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Dyeing Properties of Natural Dyes on Silk Treated with ß-Cyclodextrin

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Abstract**—**In this work, silk yarns were treated using ß-cyclodextrin (ß-CD) and cross-linked with citric acid (CA) via pad-dry-cure method. Elemental and FESEM analyses confirmed the presence of ß-CD on the treated silk samples even after five washing cycles. Then, the treated samples were dyed using natural dyes (carrot, orange and tomato). Results showed that the color strength (*K/S*) of the treated samples had been markedly enhanced compared with the control sample (after treatment with metal mordant). Finally, the color strength (*K/S* value) and color fastness (fading, staining and light fastness) of the treated samples with ß-CD were investigated and compared.

Keywords**—**ß-cyclodextrin, dyeing, natural dyes, silk yarn.

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I. Introduction

NATURAL dyes or colorants are widely considered to dyeing of natural fibers (cotton, wool and silk) due to their non-toxic, non-carcinogenic, eco-friendly and biodegradable properties [1]. Nevertheless, natural dyes have limitations such as difficulty of color matching, color reproduction, low color absorption rate, etc. [2]. In addition, natural dyes do not have good affinity for adsorption onto the fibers, thus in most cases, their fastness properties are poor. To improve these properties, various techniques have been used such as mordanting (with metal salts, etc.), post-treatment (with tannic acid, syntan, cyclodextrin, dendritic structure, etc.) and chemical modification of the natural fibers [3]-[5].

CDs are cyclic oligosaccharides commonly composed of six to eight glucopyranose units (α, β and γ-CDs). They are well known due to their unique structure (a truncated cone) that possesses hydrophobic interior cavity. Therefore, CDs can form inclusion complexes with a wide range of partially hydrophobic compounds dissolved and solubilized in water. This property of CDs has led to their application in various areas such as enzyme mimics, catalysis and encapsulation of active substances, auxiliary agents, fragrances, antimicrobial agents, colorants, drugs, etc. [6]. Hence, the use of CDs as dyeing auxiliaries that improve dye sorption onto fibers has been proposed [6].

Previous works [7] reported that preliminary modification of the natural fibers (cellulosic and proteinic fibers) with CDs and polycarboxylic acids (crosslinking agents) before the dyeing process can improve the adsorption process. It was observed that a crosslinking reaction between polycarboxylic acids and CDs occurred in situ in the fiber network and resulted in the coating of fibers by a cross-linked CD polymer.

In this work, the effect of ß-CD on silk dyeing with natural dyes was investigated in terms of colorimetric data (K/S values) and fastness properties.

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II. Experimental Procedure

A. Materials

Raw silk yarn (2 filaments, 10.5 N_m) was supplied by Iran Silk Worm Rearing Company. ß-CD was purchased from Sigma Aldrich Company and used as received without further purification. CA and sodium hypophosphite (SHP) were purchased from Merck. The degumming, bleaching and treatment with metal salt ($Al_2(SO_4)_3$) were carried out according to the previous work [8]. The natural dyes were extracted according to the well-known classic method [9]. It is worth mentioning that the extracted dyes of carrot, orange and tomato have been chose for the dyeing process, because these vegetables have a lot of ß-carotene and pectin compounds.

B. β-CD Finishing

At the first step, the silk samples were impregnated (5 min) in aqueous solutions containing CA (0, 25, 50, 75, 100 g/L), β-CD (0, 25, 50, 75, 100 g/L) and a 0.5 mole ratio to CA for the SHP catalyst. Thereafter, the impregnated samples were roll-squeezed (wet pick-up: 100 ± 2%), dried (80˚C and 5 min) and cured at 130˚C for 15 min. Finally, the samples were washed with warm water (50 ˚C) and dried at temperature room. The grafting rate was determined by weighing each the dry sample before (W_1) and after (W_2) grafting, using a Sartorius balance (model: GK1203; accuracy: ± 10^{-4} g). The grafting efficiency was calculated according to the following equation:

