calculated at 550 nm as the measured $\lambda_{max.}$

The color difference (ΔE) and relative color strength between chitosan coated dyed and uncoated dyed samples were also calculated according to Eq. (3) and Eq. (4), respectively.

$$\text{Relative colour strength (\%)} = \frac{\text{K/S of treated sample}}{\text{K/S of untreated sample}} \times 100 \quad (3)$$

$$\Delta E = \sqrt{(\Delta l)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (4)$$

Where $\Delta L=L^*_{coated} - L^*_{uncoated}$;
$\Delta a=a^*_{coated} - a^*_{uncoated}$;
$\Delta b=b^*_{coated} - b^*_{uncoated}$

'L^*' refers to lightness–darkness values from 100 to 0 representing white to black; 'a^*' represent redness if positive and greenness if negative and 'b^*' describe yellowness if positive and blueness if negative.

Morphology Observation

Treated and dyed yarns were coated with gold (Bal-Tec, Swiss) in order to observe the surface morphology by SEM-XL30, Phillips scanning electron microscope (Holland) with an accelerating voltage of 17 kV.

Determination of Physical Properties

Since chitosan is a high molecular weight polymer, its application to silk can affect its feel and other physical properties. To ensure that the chitosan treatment had no detrimental effects, the treated and dyed silk was characterized in terms of several parameters related to its appearance and feel such as handle properties, yellowness and luster. A subjective handle tests were completed by ten persons (five male and five female) through touching the anonymous yarns with hands directly. The yellowness of treated yarns was measured by b* values using UV–Vis spectrophotometer (X.rite Color-Eye7000 A, Minolta).

Determination of Fastness Properties

The treated samples were washed as stated by the conditions mentioned in the test method ISO105:3001 to determine the change in color and staining of adjacent fabrics after washing. The rating scale of washing fastness for color change was from 1 (very poor), 2 (poor), 3 (fair), 4 (good) to 5 (excellent).

Light fastness tests were carried out according to the test method ISO105:B01. The rating scale of light fastness was from 1 (very poor), 2 (poor), 3 (fair), 4 (moderate), 5 (good), 6 (very good), 7 (excellent), to 8 (outstanding).

Determination of Chitosan Durability

Laundering durability is one of the requisites for a successful finishing. The treated samples (of known weight) were laundered one time at 60˚C for 20 min in distilled water (40ml) to determine the chitosan durability in yarns. Weight loss percentage (%) was calculated by Eq. (5).

$$\text{Weight loss percentage (\%)} = ((W_1-W_2)/W_1)*100 \quad (5)$$

Where W_1 and W_2 are the weight of yarn before and after washing.

Antibacterial Efficiency

AATCC100-1999 was used to analyze the antibacterial activity of the treated silk yarns. The organisms taken for this study were *Staphylococcus aureus* (*S.aureus*) and *Escherichia coli* (*E.coli*). To evaluate the antibacterial activities of the treated yarns, the reduction in colony number between the treated and untreated samples after incubation was determined. The percentage reduction was calculated using the following equation:

$$\text{Percent reduction of bacteria (\%)} = ((A-B)/A)*100 \quad (6)$$

Where A is the number of bacteria on the un-treated silk yarns after 24 hours and B is the number of bacteria on the treated silk yarns with chitosan after 24 hours.

RESULTS AND DISCUSSION

Morphologies of Silk Yarns

Surface morphology changes of the silk yarn after surface modification with chitosan were investigated using scanning electron microscopy (SEM). The SEM micrographs of untreated and chitosan treated yarns, dyed samples without and with chitosan treatment followed by a dyeing process using reactive Red 66 and reactive Red 195 are shown in *Figure 2*. All of the treated SEM micrographs showed the presence of foreign materials attached to the surface of the silk yarns. Control sample *Figure 2(a)* showed a clean and smooth surface, while slight longitudinal flutes and small pits were appeared on the surface of treated silk yarns (*Figure 2(b), (c), (d), (e), (f)*). As it was seen in Figure 2 the chitosan alongside the dyestuff built up a rough layer on the surface of silk yarns, in which chitosan particles were supposed to disperse. The surface of silk yarns treated with chitosan and dyed with reactive Red 66 *(Figure 2(d))* was as smooth as that of unfinished silk yarns but for the silk yarns treated with chitosan and dyed with reactive Red 195 *(Figure 2(f))* the surface became rougher compared to the others caused to increase dyeability and antibacterial properties of the silk yarns.

