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Sustainable Dyeing Process for Nylon 6 Fabrics by Rhubarb Flower Using Different Bio-Mordants

Fatemeh Shahmoradi Ghaheh [1], Aminoddin Haji [2,*] and Elaheh Daneshvar [3]

1 Department of Textile Engineering, Faculty of Environmental Science, Urmia University of Technology, Urmia 5756151818, Iran; f.shahmoradi@uut.ac.ir
2 Department of Textile Engineering, Yazd University, Yazd 8915818411, Iran
3 Colour & Imaging Lab, School of Computing Sciences, University of East Anglia, Norwich NR4 7TJ, UK; e.daneshvar@uea.ac.uk
* Correspondence: ahaji@yazd.ac.ir

Abstract: The purpose of this study is to propose a fully sustainable dyeing process for nylon 6. In order to achieve this goal, Rhubarb flower parts were used to produce a brown hue on nylon 6 fabric. The effects of dyeing parameters such as dyeing time, temperature, dyebath pH, M:L, salt addition, dispersing agent, and dye concentration on color strength were investigated. Using 100%owf dye in an acidic medium at boil and the material to liquor ratio of 1:30 for 75 min was determined to be the optimal condition for dyeing nylon 6 with rhubarb flower. In order to achieve acceptable color fastness, four natural mordants were applied, including walnut husks, pistachio hulls, pine cones, and green coffee. Colorimetric measurements revealed that mordanting did not affect the hue of the color compared to the non-mordant sample. In addition, diverse natural mordants produced the same color (i.e., brown) with varying color strengths, of which 10%owf walnut husk generated the strongest color. Bio-mordanted samples were also found to have excellent color fastness, thereby providing an effective substitute for metal mordants.

Keywords: natural dyeing; polyamide; eco-friendly; tannin; color strength; fastness

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1. Introduction

In today's world, industry and scholars are emphasizing sustainability, and the textile industry is striving to adopt this approach. Dyeing is an essential process in the textile industry that utilizes numerous synthetic dyes. However, chemicals and synthetic dyes, which make up the majority of those used in the textile industry, result in the emission of vast quantities of highly polluted wastewater. Therefore, there is a current research focus on developing eco-friendly substitutes for synthetic dyes. Various reports have been published on the coloration and functionalization of different textile fibers using natural dyes. However, most studies have been focused on natural fibers such as wool, silk, and cotton [1–3], while the number of studies on natural dyeing of synthetic fibers is comparably low. Recently, several attempts have been made to apply natural dyes on synthetic fibers such as polyester [4–6].

Nylon fibers have been a game-changer in the textile and other industries since their invention in the 1930s. These synthetic fibers are known for their durability, strength, and versatility, making them ideal for a wide range of applications. In the textile industry, nylon fibers are used to create fabrics that are lightweight, breathable, and resistant to wear and tear. They are also used in the production of carpets, upholstery, and other household items. Nylon fibers have also found their way into other industries such as automotive manufacturing, where they are used to make seat belts and airbags. Nylon fibers are commonly dyed using synthetic dyes due to their ability to produce bright and vibrant colors. However, the use of synthetic dyes can have negative impacts on the environment and human health. Natural dyes, on the other hand, are derived from plant or animal sources and are considered to be more sustainable and eco-friendly. They also have the potential to produce unique and subtle shades that cannot be achieved with synthetic dyes. The use of natural dyes for dyeing of nylon fibers is important in promoting sustainable textile practices and reducing the environmental impact of textile production [7,8]. In this regard, there are some publications on utilizing natural dyes for polyamides such as madder [9,10], berberine (*Berberis vulgaris*) [11], weld and pomegranate peel [12], Henna leaves [13], onion outer shell [14], curcumin and saffron [15], mangrove bark [16], leaves of the almond tree [17], and betel nut (*Areca catechu*) [18]. However, the common point among all these natural dyes is that they were utilized with various metal mordants resulting in wastewater pollution. Nevertheless, Esfand (*P. harmala*) was employed as a natural dye in nylon dyeing and numerous bio-mordants were suggested as alternatives to the metal mordants [19]. Furthermore, in our previous study, we used the dragon's blood resin together with different bio-mordants to dye nylon 6 fabric. Our previous findings revealed that artemisia displayed the best efficiency of bio-mordanting in nylon 6 dyeing with dragon's blood resin [20]. Therefore, to mitigate the hazardous consequences of the dyeing processes, researchers are now replacing metal mordants with bio-mordants.

The introduction of new natural sources for dyes has the potential to expand the range of colors available and introduce new specific features. Rhubarb (*Rheum ribes* L.) is a member of the polygonaceae family, native to Asia, particularly Iran, Pakistan, India, and China. Rhubarb contains different tannoids such as Catechin, Glucogalline, Tetrarine, and Gallic acid, among others. Previous studies have exclusively used rhubarb (i.e., root part) as a natural colorant for natural fibers such as wool [21–23] and cotton [24]. However, there has been no research on applying rhubarb flowers on synthetic fibers. Rhubarb flowers are produced in large clusters at the end of the main stem and have a red hue due to various anthraquinone derivatives present in them. Among the various anthraquinone derivatives identified in the rhubarb flower, chrysophanol and emodin are the most abundant coloring compounds (Figure 1) [25–27]. These derivatives have great potential for textile dyeing. This paper explores using the flower component of rhubarb to achieve a deep brown hue on nylon 6 fabric. In addition, the importance of new bio-mordants to achieve a completely eco-friendly process for dyeing synthetic fibers is investigated. The objective of this study is to introduce a fully eco-friendly dyeing process for nylon 6 fabric using plant dye and mordants, exhibiting similar hues and comparable fastness properties with the metal mordants.

Figure 1. *Cont.*

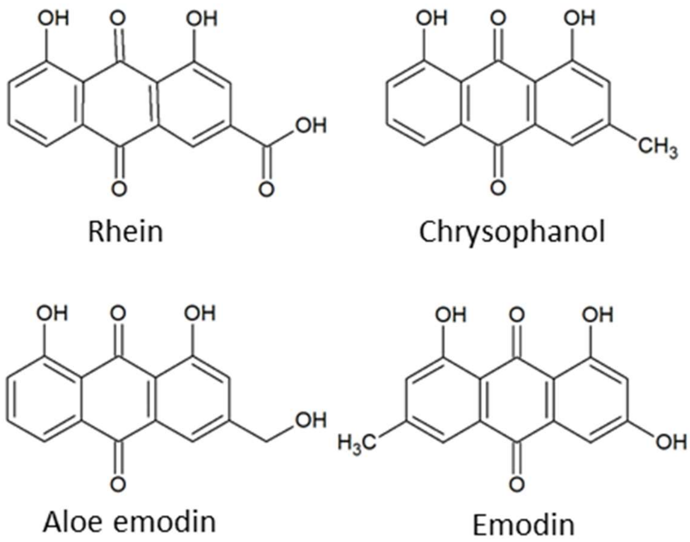


Figure 1. Rhubarb flower and its important coloring compounds.

