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Effects of various colorants on self-dyed silk properties: aspects of color, thermal stability, morphology, and degumming

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Abstract. The process of dyeing has resulted in significant water consumption and wastewater discharge by the textile industry. The study's goal is to create and characterize self-dyed silks by feeding techniques with various natural and synthetic colorants in order to decrease textile environmental risks and improve the added value of silk. In this study, Bombyx mori was given mulberry leaves that had been dyed using Nanocurcumin derived from turmeric powder, as well as dyestuffs from *Caesalpinia sappan*, Acid Red 88, and Basic Red 13. The colorimetric, morphological, and thermal characteristics of both pristine and degummed self-dyed silks were thoroughly assessed using the CIELab color, color strength K/S, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). Consequently, Acid Red 88 greatly improved the coloring effectiveness of silks when compared to another natural dye and basic red. After all of the self-dyed silk was degummed, it was discovered that it was dispersed mainly in the sericin layer rather than the fibroin. The surface morphology and temperature properties of silk threads were also changed by the self-dyeing process. This study proposed waterless and sustainable silk coloration methods with various natural and synthetic colorants, which will help to address the health and environmental dangers connected with the dyeing industry, as well as the increasing demand for greener and more sustainable long-term development choices. Besides, the effects of the degumming process on self-dyed silks were also fully depicted.

Keywords: self-dyed silk, mulberry, degumming, characterization, colorant.

Classification numbers: 1.4.8, 2.3.2, 2.9.3.

1. INTRODUCTION

Silk, a natural fiber composed of the proteins fibroin and sericin, has been used in textiles for at least 5000 years and is a commonly used and color-required textile material [1]. Silk is a valuable substance with numerous beneficial properties that is utilized for a range of applications, most notably textiles, and fashion. Silk is frequently colored to improve aesthetics using several ways such as printing or dyeing, with dyeing being the most commonly used and popular [1]. More than 90% of commercially manufactured silk is actually spun by the domesticated silkworm Bombyx mori, a monophagous insect whose diet consists of mulberry tree leaves [1]. Before spinning their cocoons, silkworms go through 5 instars, which takes roughly 28 days [1]. Hot air is used to dry cocoons, removing the pupae and preventing the moth from eclosing. Importantly, proper drying boosts both silk output and quality and is a recommended practice even in tropical places with year-round availability [1]. Reeling requires immersing the cocoons in hot water to weaken the sericin protein, which links the fibers together to create the thick cocoon shell. Softening allows brushes to locate and pull the end of the silk strand [1]. The process of degumming involves the complete removal of sericin, which is the silk gum that bonds the fibroin filaments together, in order to achieve a characteristic shiny, soft texture and other desirable properties [2]. There are various sorts of silk that are commercially known and manufactured all over the world. However, most silk contains basic colors such as white (Mulberry silk, Eri silk), green (Tasar silk), and golden-yellow (Muga silk) [3]. As a result, there is a considerable demand for dyeing silk, particularly for environmentally friendly approaches.

The use of dyes to color silk also harms the environment. Water resources have been jeopardized and polluted as a result of the amount of water utilized, effluent, and untreated dye compounds. Many environmentally friendly coloring methods have been developed and used, including dyes derived from flowers, leaves, roots, barks, and so on [1, 4–6]. Nonetheless, ongoing research and improvement efforts are addressing drawbacks such as color instability, poor color fastness, and the utilization of highly toxic metal mordants that pose environmental hazards upon release [7, 8].

Moreover, to mitigate the labor-healthy and environmental repercussions of the existing textile industry, numerous efforts are being made throughout the world for dyeing, functionalization, and the discovery of novel bio-based alternative materials (like fungus, bacterial cellulose and protein, and so on) with varied uses in fashion, medical, and other technological applications [4, 5, 9–16]. However, these studies have not focused on the reduction of water consumption and discharges of major concerns of current textile dyeing and finishing. To clarify, the textile industry has consumed a considerable quantity of water and generated massive amounts of wastewater from various phases, particularly in the dyeing process, which accounts for around 16% of textile wastewater [18, 19]. Effluent discharged by dyeing is frequently color-rich, comprising residues of reactive dyes and chemicals such as complex components, numerous aerosols, high chroma, high COD (chemical oxygen demand) and BOD (biochemical oxygen demand) concentrations, and many more difficult-to-degrade compounds [18]. With an estimated 70 billion tons of wastewater produced by the textile industry each year, the discharge of this industry has been deemed a health and environmental danger, increasing demand for greener and more sustainable alternatives [18].

In relation to waterless coloration technology in the textile industry, self-dyeing is a dyeing method achieved by feeding silkworms with a specially formulated feed made from mulberry leaves containing dye solutions [20, 21]. This process significantly reduces the need for treating wastewater generated from common dyeing processes in traditional methods [20, 21]. During the fifth instar stage, silkworms were fed with modified feed consisting of mulberry leaves immersed or sprayed with dye solutions or mulberry leaf powder feed mixed with dye solutions [21].

Numerous studies on the silkworm self-dyeing method have been conducted in an effort to address the aforementioned challenges as well as those related to wastewater. This approach, which involves feeding silkworm leaves with dyestuff, allows for a nearly 100% reduction in water use when compared to conventional dyeing techniques, especially for Rhodamine B (RhB), Congo Red, Acid Orange G, Acid Orange II, Mordant Black 17, Direct Acid Fast Red, Sudan III, N-Blue, Neutral Red, Thionin [20–23]. Prior studies demonstrated that the structure and characteristics of the dye being used have a significant impact on the color strength values [22]. Furthermore, the other applications of this self-modifying method (self-dyeing/finishing) for silk have been conducted to enhance silk performance and functions. To promote environmentally friendly practices in silk coloring and functionalization, extensive scientific research has been conducted on altering the diets of silkworms with various functional substances. These substances encompass a wide range, including single-walled Carbon Nanotubes, Graphene, Graphene oxide, Carbon-based Nanomaterials, metal and metal oxide nanoparticles, and quantum dots [24–26]. The objective is to create self-modified silk fibers that exhibit enhanced mechanical properties, making them suitable for diverse applications such as reinforcement and surgical sutures v.v [24–26]. These innovative studies contribute to the advancement of sustainable approaches for silk treatment and functionalization. Diet modification approaches will undoubtedly produce significant promise and sustainability for silk dyeing and finishing in the future.