$$\%Graftyield = (W_2 - W_1)/W_1 \times 100 \quad (1)$$

C. FTIR, ATR-FTIR, FESEM and Elemental Analyses

Fourier transform infrared (FTIR) and attenuated total reflection-FTIR (ATR-FTIR) spectra were recorded by Thermo Nicolet Nexus 670 and Bomem MB 100 spectrophotometers, respectively; at a resolution of 4 cm^{-1} over a range 400-4000 cm^{-1}. The KBr disc method was used for powder samples. The spectral analysis of the samples was done with OMNIC software. The carbonyl band absorbance in the infrared spectra was also normalized against the 2978 cm^{-1} band associated with CH_3 asymmetric vibration mode (as internal reference band). Elemental analysis was performed using a Euro EA 3000 Series Elemental Analyzer (Euro vector, Milan, Italy). Also, the morphology of the samples was observed under field emission scanning electron microscope

Open Science Index, Materials and Textile Engineering Vol:15, No:2, 2021 publications.waset.org/10011821/pdf

(FESEM) (Hitachi, model: S-4160) after gold coating.

D. Dyeing

The dyeing process was carried out in Hanau-Linitest laboratory scale dyeing machine with the dye different concentrations (0.5, 1.0, 1.5, 2 and 4% owf). Dyeing of the treated samples with the natural dyes was performed according to Fig. 1. Then, the samples were recovered for colorimetric measurements. The exhaustion of the dyeing bath was measured (using spectrophotometer Shimadzu, UV160A, Japan) by comparing the concentration of dyeing bath before and after dyeing. The wavelength of the extracted natural dyes of carrot, orange and tomato are 418 nm, 438 nm, and 516 nm, respectively.

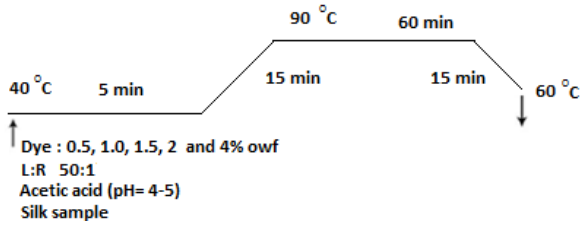


Fig. 1 Dyeing process

E. Color Measurement and Fastness

After the dyeing process, the color strength (*K/S*) of cotton samples was measured according to the well-known Kubelka-Munk equation:

$$K/S = (1-R)^2/2R \quad (2)$$

where K is the light absorption coefficient, S is the scattering coefficient, and R is the reflectance at the maximum wavelength. A Gretage Macbeth Color-Eye 7000A reflectance spectrophotometer was used to measure the reflectance of the samples.

Also, the wash, staining (ISO 105 C06: 1994) and light fastness (ISO 105 E02: 1994) of the dyed samples were determined according to an evaluation scale from 1 to 5 (fading and staining fastness) and 1 to 8 (light fastness), respectively. This evaluation is based on a comparison of the dyeing level between samples before and after standard washings.

III. Results and Discussion

A. Silk Yarn Treated with β-CD

When the silk samples are treated with CA and β-CD in presence of SHP (as a catalyst), it seems that two competitive esterification reactions occurs through the esterification of CA by: the hydroxyl groups of silk fibroin (i), and the hydroxyl groups of β-CD (ii). Researchers have suggested that bi- or polycarboxylic acids first form cyclic anhydrides as intermediates and then the anhydrides react with silk hydroxyl groups to form ester bonds [10]. It should be noted that the probably of esterification reaction of CA by (i) is rather than the amidation reaction of CA by the $-NH_2$ end groups of silk fibroin. Studies on amino acid composition have revealed that fibroin is constituted by simple amino acids such as *glycine*, *serine* and *alanine* (nearly 80% of the composition) and *serine* has a functional hydroxyl group (Fig. 2) [11]. Furthermore, the number of hydroxyl groups of β-CD is higher of hydroxyl groups of silk fibroin, and this leads to decreasing the amount of carboxylic groups of CA available for crosslinking with NH_2 of silk. Therefore, it is hypothesized that the probable sites for crosslinking of the CA with fibroin will be hydroxyl functional groups. In addition, the polyesterification reaction between CA and β-CD can be formed a cross-linked polymer of β-CD (named Poly CA-βCD hereafter), which took place a coating that was physically anchored (and not covalently grafted) to the fibers (Fig. 3).