2. Experimental Section

2.1. Materials

Naz Harir Co., Mashhad, Iran, provided a nylon 6 warp knitted raw fabric (60 g/m^2). Dried *Rheum ribes* L. flowers, collected in spring 2022, were purchased from a local store in Tehran, Iran. Four different bio-mordants which contain high amounts of polyphenols such as tannin, ellagic acid, and chlorogenic acid were utilized. Among them, pistachio hull, walnut husk, and pinecone (collected in autumn 2022) were procured from a local store in Tehran, Iran and green coffee was an import from Vietnam. All plant materials were stored in their original form in a cool and dry place, away from sunlight, and were used for dyeing in less than 6 months from the date of collecting. Furthermore, common metal salts including iron(II) sulphate ($FeSO_4$), aluminium potassium sulphate ($KAl(SO_4)_2$), zinc sulfate ($ZnSO_4$), copper sulphate ($CuSO_4$) and sodium sulphate (Na_2SO_4) were supplied by Merck (Germany). To adjust the pH of the dyebath, acetic acid and sodium hydroxide were purchased from Merck (Darmstadt, Germany). Nonionic detergent (Welly wash) and dispersing agent (Heptamol SHT) were provided by Kohan Taj Kimia, Iran.

2.2. Dye and Bio-Mordant Extraction

Initially, the rhubarb flowers were dried and then pulverized into a fine powder using a mechanical grinder. The powder was then sifted through a 40-mesh nylon screen. Next, 10 g of the rhubarb flower powder was extracted by using 200 mL of distilled water in a Soxhlet extractor for an hour. The resulting solution was filtered through a Whatman filter No. 42, and the filtrate was used as the stock solution. The same process was used to extract the bio-mordants.

2.3. Pre-Mordanting

Initially, the nylon 6 fabrics underwent scouring at 60 °C that employed distilled water and a nonionic detergent (1 g/L) with a material to liquor ratio of 40:1 for 30 min. Subsequently, the fabrics were rinsed with tap water and left to air dry. Bio-mordant baths were prepared by adding varying amounts of mordant extracts (10, 20, and 50%owf) in water at the material to liquor ratio (M:L) of 1:40. The wetted fabrics were then immersed in the mordanting solutions and the temperature was gradually raised to the boiling point at a rate of 2 °C/min. Mordanting was continued at the boil for an hour before rinsing the mordanted fabrics with tap water and drying them at room temperature.

To compare the effectiveness of bio-mordants with that of metal mordants, several common metal salts were employed. Metal mordant solutions using the aforementioned metal salts were prepared by adding 1 %owf in water at a liquor ratio of 1:30, and metal mordanting was performed similarly to the bio-mordanting procedure.

2.4. Dyeing Process

Mordanted fabrics were immersed in the dyeing solution and the dyeing was performed using exhaustion method under different conditions. In this research, dyeing variables including temperature, time, pH, M:L, dye concentration, salt addition, and dispersing agent were optimized through experimental tests. Therefore, the nylon 6 fabric was dyed at 40 °C, 60 °C, 80 °C, and 100 °C to evaluate the optimum dyeing temperature. Dyeing time was optimized at intervals of 15, 30, 45, 60, 75, and 90 min. Dye concentration was varying at different percentages including 10, 20, 30, 40, 50, and 100 %owf (on the weight of fabric). The pH of dyebath was varying at 3, 5, 7, 9, and 11, while different levels of M:L, i.e., 1:10, 1:20, 1:30, 1:40, and 1:50 were applied. In addition, different concentrations of dispersing agent were used (0, 0.5, and 1 g/L) to determine their effect on dye exhaustion. Different amounts of sodium sulfate (1, and 2.5 g/L) were applied to determine the effect of salt addition on the dyeing levelness. The temperature of the dyebath was raised from 25 °C to the desired temperature during with the rate of 2 °C/min. In addition, to adjust the pH of the dye bath, a few drops of acetic acid (1% *v*/*v*) or sodium carbonate (1% *w*/*v*) were used. A schematic presentation of the dyeing procedure is shown in Figure 2 [20].

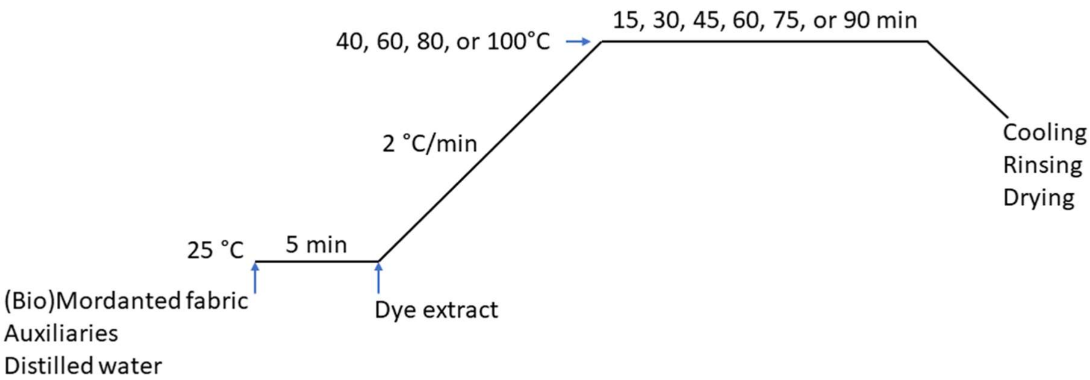


Figure 2. Schematic presentation of the dyeing procedure.

2.5. Color Measurement

The reflectance spectra of dyed samples were measured using a Color-Eye 7000 A spectrophotometer (X-rite, Grand Rapids, MI, USA) in the visible light range from 400 to 750 nm with 10 nm steps. Then, the color strength (K/S value) of the samples was calculated using the Kubelka–Munk equation according to Equation (1),

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

where R is the reflectance value at each wavelength, K is the absorbance coefficient, and S is the scattering coefficient. In addition, the CIEL*a*b* coordinates of the samples under CIE standard illuminant D65 and CIE 1964 standard observer were calculated.

2.6. Color Fastness

The wash fastness of the dyed samples was measured according to the ISO 105-C06 (A1S):2010 method [28] using a Launderometer. The light fastness was assessed according to the ISO 105-B02:2013 method [29].

3. Results and Discussion

This section first discusses the optimization of the variables of dyeing of nylon 6 fabric using Rhubarb flower without applying any mordant. Then, the efficacy of the bio-mordants as eco-friendly alternatives for metal mordants is described. Lastly, the remarkable color fastness of the samples dyed in the presence of bio-mordants is presented.