Turning to the mechanism of dye uptake inside silkworms during the self-dyeing process, a thorough evaluation of the properties of azo dyes revealed that a balance between water repellency and water affinity was necessary for the diffusion of dyes from the silkworm gut into the hemolymph and subsequently into the silk glands. The partition coefficient of dyes influences the selective binding of dyes to either sericin or fibroin proteins within the silk gland, ultimately affecting their distribution in the cocoon. Such profound understanding was crucial in developing new dye molecules that could be successfully delivered to Bombyx mori silkworm to produce internally colored silk with various hues and shades [20]. This process did not generate large amounts of wastewater containing dyes and polluting chemicals, making it an eco-friendly option. Dyes follow the biochemical pathway of the silkworm to create coloration in cocoons or silk fibers. The color intensity in the silkworm cocoons could be easily controlled by regulating the concentration of dyes in their food. These dyes were harmless to silkworms and had no adverse effects on their development [23, 27]. The derivatives of the dyes were used. A series of azo dyes were used as "model compounds" to establish important molecular structural parameters that determine the effectiveness of dyeing to produce colored silk. This approach resulted in economic benefits [20]. For each different process, there were changes in methods and implementation procedures. Compared to previous studies, this study not only assessed the dye properties and their color-producing capabilities, as most prior reports focused on, but also evaluated the characteristics of self-dyeing yarn before and after degumming to elucidate certain impacts of various dyes on the microstructural properties of the yarn. This is crucial in the research and development of a new textile material.

This study provides a scientific premise on the self-dyeing method of silk for various new natural that had not been tested before (Nanocurcumin from Turmeric powder, Caesalpinia sappan dyestuff) with the expectation of their compatibility with natural dyestuffs. Silk self-dyeing added value and significance to an eco-sustainable method of color creation. Furthermore, synthetic dyes (Acid Red 88, Basic Red 13) were also tested to expand the list of colorants applicable to this self-dyeing method. Of particular note, unlike the report on the molecular weight of dyes below 400 g/mol, which demonstrated a high color-producing capability for silk [20], the results in this study contributed to a clearer understanding of the role of molecular weight in the coloration effectiveness of the self-dyeing method. Besides, colorimetric, morphological, and thermal of these self-dyed silk fibers have been thoroughly evaluated via Commission on Illumination Lab (CIELab) color space, visible light scattering, and reflection, Scanning Electron Microscope (SEM), Thermal Gravimetric Analysis (TGA). In addition, the influences of silk degumming on these properties of self-dyed silk were also investigated and discussed.

2. MATERIALS AND METHODS

2.1. Materials

Chemicals: *Caesalpinia sappan* dyestuff was provided by Maiwa (Canada). Nanocurcumin derived from Turmeric powder was obtained from Faculty of Chemistry Engineering – Ho Chi Minh City University of Technology (Vietnam). Acid Red 88 was purchased from Sigma-Aldrich (USA). Basic Red 13 was provided by Rifa (Korea).

Bombyx mori (Mulberry species) and mulberry leaves were supplied by Bao Loc's mulberry plantations (Lam Dong, Vietnam).

2.2. Coloring mulberry leaves

Using the spraying technique, mulberry leaves were dyed with dyeing solutions such as *Caesalpinia sappan* dyestuff (286.28 g/mol), Nanocurcumin (368.4 g/mol), Acid Red 88 (400.38 g/mol), and Basic Red 13 (389.36 g/mol) at a concentration of 2000 ppm. The liquor ratio was 1.5:1 (the weight in grams of mulberry leaves to the volume in milliliters of dyeing solution). These colorful leaves were line-dried until their moisture content was in equilibrium with the surrounding air.

2.3. Self-dyeing of silkworm

Since the fourth day of the fifth instar, colorful mulberry leaves have been fed to the Bombyx mori silkworms. There was a three-day feeding period. The collected cocoons were boiled for five minutes at 90ºC before being reeled using Silk reeling M/C-KTR1 (Korea).

2.4. Characterization

2.4.1. Color analysis

Based on the Kubelka-Munk theory as shown in Equation 1 [28], the color strength (K/S) of self-dyed silk fibers was measured and estimated using an X-Rite Color i5 Spectrophotometer and Color iControl software (X-Rite, USA) in the wavelength range of 400 nm to 700 nm. The lightness of a sample is typically denoted by the L*, which is based on the percentage of light reflectance [29]. A value of zero for L* indicates a black sample, while a value of 100 indicates a white one [29]. The a* value represents the degree of redness or greenness in a sample’s color [29]. A positive a* value indicates a red color, while a negative one indicates a green color [30]. If a* is zero, the sample will appear gray and be positioned at the center of the red/green plane [29]. The b* value represents the degree of yellowness or blueness in a sample’s color [29]. A positive b* value indicates a yellow hue, while a negative value indicates a blue one [29]. However, it’s important to note that the a* and b* values do not necessarily indicate that a sample is yellow, blue, red, or green in color [29]. Color difference ΔE represents the geometrical distance between the corresponding points (of the two samples) in the color space (the distance from the test sample and the analysis sample) which was computed as Equation 2. Where K, S, and R, respectively, stand for absorbance, scattering, and reflectance; ΔL indicates any difference in brightness and is denoted by (+) if the sample that reproduces is lighter (brighter) than the witness specimen, and by (–) if it is darker than this [29]; ΔL determines the lightness/darkness difference between a sample and a standard [29]; Δa determines the red/green color distinction between the standard and the sample [29]; Δb determines the yellow/blue color difference between a standard and a sample [29].

$$\mathrm{K/S} = \frac{(1-\mathrm{R})^2}{2\mathrm{R}} \tag{1}$$

$$\Delta\mathrm{E} = \sqrt{\Delta\mathrm{L}^2 + \Delta\mathrm{a}^2 + \Delta\mathrm{b}^2} \tag{2}$$

2.4.2. Scanning electron microscope

Using a JSM-IT200 InTouchScope™ Scanning Electron Microscope (Japan), the morphology of self-dyed silk fiber was examined.