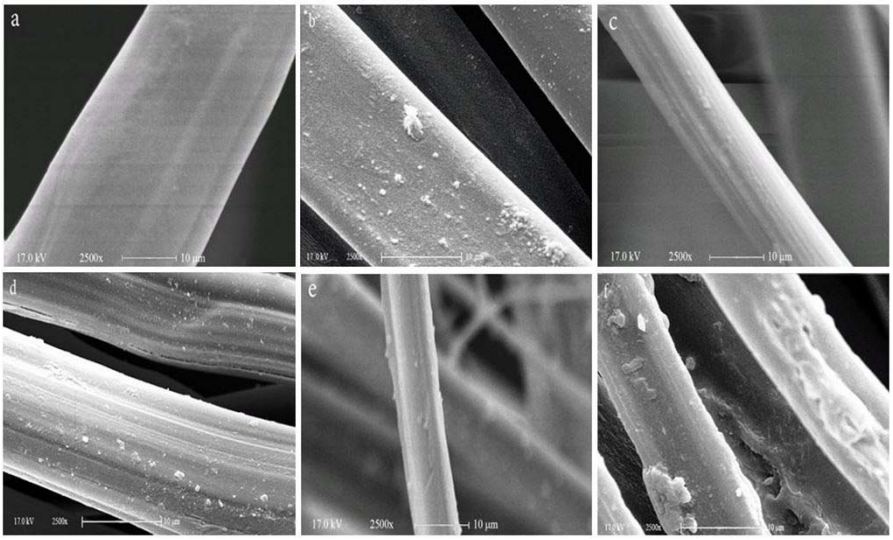


FIGURE 2. SEM photographs of the surface of silk yarns. (a) Untreated and undyed silk yarns (b) 3% chitosan treated undyed silk yarns (c) Untreated dyed silk yarns with reactive Red 66 (d) 3% chitosan treated dyed silk yarns with reactive Red 66 (e) Untreated dyed silk yarns with reactive Red 195 (f) 3% chitosan treated dyed silk yarns with reactive Red 195.

Color Strength

K/S value of a dyed material has a close relationship to the amount of dye absorbed by the yarn. K/S values and the relative color strength of silk dyed samples with reactive Red 66 and reactive Red 195 are shown in *Table I*, respectively. Regarding *Table I* it can be concluded that the K/S values of chitosan treated dyed yarns are higher than that of untreated dyed samples. As the chitosan concentration increases, the dye uptake also increases. This enhancement in (K/S) values of chitosan treated silk yarns shows that the chitosan has an incremental effect in dyeing processes. This result further affirms that chitosan increases the amount of dye uptake in the treated silk yarns.

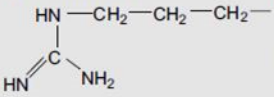
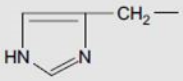
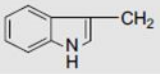
Silk is a natural protein (polypeptide) fiber, which is composed of 18 amino acids with various reactive functional groups including hydroxyl and amine groups (*Table II*) [40].

Chitin is a copolymer of N-acetyl-d-glucosamine and d-glucosamine units linked with β-(1-4) Glycosidic bond, where N-acetyl-d-glucosamine units are predominant in the polymeric chain. The deacetylated form of chitin refers to chitosan. Chitosan has three reactive groups. They are the primary and secondary hydroxyl groups on each repeat unit, and the amino group on each deacetylated unit (*Figure 3*).

TABLE I. Spectrophotometer characterization of the yarns dyed with Reactive Red 66 and Reactive Red 195.

Dyes type	Chitosan Concentration (%)	ΔE	K/S	Relative color strength (%)
Reactive Red 66	0	-	1.03	100
	0.1	3.76	2.50	242
	0.25	3.79	2.73	265
	0.3	3.81	3.10	301
	0.4	3.86	2.60	251
	0.5	3.89	2.63	255
	0.75	3.93	2.74	266
	1	3.97	2.70	262
	1.5	3.99	2.54	247
	2	4	2.61	254
	2.5	4.05	2.40	233
	3	4.23	3.06	298
	6	3.60	2.41	235
	9	3.43	1.52	148
	12	3.12	1.59	155
Reactive Red 195	0	-	6.78	100
	0.1	0.52	6.26	92
	1	0.53	7.55	111
	2	0.58	6.44	95
	3	0.69	6.67	98
	5	0.44	5.93	87
	6	0.34	5.84	86

TABLE II. The hydrogen and amine groups and the residues of the amino acids of silk [40].