3.1. Dyeing Parameters Optimization

Figure 3 shows the effect of dye bath pH in the visible range of wavelengths. The effect of dye bath pH was investigated to achieve maximum color strength of the dyed samples. The color strength decreased as the pH increased from 3 up to 11. In fact, maximum color strength was achieved when dyeing was performed at pH 3. It has been shown that the point of zero charge for nylon 6 fiber is around pH 4–5 [30]. Above this pH, the surface charge of the fibers is negative, which repels the anionic dye molecules, while at pH values less than 5, the -NH and NH_2 groups of polyamide chain gain positive charge, which attracts the anionic dye molecules causing an increase in dye exhaustion.

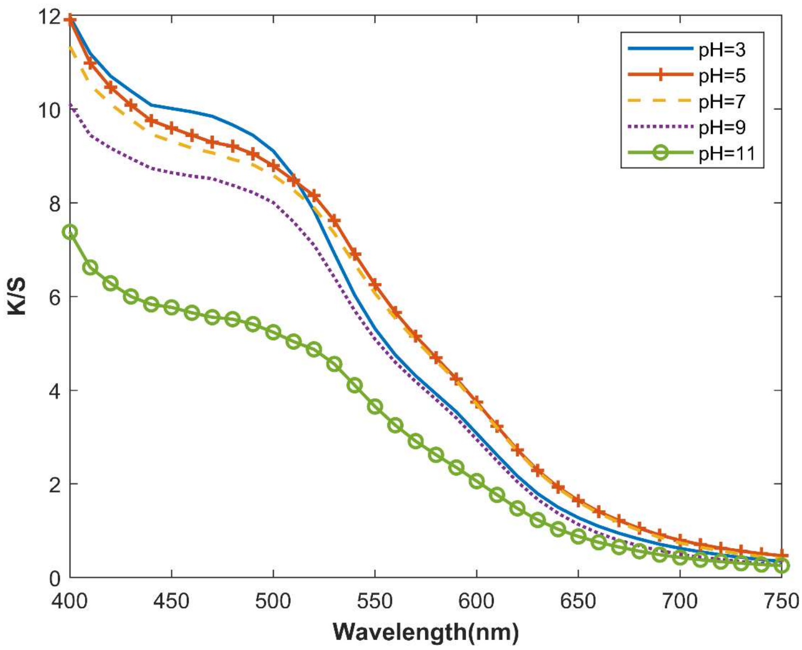


Figure 3. The effect of dye bath pH on color strength (dyeing with 50%owf dye at M:L = 1:40, and 100 °C for 1 h, without salt and dispersing agent).

The influence of dyeing temperature on color strength (K/S) was investigated for 60 min at temperatures ranging from 40 °C to 100 °C, and the results are shown in Figure 4. The color strength clearly increased as the dyeing temperature increased, and thus the maximum color strength was obtained at 100 °C. As the temperature rises, the polymeric structure of nylon 6 opens up [24] and more dye molecules becomes separated from the aggregates [31], making dye adsorption easier and yielding a greater K/S value.

According to Figure 5, the results of changing dyeing time show that the nylon 6 fabric's color strength increased until the dye exhaustion reached equilibrium at 75 min. It is well known that extending the dyeing time may increase the opportunity for dye molecules to be placed in the dyeing sites of polyamide fibers [32]. Therefore, the optimal time for dyeing nylon 6 fabrics was discovered to be 75 min since after increasing the dyeing time to 90 min, the K/S value decreased. Decreasing K/S values over a longer time may be attributed to the shift in the equilibrium leading the dye molecules to migrate from the fabric into the dye bath [33].

As for dye concentration, according to Figure 6, as the dye concentration increased, the K/S values gradually increased until at 100 %owf an extreme shift occurred, and the maximum color strength was yielded. This may reveal that the saturation point of nylon 6 has not been reached even when using 100 %owf. In fact, the defect of natural dyes is that the gaining of fiber saturation occurs at high dye concentrations [10].

Figure 7 shows the effect of the M:L ratio on the K/S values for the wavelength of 400 nm to 750 nm with 10 nm intervals. If we consider K/S curves as a metric for determining the optimal parameters, increase in M:L causes an increase in K/S until the M:L = 1:30 has the highest K/S curve. However, a further increase in M:L achieves lower K/S due to the dilution of the dye solution phase.

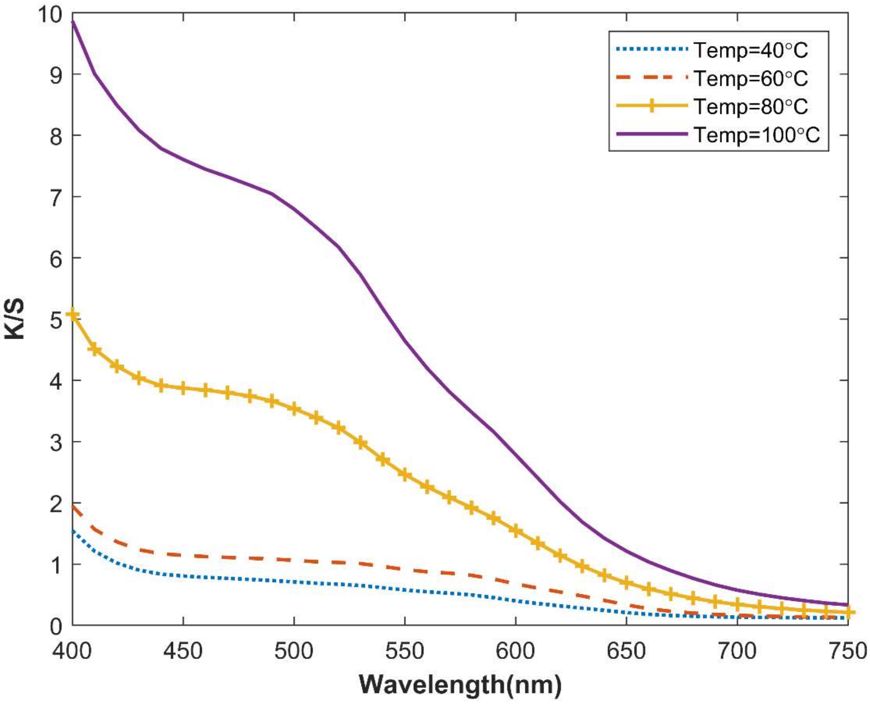


Figure 4. The effect of dyeing temperature on the color strength of dyed samples (dyeing with 50%owf dye at M:L = 1:40 and pH = 3 for 1 h without salt and dispersing agent).