2.4.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TG209 F1 thermometer (Netzch, Germany). The thermograms were produced at temperatures ranging from 25 to 1000°C in a nitrogen environment with a constant gas flow rate of 10 mL/min and a heating rate of 10 K/min.

3. RESULTS AND DISCUSSION

3.1. Coloration effectiveness of silk self-dyeing for artificial and natural colorants

Figure 1 provides images of silk samples through the self-dyeing process using natural and artificial colorants.

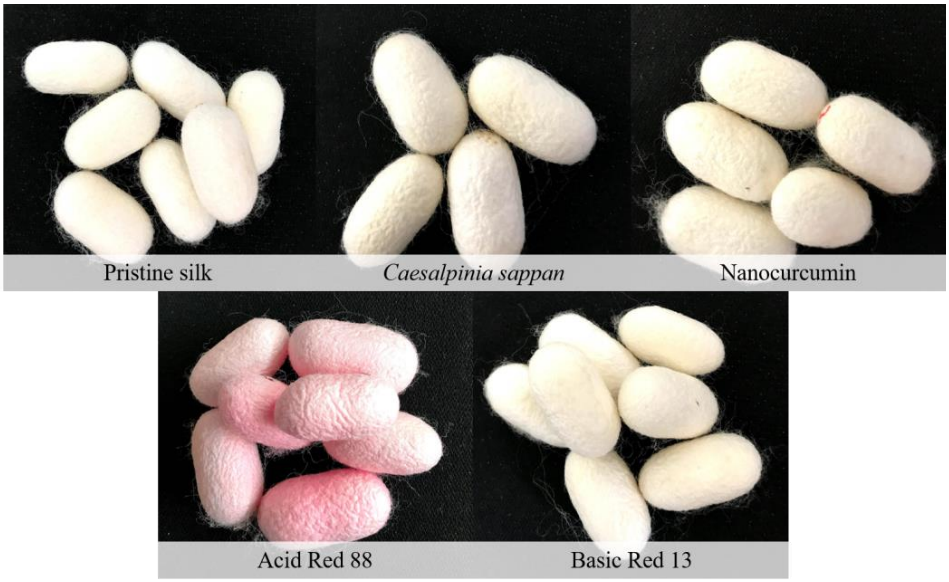


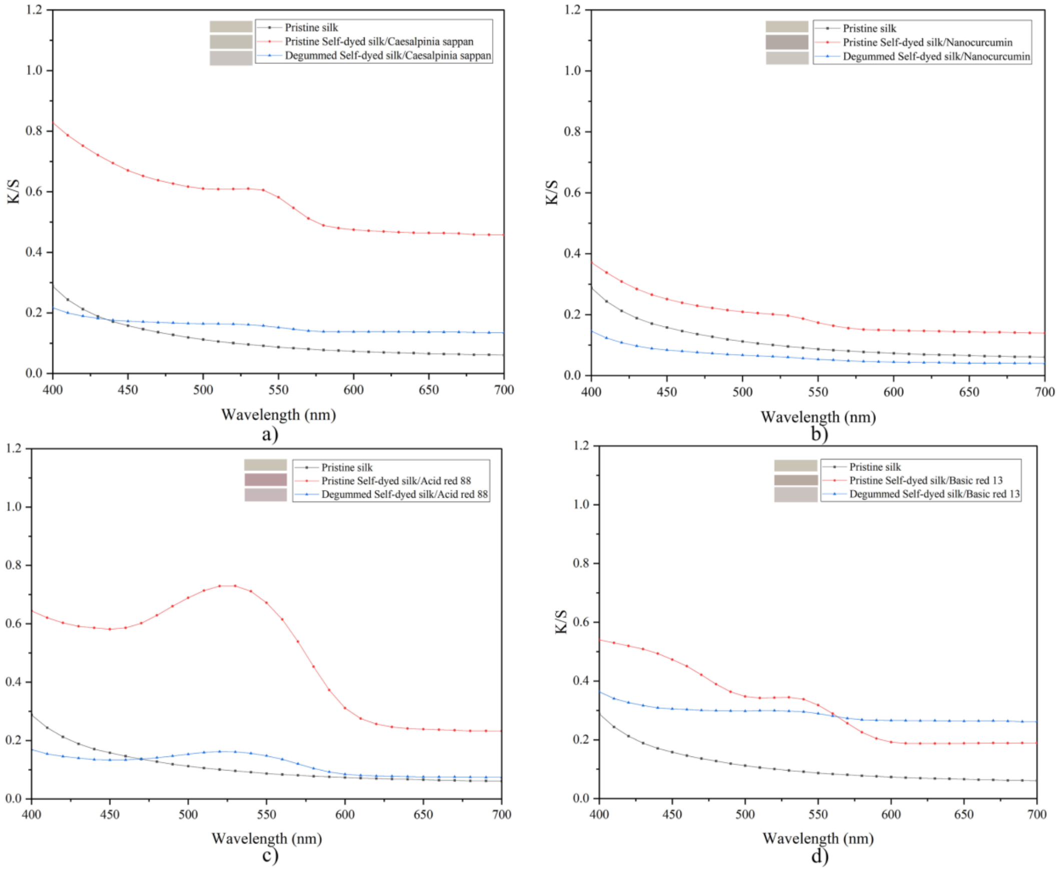
Figure 1. Self-dyed cocoons with various artificial (Acid Red 88, Basic Red 13) and natural (*Caesalpinia sappan*, Nanocurcumin) colorants.

Generally, as per visual observation (Figure 1), it is clear that natural colorants (*Caesalpinia sappan*, Nanocurcumin) didn't yield significant coloration effectiveness for cocoons of Bombyx mori via the self-dyeing process. On the contrary, in terms of artificial colorants, Acid Red 88 has prevailed over its counterparts in coloration capacity, followed by Basic Red 13. To elucidate the dyeing capabilities of silk for different dyes reports from prior studies highlighted molecular weight (around 400 g/mol) as a determining factor in the dye's permeation through the silk gut into the glands within the silkworm's body [23]. Concerning molecular weight, all the dyes used hardly exceeded but rather fluctuated around, the 400 g/mol threshold, such as

Nanocurcumin (368.38 g/mol) [31], Acid Red 88 (400.38 g/mol) [32], and Basic Red 13 (389.36 g/mol) [33]. Therefore, it can be inferred that the molecular weight of the dye is not an absolute determinant, as suggested in some previous reports, but rather a factor enabling the efficient absorption of the dye through the silk gut of the silkworm.