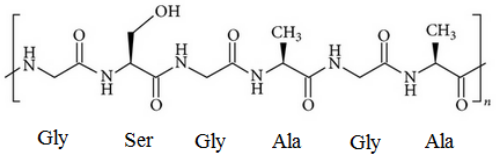


Fig. 2 The chemical structure of silk fibroin

Fig. 4 shows that the maximum yield of the functionalization reaction (24%wt) has reached by fixing the temperature of treatment at 130˚C, the curing time at 15 min, and by the 50 g/L concentrations of CA and β-CD in the impregnating bath. As can be seen in Fig. 4(c), the grafting yield increases by increasing of CA concentration; whereas, the strength of silk sample strongly decreases. Results shows that the optimum CA concentration is 50 g/L (the results of strength have not been mentioned in here). Otherwise, the grafting yield of silk slowly has increased after 50 g/L concentrations of β-CD (Fig. 4 (d)). It seems that the excess amount of the β-CD leads to formation of the poly CA-βCD (more complexes), which has not affected on the grafting yield.

B. FTIR and ATR-FTIR Analyses

Fig. 5 shows the FTIR and ATR-FTIR of the β-CD and treated silk samples. The peaks at 1652 cm^{-1}, 1521 cm^{-1} and 1229 cm^{-1} are attributed to the carbonyl stretching (C=O) of amide I, amide II and amide III of the silk fibroin, respectively (Fig. 5 (c)). Furthermore, in the spectra of silk treated with both CA and the combination of CA and β-CD, a "Shoulder" band appears at 1500-1800 cm^{-1} frequency region (Fig. 5 (b)). In order to distinguish this band, ATR-FTIR technique has been used at 1000 to 1800 cm^{-1} region. According to the result of ATR-FTIR, the C=O stretching mode of the ester carbonyl groups (-COO-) can be revealed at 1742 cm^{-1} and 1747 cm^{-1} (Fig. 5 (c)). These peaks confirm the esterification reactions of CA and hydroxyl groups of silk sample and β-CD (Fig. 5 (b)). Other peaks at 1085 cm^{-1} (C-O-C stretching vibration), 1156 cm^{-1} (C-O stretching vibration) and 2918 cm^{-1} (C-H stretching vibration) show the existence β-CD on to the silk sample (Fig. 5 (b)), which can be also observed at Fig. 5 (a).

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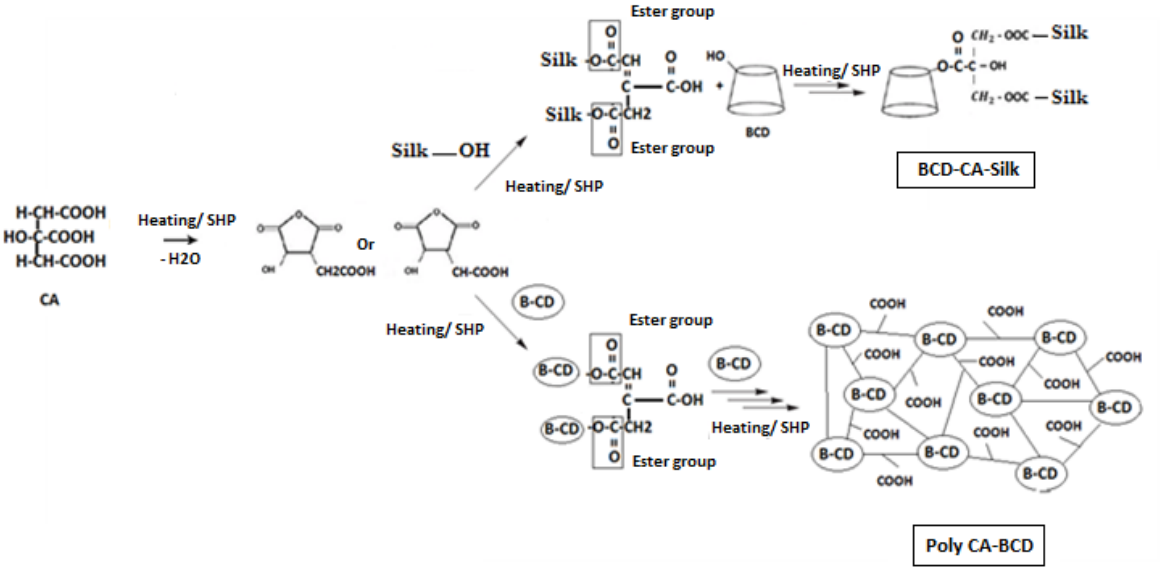