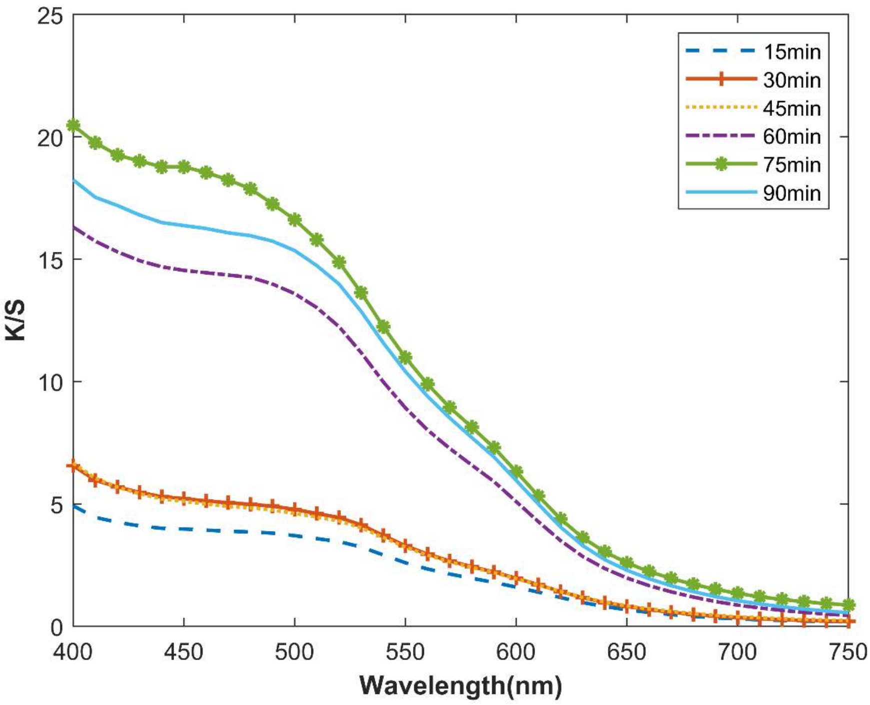


Figure 5. The effect of dyeing time on the color strength of dyed samples (dyeing using 50%owf dye at M:L = 1:40, 100 °C, and pH = 3, without salt and dispersing agent).

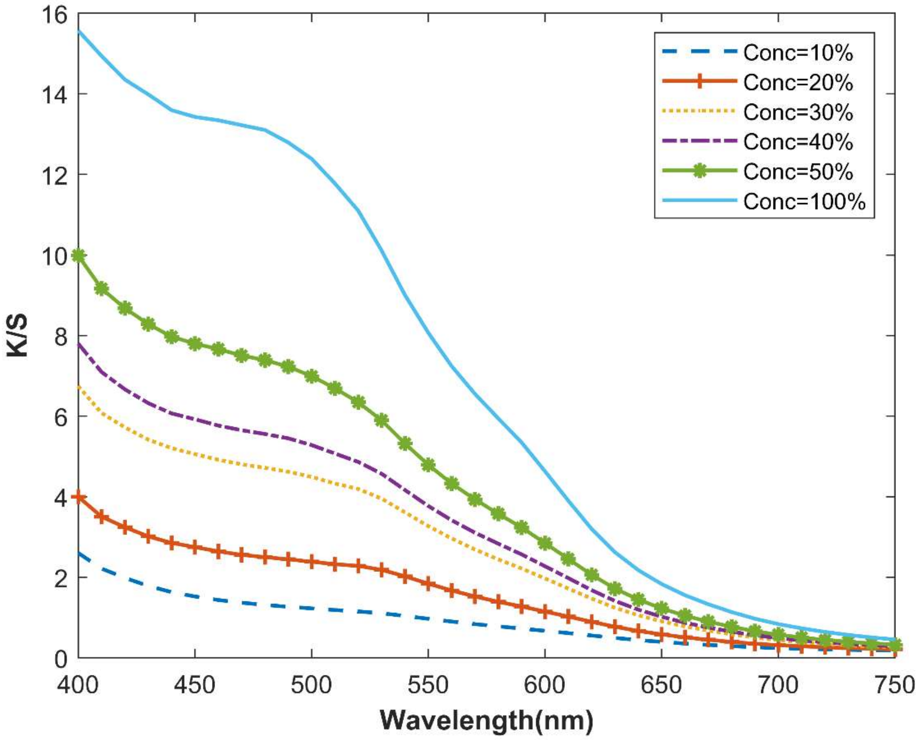


Figure 6. The effect of dye concentration on color strength (dyeing at M:L = 1:40, 100 °C, and pH = 3 for 75 min, without salt and dispersing agent).

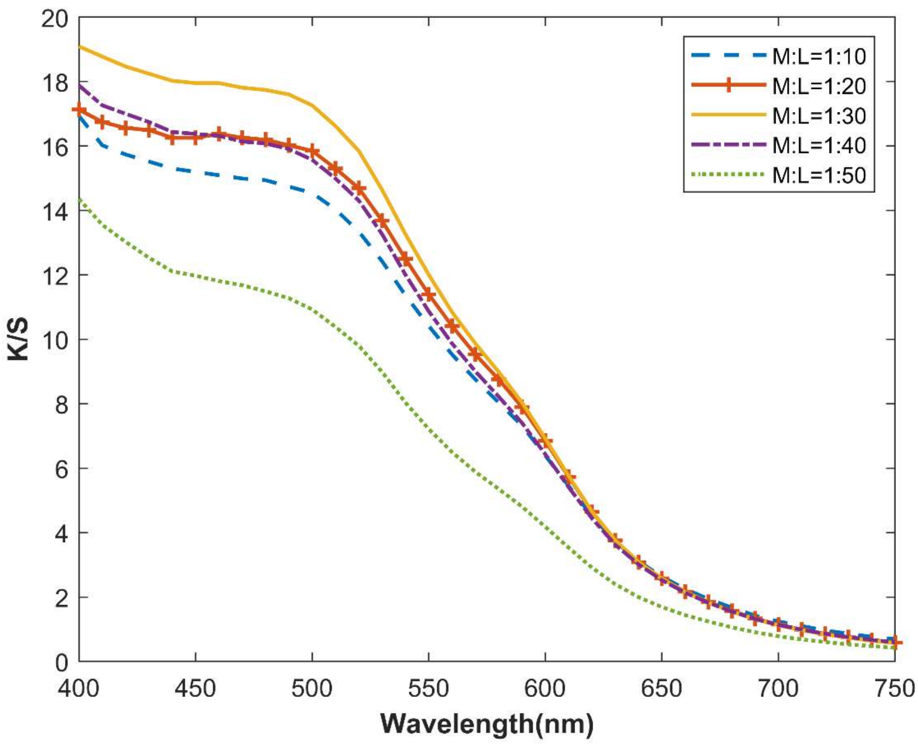


Figure 7. The effect of M:L ratio on the color strength of dyed samples (dyeing using 100%owf dye at 100 °C, and pH = 3 for 75 min, without salt and dispersing agent).