To clarify, previous studies have emphasized key elements of effective silk self-dyeing, including molecular weight (no more than around 400 g/mol), balance of hydrophobicity and hydrophilicity (hydrophobicity imparted by aromatic groups and hydrophilicity of polar groups) of silk cocoon.

Figure 2 illustrates the K/S curves of self-dyed silk samples before and after degumming, as well as in comparison with pristine silk. K/S was calculated based on the amount of light absorbed (K) and scattered (S) by the sample at a particular wavelength.



a)

b)

c)

d)

Figure 2. K/S spectra of self-dyed silk with *Caesalpinia sappan* (a), Nanocurcumin (b), Acid Red 88 (c), Basic Red 13 (d) before and after degumming.

The findings in this study were once again validated through the K/S color values of silks self-dyed with pre and post-curing dyes (Figure 2). Acid Red 88 has demonstrated a good coloring effect on the self-dyeing process compared with most of the studied dyes of both natural and artificial sources. In addition, it can be seen that after degumming with MS and Na_2CO_3, the K/S values of all dyed silk samples were significantly reduced, which proves that the surveyed natural and artificial colorants are adsorbed and distributed mainly in the sericin layers.

Before degumming, the K/S curves of self-dyed silk samples Acid Red 88 (Figure 2.c) showed a peak in the range of 500 – 550 nm, suggesting that this wavelength range was more effective in producing better color than other wavelengths outside the peak range. These peaks indicated the maximum absorption of light by the dye molecules, resulting in a more intense and evenly distributed color on the surface. However, for certain types of self-dyeing drugs such as *Caesalpinia sappan* (Figure 2.a), Nanocurcumin (Figure 2.b), and Basic Red 13 (Figure 2.d), no peak waves were observed, so it can be concluded that these samples did not produce any color during the self-dyeing process in the wavelength range of 400 – 700 nm. The K/S curves also showed a gradual decrease in K/S values as the wavelength increased from 400 to 700 nm. This decrease in K/S values indicated a decrease in the amount of color strength by the dye molecules at longer wavelengths.

Prior to degumming, a notable peak was observed in Acid Red 88, with peak wavelengths ranging from 525 to 535 nm, respectively. This peak exhibited higher K/S values compared to the other self-dyed silk samples, indicating that Acid Red 88 (with a peak of 0.73 ± 0.42 K/S at a wavelength of 530 nm) was more effective in coloring the silk prior to the removal of the sericin layer.

After degumming, the K/S curves of all self-dyed silk samples showed a significant decrease, indicating a decrease in the amount of dye molecules present in the silk samples. The K/S values of the self-dyed silk samples after degumming were similar to those of Pristine silk, indicating that the dye molecules were primarily located in the sericin layer of silk. The peaks of *Caesalpinia sappan* (Figure 2.a), Acid Red 88 (Figure 2.c), Basic Red 13 (Figure 2.d), and Nanocurcumin (Figure 2.b) observed in the K/S curves before degumming gradually disappeared after degumming, indicating that the dye molecules were removed from the silk samples during the degumming process. The K/S values of *Caesalpinia sappan* (Figure 2.a), Acid Red 88 (Figure 2.c), Basic Red 13 (Figure 2.d), and Nanocurcumin (Figure 2.b) decreased to only about 0.2 to 0.4, much lower than before degumming.

The results from Table 1 indicated that the L*, a*, b* values and the color difference (ΔE) of the self-dyed silk samples before and after degumming, compared to the undyed silk, demonstrated color variations. The findings also revealed differences in color between the silk samples before and after degumming. This indicates that the degumming process affects the color system of the samples, although the extent of change varied for each dye.

Prior to degumming, the Nanocurcumin, *Caesalpinia sappan*, and Basic Red samples had similar average L* values, indicating that their brightness was approximately the same. Among them, *Caesalpinia sappan* had the highest brightness with a value of 80.22 ± 3.86, so the brightness of this sample stood out more compared to the other four samples. Acid Red 88 had a lower brightness (67.57 ± 2.23), this sample had the lowest brightness among the 4 dye samples. After degumming, the L* values of all samples increased significantly, indicating that the sericin coating had darkened the colors of the samples. Among them, the Nanocurcumin sample had the highest (88.37 ± 0.66) and Acid Red 88 had the greatest increase in average L* value after degumming (83.22 ± 0.63). Nanocurcumin had the least and lowest increase in average L* value (76.79 ± 0.43), and the difference in L* between measurements of this sample was very large.

Table 1. L*,a*,b*, and ΔE measurement results with 4 dye samples before and after degumming.

	Before degumming			
	Caesalpinia sappan	Nanocurcumin	Acid Red 88	Basic Red 13
L*	80.22 ± 3.86	76.79 ± 0.43	67.57 ± 2.23	74.94 ± 0.98
a*	0.61 ± 0.22	2.49 ± 0.37	13.71 ± 0.77	4.02 ± 0.50
b*	6.45 ± 1.96	7.26 ± 2.15	2.33 ± 2.00	6.48 ± 0.43
ΔE	6.24 ± 3.60	9.60 ± 0.58	21.92 ± 1.74	14.27 ± 5.53
	After degumming			
L*	85.57 ± 1.40	88.37 ± 0.66	83.08 ± 0.88	82.10 ± 1.87
a*	1.19 ± 0.17	0.70 ± 0.16	5.58 ± 0.75	1.66 ± 0.70
b*	2.68 ± 0.38	4.78 ± 0.72	1.49 ± 0.62	3.33 ± 2.04
ΔE	5.16 ± 0.45	3.86 ± 0.48	8.59 ± 0.94	6.37 ± 1.25

Before degumming, the ΔE values of the samples were relatively large, ranging from 6.24 ± 3.60 to 21.92 ± 1.74, with Acid Red 88 being the most effective with a ΔE of 21.92 ± 1.74 and *Caesalpinia sappan* being the least effective with a value of 6.24 ± 3.60. However, after degumming, the ΔE values decreased significantly, ranging only from 3.86 ± 0.48 to 8.59 ± 0.94. Before degumming, Acid Red 88 was evaluated as having the best color efficiency, but after the degumming process, its color efficiency decreased significantly. This indicates that the color efficiency of the samples is very high when the sericin layer is not removed. The dyes mainly bond with the sericin layer, which is difficult to bond and penetrate deep into the fibroin.