Functional group	Residue (R)	Amino acids	Composition (mol%)
–OH	$CH_3CH(OH)–$	Threonine	0.91
	$HOCH_2–$	Serine	12.10
$–NH_2$ or –NH–	$H_2NCH_2CH_2CH_2CH_2–$	Lysine	0.32
		Arginine	0.47
		Histidine	0.14
		Tryptophan	0.11

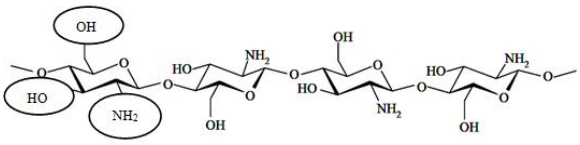


FIGURE 3. Chemical Structure of chitosan.

As a kind of protein fibers, 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 (*Figure 4*).

As shown in *Figure 1(a),* four features of a typical reactive dye molecule are a reactive group (R) containing leaving group (X), a chromophoric group (C), a bridging group (B) and a solubilising group (S).Chitosan can easily absorb anionic dyes, such as direct, acid and reactive dyes, by its electrostatic attraction characteristics which are the result of its cationic nature in an acid environment [15, 16].

The possible mechanism of the adsorption process of chitosan and reactive dye is electrostatic attraction between protonated $–NH_2$ of chitosan and anion of dye (Cl) as follows:

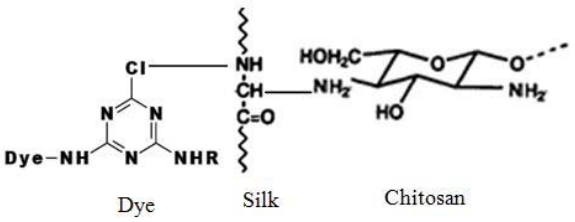


FIGURE 4. One possible mechanism of binding Silk-Chitosan-Dye.

It is observed (*Table I*) that by increasing the chitosan concentration the (K/S) values has been increased up to 3% and then decreased. This detraction in (K/S) values of chitosan treated silk yarns is associated with the saturation of silk yarns by chitosan while it is shown that the chitosan molecules have the competitive effect against dyes molecules which caused dye precipitation thus the silk yarns do not absorb dye evenly.

The color difference (ΔE) values are also given in *Table I.* From *Table I* and *Figure 5*, it can be clearly seen that up to 3%, by increasing in chitosan concentration there is no significant color difference between the samples.

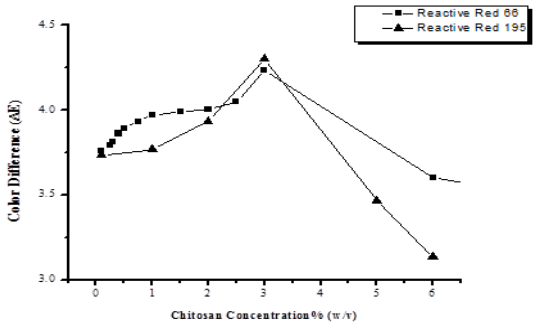


FIGURE 5. Relationship between chitosan concentration and color difference of dyed silk yarns treated with different amounts of chitosan on silk yarns dyed with reactive red 66 and reactive red 195.

Fastness Properties

Textiles are subjected to frequent treatments such as washing and exposure to light during their usage. As the durability of the finish applied on the textile material is extremely important in these conditions, it has been assessed and is given in *Table III* for reactive Red 66 and reactive Red 195, respectively.

TABLE III. Fastness rating of the yarns dyed with Reactive Red 66 and Reactive Red 195.