Fig. 3 Possible mechanism of the silk sample with β-CD by using CA: CA-β-CD polymer is obtained, consisting of β-CD cavities and COOH groups carried by crosslinking residues

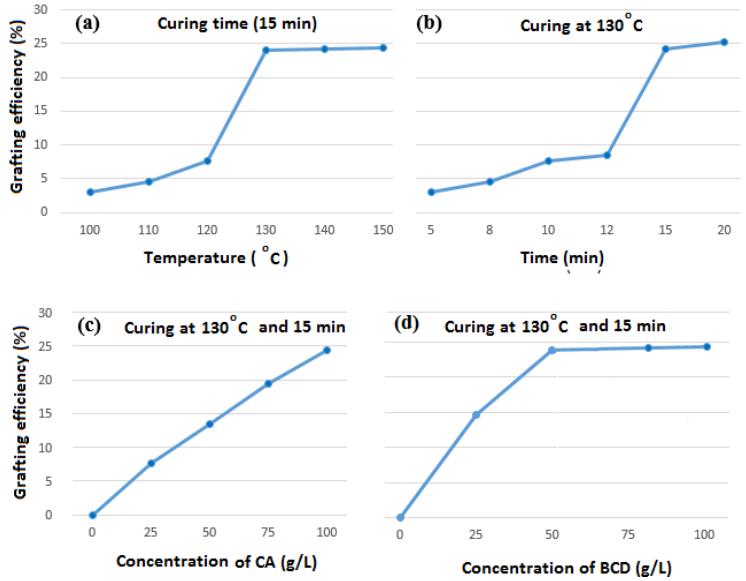


Fig. 4 Influence of: (a) curing temperature (b) curing time (c) CA concentration (d) β-CD concentration, on grafting efficiency

TABLE I
ELEMENTAL ANALYSIS OF THE SILK SAMPLES

Sample		Carbon (%)	Oxygen (%)
Untreated Silk	Before washing cycles	47.2	28.4
	After 5 washing cycles	46.6	26.3
Silk treated with CA	Before washing cycles	53.2	29.6
	After 5 washing cycles	52.1	28.9
Silk treated with CA/β-CD	Before washing cycles	63.3	25.2
	After 5 washing cycles	59.7	24.1

C. FESEM Analysis

The morphology of the treated silk samples was observed under field emission scanning electron microscope. Fig. 6 shows FESEM micrographs of the samples. It is clear that the surface morphology of the grafted silk sample with β-CD differs from that untreated sample. The presence of β-CD can be confirmed with scattered accumulation particles on the silk fibers surface.

D. Elemental Analysis

Table I shows elemental percentages of the samples. The higher carbon and oxygen contents of the treated silk samples confirm the presence of CA and β-CD even after the domestic washing cycles. It seems that the CA-β-CD polymer cannot remove easily by washing cycles; because carbon and oxygen contents of the samples have not changed. Therefore, the β-CD cavities play an important role in dye absorbance process.