Prior to degumming, the average a* color parameter of the 4 dye samples was located on coordinates of red colors with values ranging from 0.61 ± 0.22 to 13.71 ± 0.77. The a* parameter with high positive values reflected the predominance of red over green [34]. So, Acid Red 88 had the highest red color with an a* value of 13.71 ± 0.77, and the lowest was *Caesalpinia sappan* with a value of 0.61 ± 0.22. After degumming, the average a* values of the 4 samples tended to decrease but remained positive, indicating that the red color of the samples would become lighter.

Before degumming, the average b* value of the other samples was located on coordinates of yellow-blue colors with values ranging from 2.33 ± 2.00 to 7.26 ± 2.15. Since all b* values were positive, it could be concluded that, in the tested samples, yellow hues were dominant over blue hues (as mentioned in Figure 1). After degumming, the average b* values decreased to around 1.49 ± 0.62 to 4.78 ± 0.72. Combining L*, a*, and b* values, it can be seen that all 4 samples had a strong yellowish-red color before degumming, which became lighter after 4 rounds of degumming, with an increase in brightness. The degree of change varied for each sample, with Acid Red 88 being the most noticeably altered.

3.2. Surface morphological properties of self-dyed silk with natural and artificial colorants

Figure 3 shows the surface morphology of self-dyed silk samples before and after degumming at 1000 magnification.

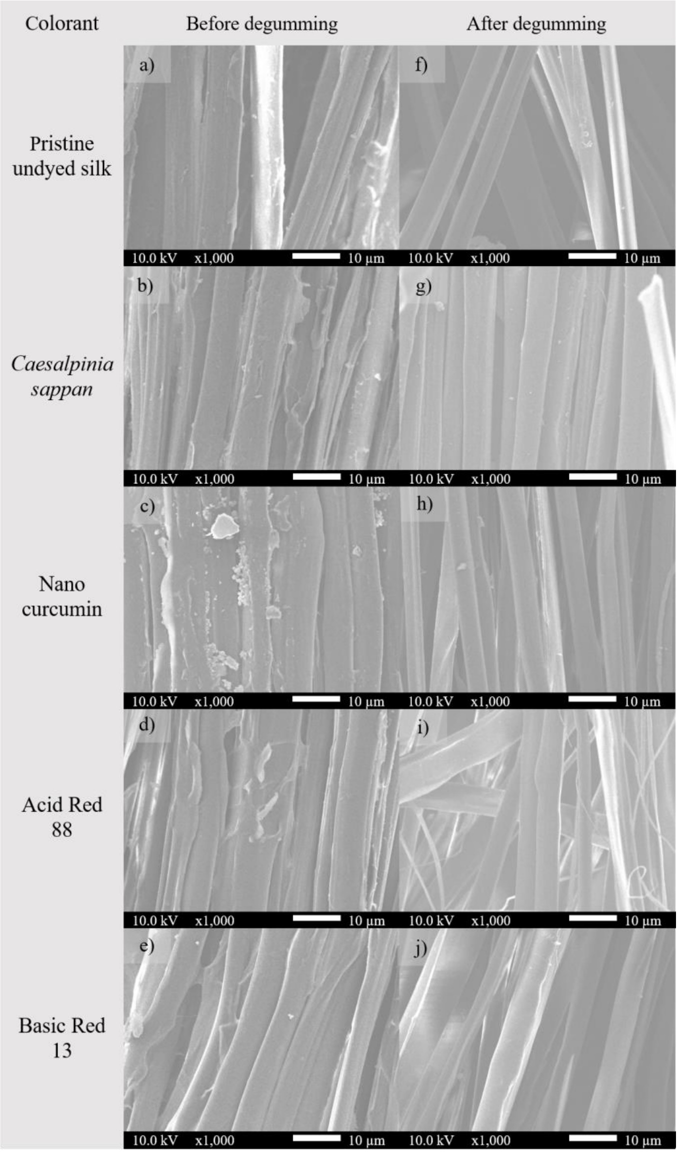


Figure 3. SEM images of silk samples before and after degumming.

In general, the surface morphology of silks before and after degumming did not change significantly displayed in Figure 3. However, for self-dyed silk before degumming (Figure 3.a,b,c,d,e), because most of the colorants are eliminated during biosynthesis in silkworms, the self-dyeing process with various colorants is said to be less efficient such as *Caesalpinia sappan*, Nanocurcumin, and Basic Red 13 (Figures 3.b,c,e). Self-dyeing with these ineffective colorants did not produce any difference in the surface morphology of silk compared with pristine undyed silks (Figure 3.a). However, for the effective colorant in self-dyeing as Acid Red 88, the surface morphology of silk changed remarkably, especially the discontinuity in the sericin layer (Figures 3.d). Corresponding to the conclusion about the coloring efficiency of self-dyeing with various dyes, the higher the colorant is mainly distributed in the sericin layer, the higher the amount of colorant will cause the sericin layer to become disrupted.

After degumming (Figure 3.f,g,h,i,j), most of the sericin layer was removed, therefore, silk surface is smoother with no obvious difference between self-dyed silk and conventional undyed silk. However, it can be observed that for the effective colorants in self-dyeing and Acid Red 88, many fibrils appear in the silk structure (Figures 3.i), which could not be observed in either undyed silk or self-dyed silks with colorants with poor coloring efficiency (Figures 3.f,g,h,j). It can be seen that, although effective colorants such as Acid Red 88 are mainly distributed on the sericin layer, they still have a significant effect on the fibroin structure of silk during biosynthesis. The results of this morphological surface are analogous to a previous study [21]. Based on the findings, it can be concluded that the self-dyed process does not have a significant impact on the morphology of silk. This finding can pave the way for future studies on modifying the fibroin structure of silk for various applications.

3.3. Thermal stability of self-dyed silk with natural and artificial dyes

Figure 4 presents TGA analysis of self-dyed silk samples before and after degumming that provided information on the thermal stability of self-dyed silks with various synthetic and natural colorants.