It is well known that salt addition in dyeing is necessary in the case of using high-affinity dyes as it retards the dye migration, thus obtaining better level dyeing. Sodium sulfate is the common leveling agent in dyeing synthetic fibers, and thus we investigated the effect of salt in the dyeing procedure of nylon 6 with a natural dye. According to Figure 8, it is clearly indicated that in the absence of salt, the color strength is higher than it is when using a 1 and 2.5 g/L salt, in which when the salt concentration increases, the color strength decreases slightly. Sodium sulfate releases Na^+ and $SO_4{}^{2-}$ as free ions in the dyebath. The interaction of sulfate anion with cationic sites on the nylon 6 fiber may cause their neutralization and consequently reduce dye ionic attraction between the fibers and anionic dye molecules. In addition, charge neutralization of the dye anions by the electrolyte cations (Na^+) affects the dye substantivity and inhibits the interaction with the nylon 6 fiber cations. Increase in salt concentration therefore inhibits dye exhaustion and consequently decreases the color strength of the dyed nylon 6 fabric [34,35].

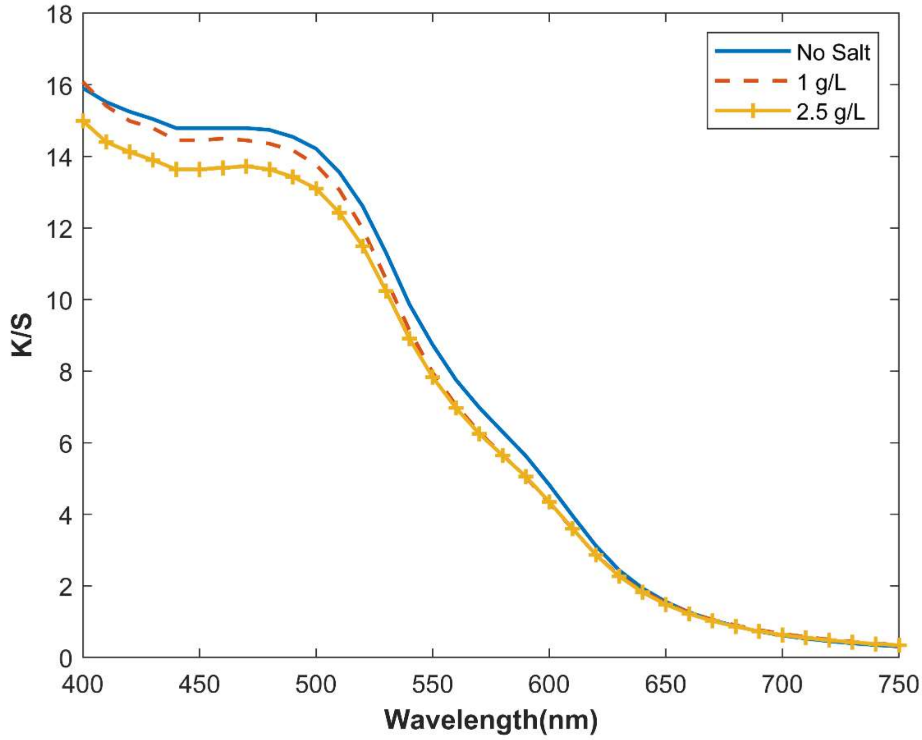


Figure 8. The effect of salt addition on color strength of dyed samples (dyeing using 100%owf dye at M:L = 1:30, 100 °C, and pH = 3 for 75 min, without dispersing agent).

Applying a dispersing agent in natural dyeing is important as the dye molecules may be aggregated. Therefore, the effect of dispersing agent addition on the color strength of dyed samples is shown in Figure 9. Expectedly, using a 0.5 g/L dispersing agent increased the color strength, and a further increase had a negative effect on the dyeing performance, probably due to the increase in the water solubility of dyes by formation of micelles with a hydrophilic outer shell and keeping the dye molecules in the solution led to these molecules avoiding the penetration into nylon 6 as a hydrophobic fiber [36]. Therefore, using a 0.5 g/L of dispersing agent may result in slight improvements in the dyeing yield.

3.2. Statistical Analysis

To analyze whether dyeing parameters have a significant effect on color strength, one sample *t*-test analysis (α = 0.05) was employed based on the maximum values of color strength (λ_{max}). The t-statistic, degree of freedom, and *p*-value of dyeing parameters are listed in Table 1. It is clear that except for dyeing temperature, other parameters are significant in the case of color strength. Therefore, to achieve the desired shade, controlling dye bath pH, concentration, M:L, and dyeing time should be considered carefully. Meanwhile, dyeing temperature is the least significant parameter in dyeing nylon 6 with Rhubarb dye.

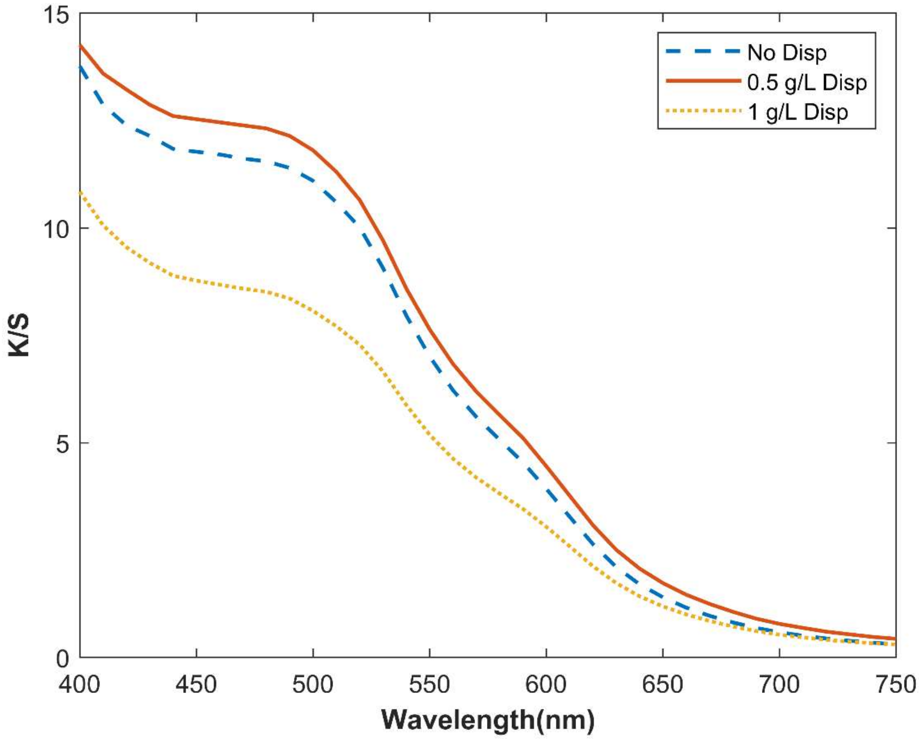


Figure 9. The effect of dispersing agent on color strength of dyed samples (dyeing using 100%owf dye at M:L = 1:30, 100 °C, and pH = 3 for 75 min, without salt).