Dyes type	Chitosan Concentration (%)	Light fastness	Wash fastness		
			Assessment of change in color	Assessment of staining	
				silk	cotton
Reactive Red 66	0	4-5	4	4-5	4-5
	0.1	5	4	4-5	4-5
	0.25	5	4	4-5	4-5
	0.3	5	4	4-5	4-5
	0.4	5	4	4-5	4-5
	0.5	5	4	4-5	4-5
	0.75	5	4	4-5	4-5
	1	5	4	4-5	4-5
	1.5	5	4	4-5	4-5
	2	5-6	4	4-5	4-5
	2.5	5-6	4	4-5	4-5
	3	5-6	4	4-5	4-5
	6	5	3-4	4-5	4-5
	9	5	3-4	4-5	4-5
	12	5	3-4	4-5	4-5
Reactive Red 195	0	5	4	5	5
	0.1	5	4-5	5	5
	1	5	4-5	5	5
	2	5	4-5	5	5
	3	5	4-5	5	5
	5	4-5	4-5	5	5
	6	4-5	4-5	5	5

Between these two types of reactive dyes, bi-functional reactive dyes (C.I. Reactive Red 195) had better fastness properties than mono-functional one (C.I. Reactive Red 66) due to formation of a greater number of crosslinking bondings within silk fiber molecules because of the existence of reactive group. Moreover, by increasing the concentrations of both reactive dyes up to 3%, the fastness properties of dyed silk yarns were somehow improved.

The add-on percentage after treatment with chitosan and dyed with bi-functional reactive dye (C.I. Reactive Red 195) and mono-functional one (C.I. Reactive Red 66) was reported in *Table IV*. By increasing the chitosan concentration, the variation of add-on percentage of silk yarns was negligible but for both reactive dyes the add-on obtained in 3% chitosan is slightly higher than the others.

TABLE IV: Weight loss and Add-on percent of chitosan treated samples and chitosan-treated dyed yarns, respectively.

Chitosan Concentration (%)	Weight loss (%)	Add-on (%)	
		Reactive Red 66	Reactive Red 195
0.1	4.29	10.07	18.78
1	5.25	10.09	18.8
3	6.09	10.1	19
6	0.62	10.08	18.97

Table IV shows a weight loss of chitosan treated yarns after washing. It is evident that the lower amount of weight loss shows higher textile durability to washing processes. It can be concluded that the inferior amount of

weight loss is due to the chemically bound of chitosan to the silk yarn, which limited the loss of chitosan in the process of the launderings.

Color Change

Table V shows the changes in color of silk yarns modified with different concentrations of chitosan before dyeing.

From b* values it is found that by increasing the chitosan concentrations, there is slight increase in yellowness values of silk samples compared to the untreated one and the reverse of these results holds true for whiteness trend. These can be attributed to introducing amino groups with chitosan treatment and the natural coloration of chitosan that appears yellowish to some extent increase yellowness with increasing the concentrations of chitosan.

TABLE V. The change in color of silk yarns treated with different concentrations of chitosan.

Chitosan Concentration (%)	L*	a*	b*
0	91.634	-0.556	2.810
0.1	90.939	-1.213	3.668
1	90.738	-0.983	4.674
3	90.251	-1.356	5.307
6	90.432	-0.927	5.314

Also, the L* results indicate that there is a very slight gradual decrease in lightness values with increasing chitosan concentrations so it could be concluded that the luster of silk was unchanged.

Handle Properties

A qualitative test was designed to determine the handle properties of the chitosan treated yarns and the chitosan treated dyed samples. For this purpose, the subjective assessment was performed by a group of ten persons (five male and five female) through touching the mark-free samples directly and giving out their handle feeling.

Based on the subjective handle assessments, it was concluded that the handle properties of the chitosan treated dyed samples were better than the chitosan treated yarns. Also, it was deduced that by increasing in chitosan and dye concentration the handle properties of the chitosan treated yarns and chitosan treated dyed samples were not significantly changed.

Antibacterial Activity

The antibacterial activities of silk yarns have been tested for the various possible treatment combinations, treatment with chitosan alone; dyeing with reactive Red 66 and reactive Red 195 without chitosan treatment and treatment with chitosan followed by dyeing with reactive Red 66 and reactive Red 195.

Figure 6 and 7 represent the reduction values for treated samples against both *E. coli* and *S. aureus*. These data show that in case of *E. coli* for treated yarns the bacterial reduction is better against *S. aureus*. The antibacterial activity of the silk treated with chitosan was considerably decreased after dyeing due to the blocking of the cationic groups of the chitosan and yarns by dye molecules. But for *S. aureus*, the reduction values exhibited by chitosan treated and subsequently dyed yarns are higher than un-dyed samples which prove that chitosan treatment enhances the antibacterial activity of the dyed yarns when reactive dyes are applied to yarns.