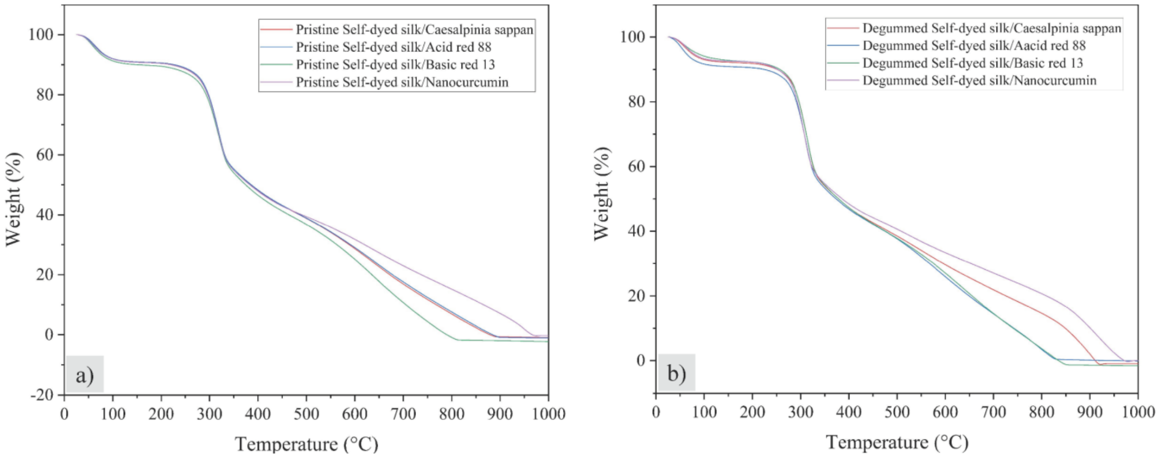


Figure 4. Thermal gravimetric analysis (TGA) of self-dyed silks before (a) and after (b) degumming.

TGA analysis confirmed that the self-dyeing of the above dyes changed the thermal properties of silk both before and after degumming. The thermal stability of the self-dyed silks is markedly different over the entire temperature range from about 25 to 1000ºC. Most of the thermal stability between the self-dyed silk samples before and after degumming exhibited similar thermal properties below 350ºC, and the difference was significantly different when the temperature was raised above 350ºC. It can be said that this finding is related to various factors such as the amount of carbon and other substances, as well as changes in amino acids within silk. This relationship was previously demonstrated through the analysis of amino acid content in self-dyed silk compared to regular white silk [21]. Furthermore, the presence of various dye types and their individual characteristics is also a contributing factor to the differences observed in the thermal properties of various self-dyed silk threads and so forth due to the existence of different colored compounds in the biosynthesis of sericin and fibroin. More specifically, the main cause of the mass loss of silk fibers at temperatures below 100ºC is water evaporation, while the bulk loss above 200ºC is related to the loss of gases that have low molecular weight (H_2O, CO_2, and NH_3) [35]. These gases are attributed to the disruption of amino acid side chain residues and the cleavage of peptide bonds in the amorphous region of the silk [36, 37]. The fibroin of Bombyx mori silk exhibits a degradation step with a maximum decomposition temperature of 350ºC. However, there are differences in the thermal properties between raw silk (containing sericin) and degummed silk (sericin removed), with corresponding thermal decomposition steps at 325 – 350ºC and 340 – 360ºC for sericin-containing and sericin-free fibers, respectively. Variations in thermal properties are also evident among different post-degumming samples, possibly linked to the type of dye ingested by the silkworms along with alterations in the silk synthesis process during fiber formation. The results demonstrate chemical and physical changes in self-dyed silk samples using different dyeing methods. However, it’s observed that silk doesn’t completely decompose even at temperatures as high as 1000ºC due to its characteristic semi-crystalline structural features and the phase transition kinetics from amorphous regions within the silk to crystalline after the heating process concludes [38–40]. Therefore, it can be said that the difference in thermal stability between the self-dyed silks is due to the quantitative change of carbon, nitrogen, oxygen, and hydrogen in the protein composition of the silk. Degradation of fibroin molecules has been recorded which can be observed at about 350ºC - the decomposition temperature of Bombyx mori silk [37].

4. CONCLUSION

This research offers a scientific foundation for the self-dyeing of silk using a variety of novel natural and synthetic colorant sources, such as Nanocurcumin from turmeric powder, *Caesalpinia sappan* dyestuff, Acid Red 88, and Basic Red 13. Acid Red 88 proved to be highly effective in coloring silk through the self-dyeing process, outperforming most of the other dyes studied including both natural and artificial dyes such as *Caesalpinia sappan*, Nanocurcumin, and Basic Red 13. Acid Red 88 exhibited a significant color enhancement at the wavelength of 525 – 535 nm before degumming compared to the other samples, with a K/S value of 0.73 ± 0.42 K/S at 530 wavelengths.

After degumming, the brightness of all samples increased significantly, with Nanocurcumin showing the highest increase with a value of 88.37 ± 0.66. The redness of the samples decreased, while the yellowness increased. The color effectiveness of Acid Red 88 was the highest, with ΔE value of 8.59 ± 0.94.

Acid Red 88 demonstrated high effectiveness as a colorant for self-dyeing. Consequently, significant changes were observed in the surface morphology of silk, particularly in the discontinuity of the sericin layer. The properties of Acid Red 88 could be further investigated due to its excellent color absorption ability. In contrast, *Caesalpinia sappan* (a), Nanocurcumin (b) and Basic Red 13 (e) did not yield any coloration after the self-dyeing process. The surface of the silk appeared smoother, and there was minimal noticeable difference between the self-dyed silk and the conventional undyed silk.