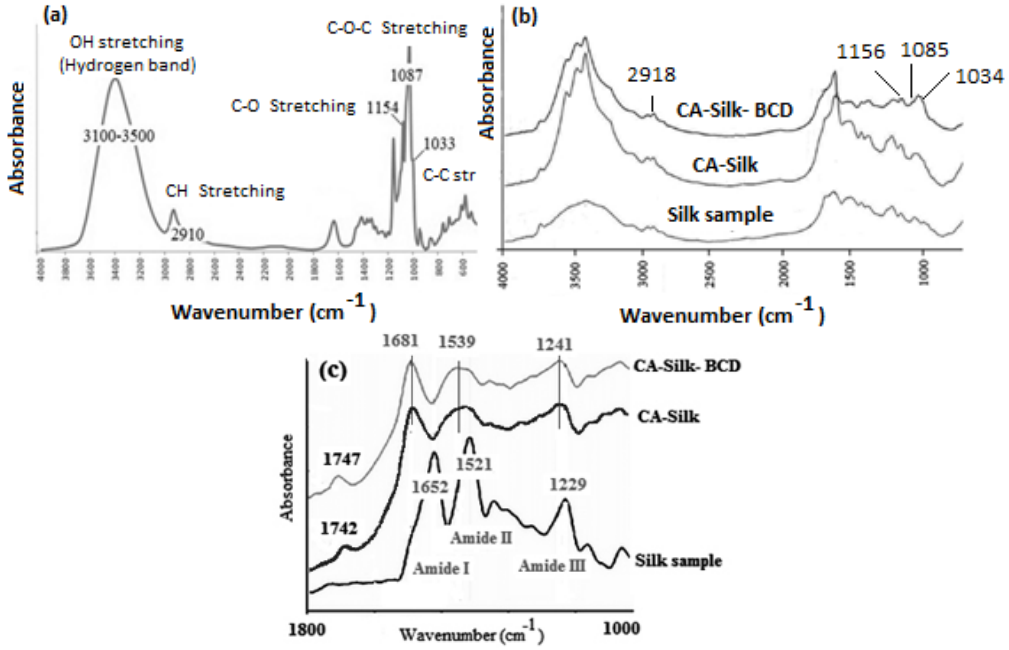


Fig. 5 (a) FTIR of β-CD (b) FTIR of the silk samples (c) ATR-FTIR of the silk samples

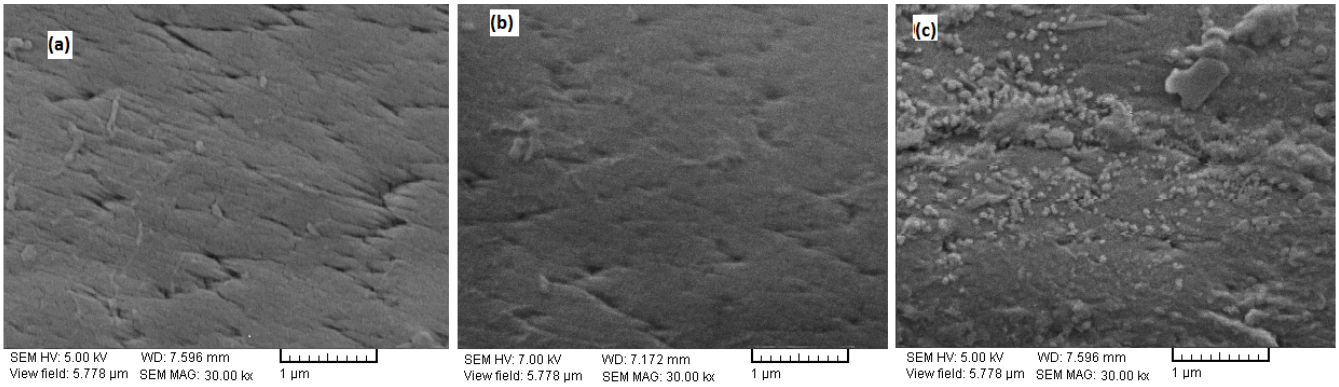


Fig. 6 FESEM micrographs of (a) the untreated silk (b) the silk treated with CA (c) the silk treated with CA/β-CD