A considerable amount of literature demonstrated that antibacterial activity of chitosan arises from its polycationic nature, which is caused by protonation of the amino groups at the carbon atoms of the glucosamine units; positively charged amino groups can bind to the anionic components (lipo-polysaccharides and proteins of microorganism surface), resulting in the disruption of the cell membrane leading to an increase in its permeability which causes death of the cell by inducing leakage of intracellular components. Chitosan can also interact with the DNA of microorganisms to prevent protein synthesis [33-38].

In general, for un-dyed samples a higher reduction was observed for *E.coli* as compared to *S.aureus*. *S. aureus* is a Gram-positive bacterium and has a thicker cell wall hence is more resistant to chitosan than *E.coli* but for dyed samples a higher reduction was observed for *S.aureus* as compared to *E.coli*, particularly at higher concentrations because the antibacterial action of chitosan and reactive dyes work simultaneously in these samples.

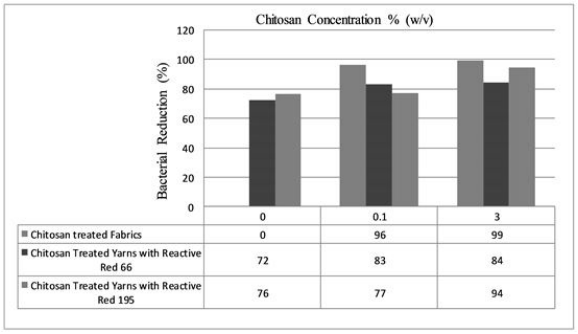


FIGURE 6. Bacterial reduction (%) of various yarns against *Escherichia Coli*.

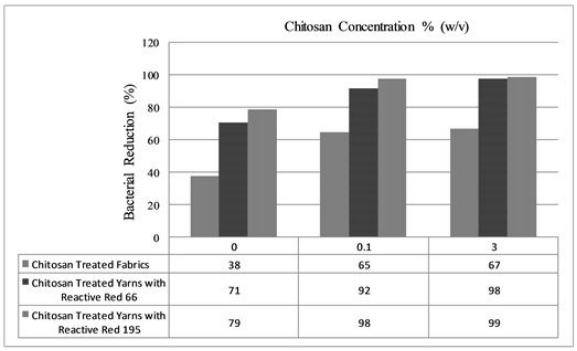


FIGURE 7. Bacterial reduction (%) of various yarns against *Staphylococcus aureus*.

From the *Figures 6 and 7*, it could be concluded that even yarns dyed with reactive dyes alone without chitosan application do exhibit significant antibacterial activity. This is due to the inherent antibacterial characteristics of these dyes. As it was shown in *Figure 1*, these reactive dyes are anionic dyes, which have sulfonate groups ($-SO^{3-}$, as water-solubilizing groups), bromine and chlorine groups in their structures. Halogen biocides such as Cl_2, Br_2 and I_2 are powerful oxidizing agents which having bactericidal, sporicidal and fungicidal activity. Halogen compounds affect micro-organisms by attacking the cell membrane to get into the cytoplasm and affect the enzymes of the microorganisms [39]. Moreover, the better antibacterial activities of treated yarns dyed with reactive Red 195 compare to the reactive Red 66 can be explained by the fact that the chlorine groups in this dye has higher activity and electronegativity in comparison with bromine group.

CONCLUSION

In this study, the dye-ability of silk yarns through pre-treatment with chitosan has been investigated. For this purpose, the silk yarns were treated with different amounts of chitosan and dyed with mono and bi-functional reactive dyes. It was found that the pretreatment of silk yarns with aqueous solutions of chitosan enhanced the dye uptake and also increased the antibacterial activity of silk yarn compared with untreated silk yarn. Based on the depth of shade values, it was found that for both reactive dyes by increasing in chitosan concentration up to 3% (w/v), there was no significant color difference between the samples. Increasing the chitosan concentration did not always yield higher depth of shade (K/S), it also caused dye precipitation and uneven dyeing. Moreover, colorfastness properties to light and washing of the treated silk samples with chitosan were improved.

There is a very slight gradual increase in yellowness of silk samples with increasing chitosan concentrations. In the subjective handle assessment, it was found that the chitosan treated silk yarns showed stiffer handle compared to the chitosan treated dyed samples.

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