Based on the results of this study, the self-dyeing technology could be further investigated for its thermal properties using various analytical methods (Differential Scanning Calorimetry, Difference Thermogravimetry, etc.) to provide a better understanding of material modification. The study’s results suggest several avenues for expanding the commercialization of self-dyeing. One promising direction is pilot-scale production, which involves further refining and optimizing the formulation and process parameters to improve the quality and consistency of the dyeing. Another potential application is in fashion design, where self-dyeing products can create custom and sustainable textile products. This study solely focused on investigating four types of self-dyeing, including the use of certain natural dyes such as turmeric and wood powder, with the anticipation of their compatibility with the silk self-dyeing technique. This aimed to enhance the value and significance of a nature-friendly and sustainable coloration method. The efficacy of this method significantly relies on the biological characteristics and natural selective absorption of silk. Hence, while not yielding vibrant colors for silk, this research still holds significance in diversifying theoretical knowledge for referencing suitable dye materials for this self-dyeing approach. Additionally, discoveries regarding the morphology, structure, and thermal properties of self-dyed silk in this study serve as a foundation to establish and select appropriate technological parameters for manufacturing and utilizing this new material in various applications. Expanding the research scope to encompass other forms of self-dyeing could offer a more comprehensive insight into the efficacy of self-dyeing technology.

For future perspective studies, delving deeper into natural dye has the potential to advance the silk dyeing compounds within the global textile industry as well as learn more about dyeing mechanisms. Self-dyeing helps reduce water consumption and environmental pollution, which is what the textile industry aims for. Based on this research, new dyes can be tested such as natural dyes, acid dyes, reactive dyes, and insoluble vat dyes that can be evaluated to evaluate their effectiveness through process self-dyeing to find the most optimal dyeing process. In addition, research on the dye absorption mechanism of silkworms is very important, so it is necessary to consider the ability of dyes to absorb and bind to silk during the self-dyeing process. In addition, other influencing factors such as the partition coefficient, concentration, hydrophobicity, hydrophilicity, and physical and chemical properties need to be evaluated.

Consequently, Acid Red 88, in contrast to another natural dye and basic red, significantly increased the coloring efficacy of silks. However, it was verified that self-dyed silk was distributed primarily in the sericin layer rather than the fibroin after all of the self-dyed silk had been degummed. The surface morphology and temperature characteristics of silk strands were also altered by the self-dyeing procedure. This research suggested sustainable and waterless techniques for silk coloration, which will help to address health and environmental risks associated with the dyeing industry, as well as the growing demand for cleaner and more sustainable options for long-term growth.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Astudillo M.F., Thalwitz G., Vollrath F. **-** Life cycle assessment of Indian silk. J. Clean. Prod. **81** (2014) 158–167. https://doi.org/10.1016/j.jclepro.2014.06.007
2. Freddi G., Mossotti R., Innocenti R. **-** Degumming of silk fabric with several proteases. J. Biotechnol. **106** (2003) 101–112. https://doi.org/10.1016/j.jbiotec.2003.09.006
3. DR T., TK K. **-** Mulberry and Silk Production in Kenya. J. Text. Sci. Eng. **05** (2015). https://doi.org/10.4172/2165-8064.1000220
4. Pham C.T.N., Phan H.N., Hoang T.T., Dao T.T.T., Bui H.M. **-** A study on the coloration effectiveness of Chromolaena odorata on the worsted wool fabric. Res. J. Text. Appar. (2022). https://doi.org/10.1108/RJTA-07-2022-0089
5. Dapson R.W., Bain C.L. **-** Brazilwood, sappanwood, brazilin and the red dye brazilein: From textile dyeing and folk medicine to biological staining and musical instruments. Biotech. Histochem. **90** (2015) 401–423. https://doi.org/10.3109/10520295.2015.1021381
6. Yusuf M., Shabbir M., Mohammad F. **-** Natural Colorants: Historical, Processing and Sustainable Prospects. Nat. Products Bioprospect. **7** (2017) 123–145. https://doi.org/10.1007/s13659-017-0119-9
7. Mitra A. **-** Natural dye mordants and their health hazards. J. Text. Assoc. **75** (2015) 405–

410.

8. Samanta A.K. - Fundamentals of Natural Dyeing of Textiles: Pros and Cons. Curr. Trends Fash. Technol. Text. Eng. **2** (2018) 69–76. https://doi.org/10.19080/ctftte.2018.02.555593 https://doi.org/10.19080/ctftte.2018.02.555593
9. Phan H.N., Vu N.K., Bui H.M. - Fabrication and characterization of patterned leather-like biomaterial derived from Brazilein/Glycerol-finished Bacterial Cellulose by using 3-in-1 textile finishing process. Cellulose. **30** (2023) 5217–5237. https://doi.org/10.1007/s10570-023-05193-w
10. Phan H.N., Bui H.M., Vu N.K., Trinh H.T.K. - Fabrication of fabric-like Bacterial Cellulose/Collagen membranes by applying textile padding method for wound dressing applications. Cellulose. **30** (2023) 2289–2321. https://doi.org/10.1007/s10570-022-05003-9
11. Phan H.N., Bui H.M., Vu N.K. - F Fabrication of fabric-like Bacterial Cellulose/Collagen membranes by applying textile padding method xtile padding method. Res. J. Text. Appar. (2023). https://doi.org/10.1108/RJTA-06-2022-0071
12. Rathinamoorthy R., Kiruba T. - Bacterial Cellulose - A Sustainable Alternative Material for Footwear and Leather Products, Springer Singapore, Singapore (2020)
13. Salauddin Sk. M., Rony M.I.A., Haque M.A., Shamim A.M. - Review on Extraction and Application of Natural Dyes. Text. Leather Rev. **4** (2021) 218–233. https://doi.org/10.31881/TLR.2021.09
14. Wijayarathna E.R.K.B., Mohammadkhani G., Soufiani A.M., Adolfsson K.H., Ferreira J.A., Hakkarainen M., Berglund L., Heinmaa I., Root A., Zamani A. - Fungal textile alternatives from bread waste with leather-like properties. Resour. Conserv. Recycl. **179** (2022). https://doi.org/10.1016/j.resconrec.2021.106041
15. Meyer M., Dietrich S., Schulz H., Mondschein A. - Comparison of the technical performance of leather, artificial leather, and trendy alternatives. Coatings. **11** (2021) 1–15. https://doi.org/10.3390/coatings11020226
16. Muthu S.S., Rathinamoorthy R. - Sustainability and Fashion, Springer Singapore, Singapore (2021).
17. Hernandez Alvarez, B., Bassler, J., Lupas, A.N. - Structural diversity of coiled coils in protein fibers of the bacterial cell envelope. Int. J. Med. Microbiol. **309** (2019) 351–358. https://doi.org/https://doi.org/10.1016/j.ijmm.2019.05.011
18. Wang Z., Xue M., Huang K., Liu Z. - Textile Dyeing Wastewater Treatment, IntechOpen, Rijeka (2011).
19. Kant R. - Textile dyeing industry an environmental hazard. Nat. Sci. **04** (2012) 22–26. https://doi.org/10.4236/ns.2012.41004
20. Nisal A., Trivedy K., Mohammad H., Panneri S., Sen Gupta S., Lele A., Manchala R., Kumar N.S., Gadgil M., Khandelwal H., More, S., Laxman R.S. - Uptake of azo dyes into silk glands for production of colored silk cocoons using a green feeding approach. ACS Sustain. Chem. Eng. **2** (2014) 312–317. https://doi.org/10.1021/sc400355k
21. Tran U.N.T., Phan H.N., Hoang T.T., Le N.T.H., Bui H.M. - Characterization of self-dyed silk yarn with Rhodamine B dye for fashion applications. Int. J. Cloth. Sci. Technol. **35** (2023) 477–492. https://doi.org/10.1108/IJCST-10-2022-0147
22. Kang P.D., Kim M.J., Jung I. Y., Kim K.Y., Kim Y.S., Sung G.B., Sohn B.H. - Production of Colored Cocoons by Feeding Dye-Added Artificial Diet. Int. J. Ind. Entomol. **22** (2011) 21–23. https://doi.org/10.7852/ijie.2011.22.1.21