Table 1. One-sample *t*-test of dyeing parameters.

Dyeing Parameter	T Statistic	Degree of Freedom	*p*-Value (Significance)
Dye bath pH	11.6270	2	3.1×10^{-4}
Dyeing Temperature	2.2589	3	0.1090
Dye Concentration	3.8582	5	0.0119
M:L ratio	19.1920	4	4.3×10^{-5}
Dyeing Time	4.1610	5	0.0088

3.3. Effect of Mordanting on Color Strength

3.3.1. Effect of Metal Mordants

Most natural dyes have a poor affinity for synthetic fibers. Therefore, applying mordants is necessary to increase the dye affinity. Figure 10 shows the effect of using different metal mordants on color strength. It is clear that Iron enhances the color strength while Copper, Zinc, and Aluminium decrease the color strength. The formation of a complex between the metal ions and dye molecules affects the L*, a*, and b* color coordinates of the dyed samples. Previous studies have shown that some mordants such as aluminium can lead to a decrease in color strength and cause an increase in the lightness and increase the a* and b* values. As can be seen in Table 2, the same results have been obtained when applying Cu, Zn, and Al mordants on nylon 6. This means a hypochromic shift caused by the formation of the complex between the dye molecules and Cu, Zn, and Al ions. Similar results have been reported elsewhere [37–39].

Finally, Iron achieves the highest color strength among the other metals used. It can be attributed to the chelation of the dye molecules with iron to generate a complex with hyperchromic shift in the spectrum as schematically illustrated in Scheme 1 [40,41]. The -COOH group of Rhein can be ionized and form an ionic bond with the positively charged amine end groups of nylon 6 fibers under acidic condition.

Table 2. Color difference in mordanted sample compared to unmordanted sample (dyeing was performed using 100%owf dye at M:L = 1:30, 100 °C, and pH = 3 for 75 min, without salt and dispersing agent).

Mordants	L*	a*	b*	K/S (λ_{max})	ΔE
Unmordanted	29.2	16.17	14.32	15.7	Control sample
Zn	29.75	17.35	15.37	15.3	1.7
Cu	29.45	17.38	16.18	16.87	2.2
Fe	28.03	15.15	13.92	16.87	1.6
Al	31.04	18.07	17.1	15.3	3.8
Pistachio hull	29.67	17.52	15.66	16.07	1.9
Walnut husk	26.64	15.1	13.52	18.77	2.8
Green coffee	31.47	16.89	15.76	13.94	2.7
Pinecone	27.19	16.86	14.55	18.62	2.1

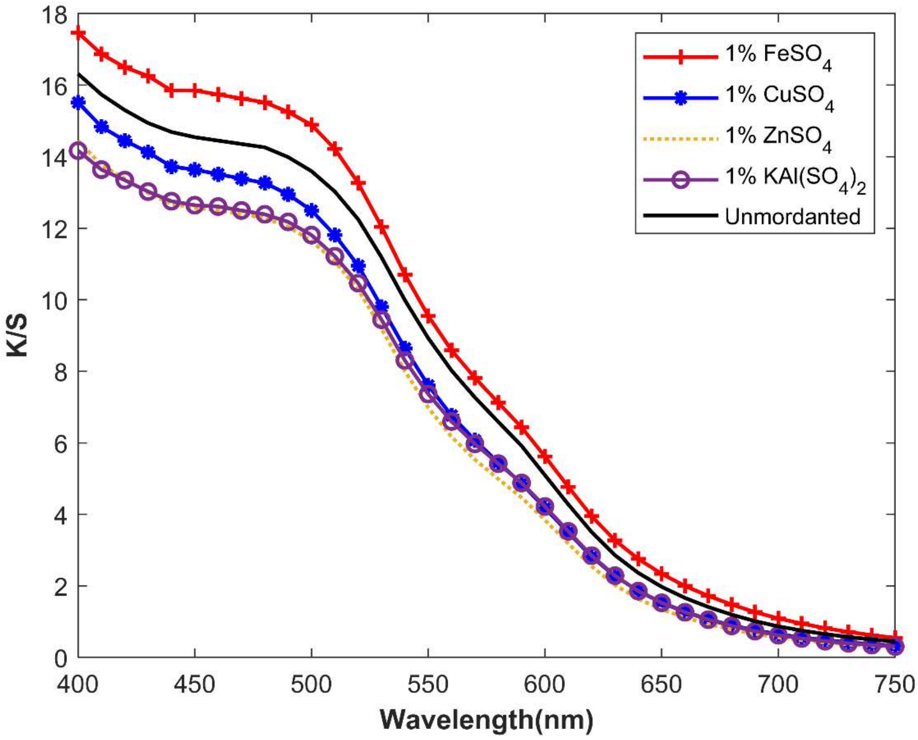


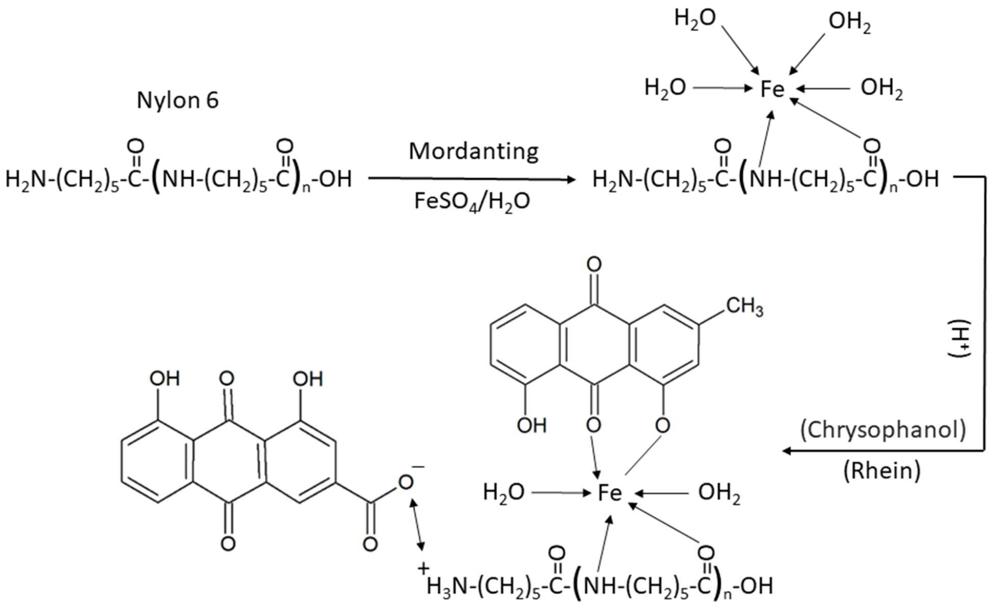
Figure 10. Color strength of dyed samples with pre-mordanting method using different metal mordants (dyeing was performed using 100%owf dye at M:L = 1:30, 100 °C, and pH = 3 for 75 min, without salt and dispersing agent).