E. Build- Up Properties

An enhancement of the color strength is expected when the dye concentration is increased, since a higher number of dye molecules would be available in the vicinity of the silk at higher concentrations. However, the dye build-up on the treated silk is limited to its saturation sorption value, which is related to the amount of β-CD grafted onto the silk samples.

Fig. 7 shows that the silk grafted with β-CD obtained good color strength at all depths of shades below 1.5% owf, which is below the saturation value of the sample (1.5% owf). Above the saturation value of the silk, there was a slight increase in color strength with increasing dye concentration. However, the color strength on the treated samples dyed with 1.5% owf natural dyes is similar to that of the color strength of a 4% owf conventional dyeing. Therefore, 1.5% owf dye was used in the dyeing procedure.

F. Color Strength

Silk samples treated with β-CD (50 g/L) in impregnating bath, constant temperature (130 °C) and curing time (15 min) were dyed according to the method described in Fig. 1. Fig. 8 shows the evaluation of the color intensity. The results of obtained reveal a significant difference in the dyeing level between the silk treated with metal salt and the silk treated with β-CD. On other hand, the enhancement of the dye shade of silk after its treatment with β-CD has clearly evidenced.

Fig. 9 shows the color strength (*K/S*) of the treated silk samples dyed with the natural dyes. It is clear that the color strength of the samples treated with β-CD and then dyed with natural dyes is higher than that of untreated silk. This result probably due to spaces (or hydrophobic interior cavities) of the β-CD, which can encapsulate (or imprison) guest dye molecules [6]. Although, the natural dyes have no distinct chemical structure, it seems that the sorption of these dyes onto the treated silk samples can occur through both chemical (ionic and hydrogen bonding) and physical (dye encapsulating) processes. Interestingly, the color strength of the silk sample dyed with the orange natural dye was also

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rather than that of the other dyes.

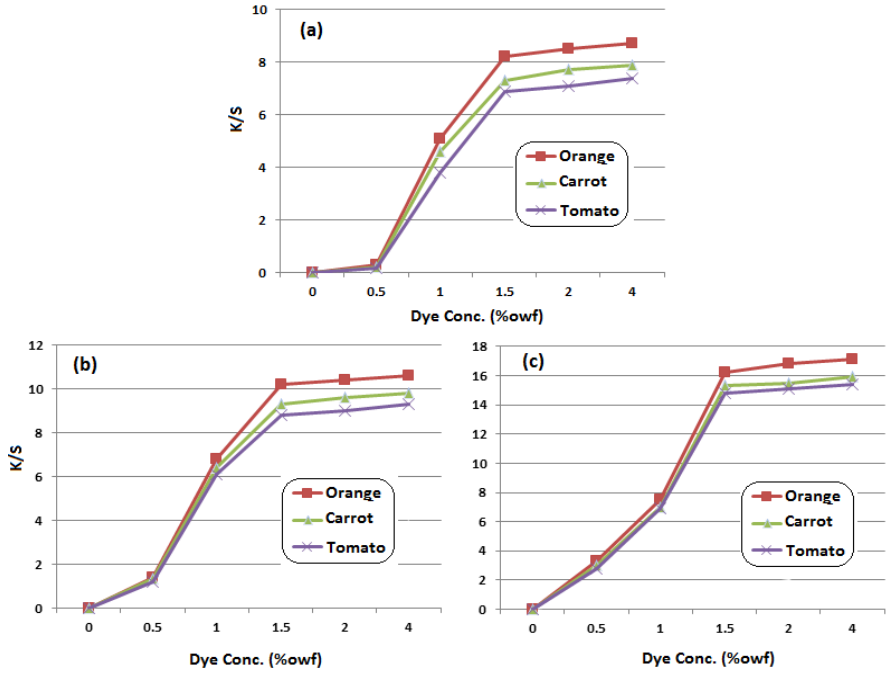


Fig. 7 Build-up properties of the natural dyes: (a) Untreated silk (b) Silk treated with metal mordant (c) Silk treated with β-CD