23. Tansil N.C., Li Y., Koh L.D., Peng T.C., Win K.Y., Liu X.Y., Han M.Y. - The use of molecular fluorescent markers to monitor absorption and distribution of xenobiotics in a silkworm model. Biomaterials. **32** (2011) 9576–9583. https://doi.org/10.1016/j.biomaterials.2011.08.081
24. Wang Q., Wang C., Zhang M., Jian M., Zhang Y. - Feeding Single-Walled Carbon Nanotubes or Graphene to Silkworms for Reinforced Silk Fibers. Nano Lett. **16** (2016) 6695–6700. https://doi.org/10.1021/acs.nanolett.6b03597
25. Ramos N., Miranda M.S., Franco A.R., Silva S.S., Azevedo J., Dias I.R., Reis R.L., Viegas C., Gomes M.E. - Toward Spinning Greener Advanced Silk Fibers by Feeding Silkworms with Nanomaterials. ACS Sustain. Chem. Eng. **8** (2020) 11872–11887. https://doi.org/10.1021/acssuschemeng.0c03874
26. Qu J., Dai M., Ye W., Fang Y., Bian D., Su W., Li F., Sun H., Wei J., Li B. - Study on the effect of graphene oxide (GO) feeding on silk properties based on segmented precise measurement. J. Mech. Behav. Biomed. Mater. **113** (2021) 104147. https://doi.org/10.1016/j.jmbbm.2020.104147
27. Tansil N.C., Li Y., Teng C.P., Zhang S., Win K.Y., Chen X., Liu X.Y., Han M.Y. - Intrinsically colored and luminescent silk. Adv. Mater. **23** (2011) 1463–1466. https://doi.org/10.1002/adma.20100386028.
28. Gangakhedkar N.S. - Colour measurement of paint films and coatings, Woodhead Publishing, Cambridge (2010).
29. Systems R. - Color & the CIELAB System. An Interpret, CIELAB Syst.1.
30. Karthikeyan A., Senthil N., Min T. - Nanocurcumin: A Promising Candidate for Therapeutic Applications. Front. Pharmacol. **11**, (2020). https://doi.org/10.3389/fphar.2020.00487
31. Deshannavar U.B., Kumar Singa P., Gaonkar D., Gayathri A., Patil A., Malade L. V. - Removal of Acid Violet 49 and Acid Red 88 dyes from Aqueous Solutions using Advanced Oxidation Process. Mater. Today Proc. **24** (2020) 1011–1019. https://doi.org/10.1016/j.matpr.2020.04.414
32. Bayram, T., Bucak, S., Ozturk, D. - BR13 dye removal using sodium dodecyl sulfate modified montmorillonite: Equilibrium, thermodynamic, kinetic and reusability studies. Chem. Eng. Process. - Process Intensif. **158** (2020) 108186. https://doi.org/10.1016/j.cep.2020.108186
33. Atodiresei G.V., Sandu I.G., Tulbure E.A., Vasilache V., Butnaru, R. - Chromatic characterization in cielab system for natural dyed materials, prior activation in atmospheric plasma type DBD. Rev. Chim. **64** (2013) 165–169
34. Nakamura S., Magoshi J., Magoshi Y. - Thermal Properties of Silk Proteins in Silkworms. Presented at the (1993)
35. Tsukada M., Nagura M., Ishikawa H. - Structural changes in poly(L- alanine) induced by heat treatment. J. Polym. Sci. Part B Polym. Phys. **25** (1987) 1325–1329. https://doi.org/10.1002/polb.1987.090250610
36. Mhuka, V., Dube S., Nindi M.M. - Chemical, structural and thermal properties of Gonometa postica silk fibroin, a potential biomaterial. Int. J. Biol. Macromol. **52** (2013) 305–311. https://doi.org/10.1016/j.ijbiomac.2012.09.010
37. Fu C., Porter D., Chen X., Vollrath F., Shao Z. - Understanding the mechanical properties of Antheraea pernyi Silka-From primary structure to condensed structure of the protein. Adv. Funct. Mater. **21** (2011) 729–737. https://doi.org/10.1002/adfm.201001046

38. Prasong S., Yaowalak S., Wilaiwan S. - C haracteristics of silk fiber with and without sericin component:A comparison between Botnbyx tnori and Philosamia ricini silks. Pakistan J. Biol. Sci. **12** (2009) 872–876. https://doi.org/10.3923/pjbs.2009.872.876
39. Bawazeer T.M., Alsoufi M.S. - Surface Characterization and Properties of Raw and Degummed (Bombyx mori) Silk Fibroin Fiber toward High Performance Applications of “Kisswa Al- Kabba.” Int. J. Curr. Res. **9** (2017) 48335–48343