3.3.2. Effect of Bio-Mordants

To investigate the effect of using different concentrations of bio-mordants on the color strength, the K/S plots of samples dyed after being mordanted with different bio-mordants including walnut husk, pistachio hull, pinecone, and green coffee are shown in Figure 11. It can be seen that the λ_{max} of all mordanted samples as well as unmordanted sample occurs at 400 nm and the shapes of the K/S curves are similar.

Except for green coffee, all used natural mordants enhanced the color strength of the dyed samples. However, pistachio hull has the least effect on enhancing color strength among the other used mordants. Walnut husk and pinecone reveal considerable performance in increasing color strength. In fact, all concentrations of walnut husk increased the color strength, of which 10%owf had the highest efficiency.

All the mentioned bio-mordants in this research contain several hydroxyl functional groups. For example, the green walnut husk contains two hydrolyzable tannins, i.e., ellagic acid and tannic acid. These tannins contain a lot of -OH groups that have the potential for hydrogen bonding with the dye molecules as well as the nylon 6 fiber [42]. Therefore, the -OH groups of these bio-mordants link with the amide group of nylon 6 and also form hydrogen bonding with the -OH groups of Emodin and Chrysophanol of Rhubarb dye (see Scheme 2). The mentioned mechanism leads to increasing the color strength of bio-mordanted samples compared with the unmordanted sample [20,43].



Scheme 1. Schematic presentation of the interactions between metal mordant, nylon 6 fiber, and dye molecules.

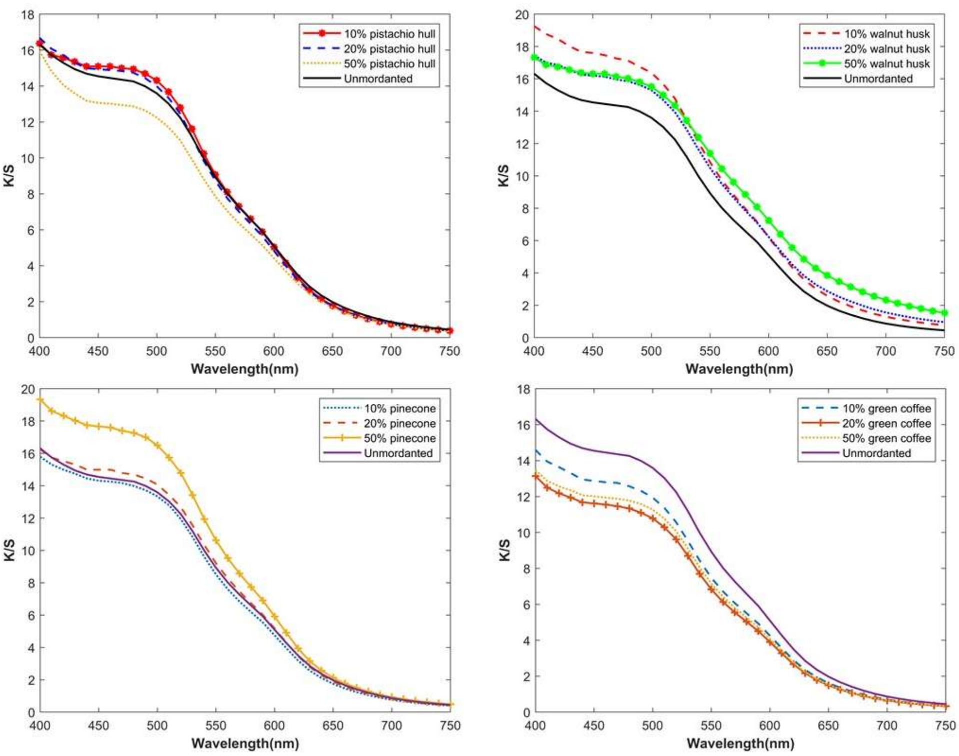
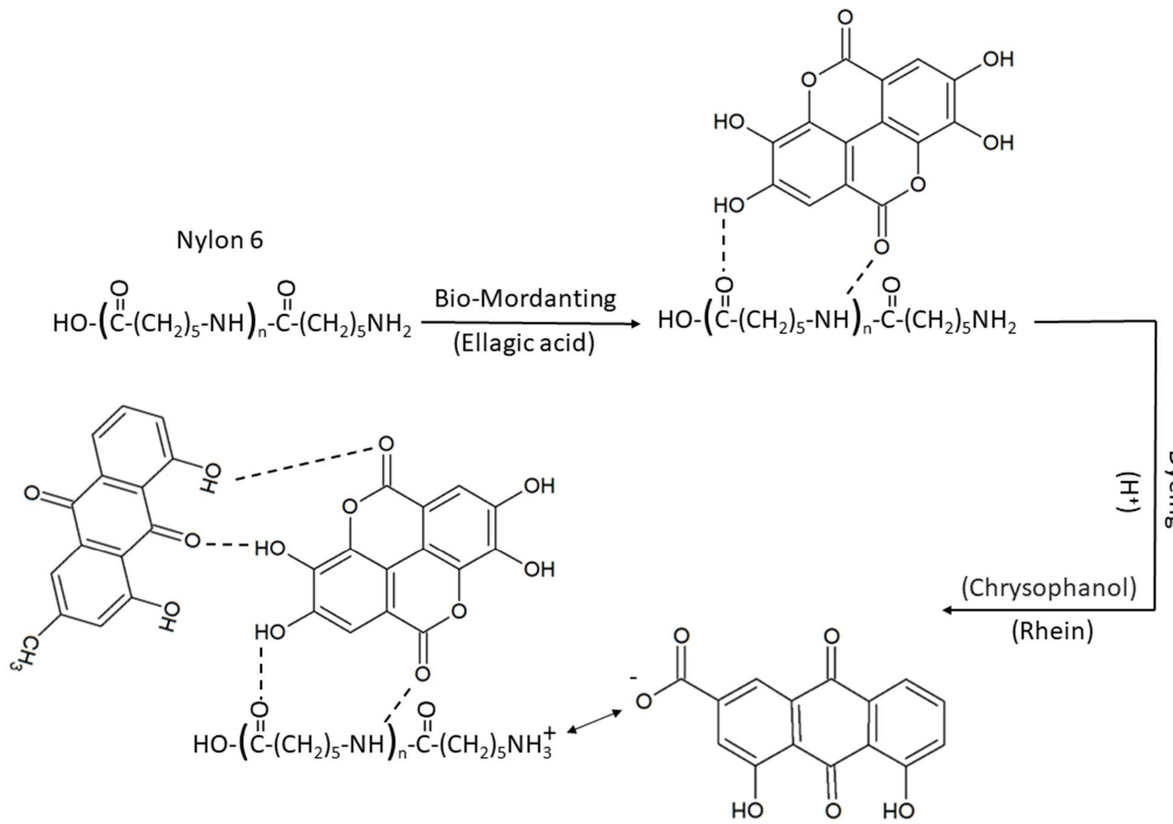


Figure 11. The effect of various concentrations of different bio-mordants on color strength of dyed samples (dyeing was performed using 100%owf dye at M:L = 1:30, 100 °C, and pH = 3 for 75 min, without salt and dispersing agent).