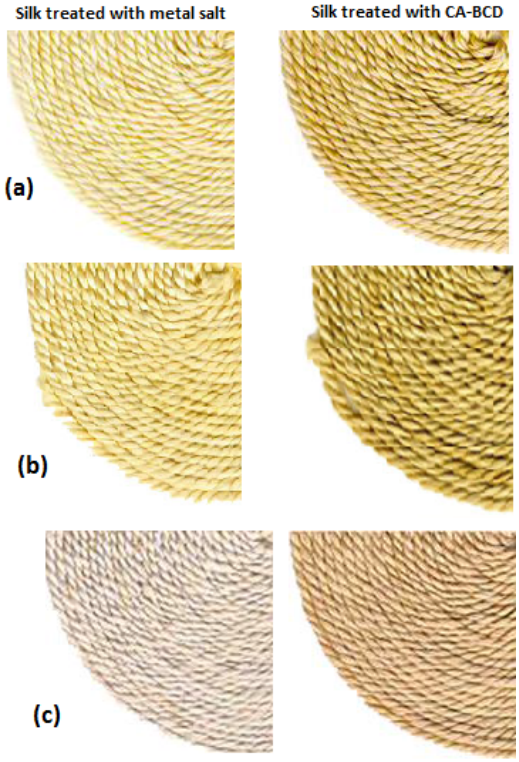


Fig. 8 Silk dyed with natural dyes extracted of: (a) Carrot (b) Orange (c) Tomato, and washed according to standard test

G.Fastness Properties

The fastness properties (washing, staining and light fastness) of the silk samples are reported Table II. The result indicates that fastness of the silk samples treated with β-CD has improved compare with that of the other samples. It seems that the grafting of silk with β-CD have a positive effect on the fastness.

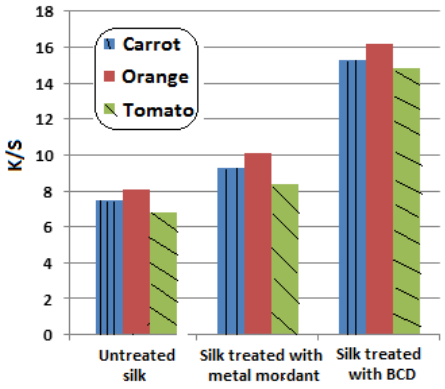


Fig. 9 Color strength (*K/S*) of the dyed silk samples

TABLE II
FASTNESS PROPERTIES OF SAMPLES[8]

Samples		Wash fastness		Light fastness
		Fading	Staining (on cotton)	
Untreated silk	*Orange*	3-4	2-3	6
	Carrot	3-4	2-3	5-6
	Tomato	2-3	1-2	4-5
Silk treated with metal salt	*Orange*	4-5	4-5	6-7
	Carrot	4-5	4-5	6
	Tomato	4-5	3-4	6
Silk treated with β-CD	*Orange*	5	5	8
	Carrot	5	5	8
	Tomato	5	4-5	7-8

[8] Silk samples treated with 50g/L CA, 50g/L β-CD, temperature 130^{0}C and curing time 15 min.

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IV. Conclusion

In the present research, it was found that the treated silk sample gave better color strength than comparable dyeing of the untreated silk by the conventional method. In addition, the β-CD did not have any negative effect on the wash and staining fastness of the silk dyed with the natural dyes. It seems that the β-CD can concurrently endow the higher color strength together with a range of improvements of the silk (such as encapsulation of active substances, auxiliary agents, fragrances, antimicrobial agents, colorants, drugs, etc.) because of their unique structure.

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