3.4. Color Coordinates of Mordanted Samples

Figure 12 indicates the color chromaticity of mordanted samples to investigate whether mordanting process changes the hue of dyeing. Except for Aluminum, all mordants including metal and natural types are close to the unmordanted sample in the chromaticity diagram indicating mordanting did not change the hue of rhubarb applied on nylon 6. Furthermore, the color coordinates of the pistachio and Cu are so close together, and thus the pistachio could be an excellent substitution for copper metal. It is clear that walnut could be a good alternative for iron metal as the same color is generated. To clarify this result, Table 2 shows the value of the CIELAB color difference between mordanted and unmordanted samples. It could be seen that the color differences are fair in the field of natural dyeing as the maximum color difference is 3.8 in the case of aluminum. Meanwhile, other color differences are close to 2, which proves the pre-mordanting process did not change the color of rhubarb on nylon 6 fabric significantly.



Scheme 2. Schematic presentation of the interactions between bio-mordant, nylon 6 fibers and dye molecules.

3.5. Evaluation of Color Fastness

There are multiple factors that affect the fastness properties such as the chemical structure of dye and mordant, the physical property of fiber, the interaction between dye–mordant–fiber, and the mordanting method that should be considered during the dyeing procedure. Therefore, selecting appropriate mordants based on the dye structure has high importance to achieve high efficiency in color strength and fastness. Therefore, we used proper bio-mordants as well as metal mordants to compare the color fastness of different types of mordants.

We investigated the effect of four common metallic mordants on fastness to washing and light using the bottom mordanting process. The results are shown in Table 3. The washing fastness of unmordanted nylon 6 fabric is evaluated as fair (i.e., 3), which reveals that the mordanting procedure is a necessary step for this natural dye. It is clear that all of the metal and natural mordants alter the wash fastness score from fair to excellent, which is due to the strong bonding between dye, metal or bio-mordant, and fiber as indicated schematically in Schemes 1 and 2. Therefore, it is concluded that the used bio-mordants could be excellent substitutions for metal mordants since the same color fastness is provided and, in addition, they do not lead to environmental hazards.

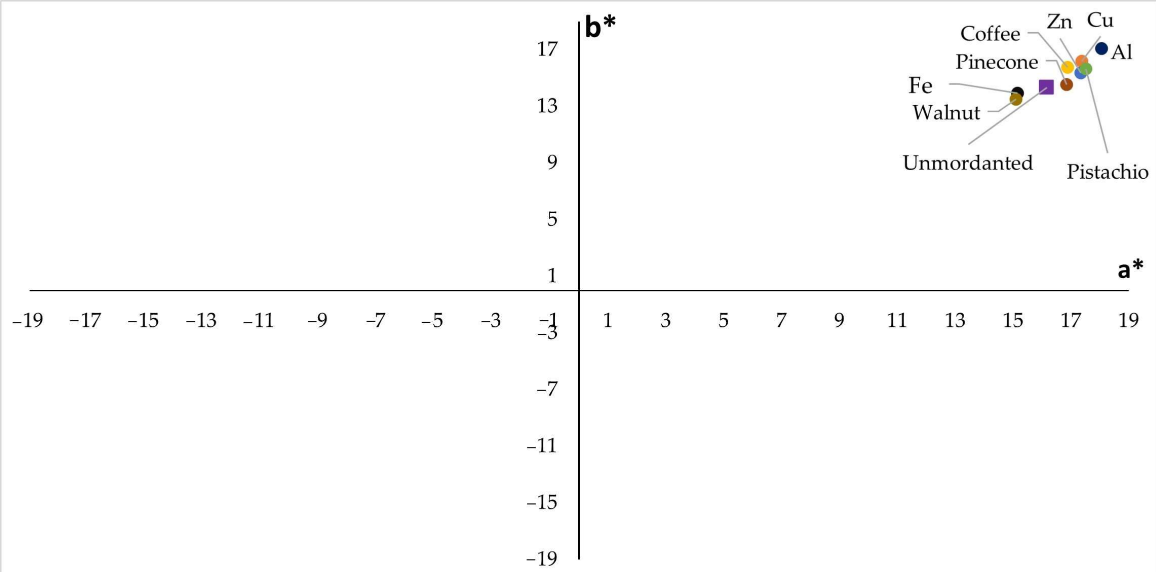


Figure 12. Chromaticity coordinates of different bio-mordants used.

Table 3. Colorfastness of nylon 6 fabric dyed with and without different mordants.

Mordant Type	Wash Fastness			Light Fastness
	Color Change	Stain on Nylon 6	Stain on Cotton	
Unmordanted	3	4	4	2
Zn	5	5	5	8
Cu	5	5	5	8
Fe	5	5	5	8
Al	5	5	5	8
Pistachio hull	5	5	5	8
Walnut husk	5	5	5	8
Green coffee	5	5	5	8
Pinecone	5	5	5	8

Like washing fastness, all mordants including metal and natural mordants enhanced the light fastness in which an excellent rating (i.e., 8 score) was achieved. Regarding light fastness, there was an amazing result in which light exposure increased the color strength of the samples compared to the unexposed samples.

4. Conclusions

In this paper, the feasibility of dyeing the nylon 6 fabric with the *Rhubarb* flower as a natural dye was investigated. The optimal conditions for dyeing nylon 6 with *Rhubarb* were found to be the 100 %owf dye at boiling temperature in an acidic environment for 75 min. Various metallic and bio-mordants were employed to improve the dyeability and fastness properties. The results showed that almost all mordants (except Al, Zn, and green coffee) increased the color strength of the dyed samples. However, the 10%owf walnut husk has the best efficiency in case of increasing the color strength. In addition, the color coordinates were not affected significantly by mordanting, especially in the case of bio-mordanting. Mordanting enhanced the fastness against washing and light significantly. The results of this study confirm that the mentioned bio-mordants can be used as excellent substitutes of metal mordants and natural dyeing can be performed in a more environmentally friendly way to avoid wastewater pollution and hazards.

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