

New Erbium(III) Complexes as Mordants for Natural Dyeing of Silk

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(Received 25 May 2020, Accepted 27 June 2020)

This research aims to develop new mordants and a wide range of colors for natural dyeing of silk. For this purpose, two new erbium(III) complexes, $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (AO = acridine orange, AMH = azomethine-H, and OAc = acetate anion), were synthesized, characterized, and used as the mordant for the natural dyeing of silk yarns with green walnut husk extract. The mordanting method and the effective dyeing parameters, including the quantity of the dye, pH, and temperature of the dyeing bath, mordant concentration, and dyeing time, were optimized. The colorimetric properties (L^* , a^* , b^* and K/S) and color fastness characteristics (light and washing) of the dyed samples were also investigated. The mordanted silk yarns with the synthesized erbium(III) complexes were compared to the unmordanted dyed samples, as well as the mordanted dyed samples only with the pure salts, including starting erbium salt (erbium(III) acetate), stannous chloride, and aluminum potassium sulfate. The results indicated that the dyeing of silk in the presence of $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ as the mordant provides the most eminent color contrast, whereas the treated silk with $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ exhibits the most color strength value (K/S). Furthermore, all mordanted and unmordanted samples exhibited proper color fastness characteristics.

Keywords: Natural dyeing, Erbium(III) complexes, Silk, Color fastness, Mordant

INTRODUCTION

Humans have applied dyes derived from plants, animals, insects, and minerals to dye clothes or fabrics and to prepare cosmetic products from prehistoric times. However, over the last 150 years, synthetic dyes have mostly replaced natural colorants in the textile industry due to the redundancy of farming and enhanced fastness properties, wide variety in color depth and shade, bright colors, effortless handling, extended repeatability, and various applications [1-4]. Nowadays, natural dyes are only utilized in handicrafts and folk arts. However, the production and application of synthetic dyes have been limited due to economic and environmental reasons. For example, the global rise in oil prices is one of the economic reasons, because crude oil is required to produce synthetic dyes and

to supply the energy in dyeing and finishing processes, therefore affecting production costs [5]. Furthermore, owing to the toxicity nature, mutagenicity, and carcinogenicity of some synthetic dyes, in many countries, new government regulations have been approved to prevent the release of these compounds into the wastewater system. This limitation can cause additional expenses due the necessity of adequate wastewater treatment in the textile industry [6]. The ethical and environmental reasons improve the social awareness of the environment and health concerns, developing public interest in sustainable products. The use of renewable raw materials helps to reserve fossil resources and to reduce environmental impacts and also eliminates the wastewater disposal problems [5].

Nowadays, in addition to the extraction of dyestuff from plants to preserve the natural resources and to reduce the wastes during the manufacturing process, the isolation of coloring compounds from the residues and by products of

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timber products as well as food industries has remained of interest to both researchers and manufacturers [7]. One of the solid waste byproducts in agriculture is the green husk of walnuts. The husk contains a natural brown dye called juglone (5-hydroxy-1,4-naphthalenedione). Our country, Iran, is the third largest world producer of walnuts (450,000 tons of walnuts per year) and contains a vast number of natural resources of juglone. Recently, the antimicrobial, antioxidant, and dyeing properties of the walnut husk extract have been investigated in different applications [8-10]. Since some wastes and byproducts can be used as natural dyeing materials, this field is particularly economical, environmentally friendly, safe, and dependable.

Furthermore, the use of mordants in natural dyeing is common to improve the fastness properties of the dyed textiles and to provide various shades and colors using a natural colorant. A mordant is usually a metal salt, which forms coordinate covalent bonds with the functional groups of the dye molecules and textile fibers. These coordination bonds increase the color fastness of the dyed textiles and extend the color range. The most widely used mordants are aluminum potassium sulfate, potassium dichromate, stannous chloride, ferrous sulfate, and copper sulfate [11]. Numerous studies were conducted to investigate natural dyeing using new metal salts as mordants [12-14]. The rare-earth metals (*viz.*, Sc, Y and the lanthanides or lanthanoides) are eco-friendly mordants, which have a higher coordination number than *d*-block transition metals, and are also used to prevent waste pollution and to extend the design flexibility in the dyeing process [15,16].

To the best of our knowledge, there is no research on the natural dyeing of fibers using rare-metal complexes as mordants in literature. In this study, two new erbium(III) complexes, $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$, (AO = acridine orange, AMH = azomethine-H, and OAc = acetate anion) were synthesized and characterized. The complexes were utilized as the mordant in the dyeing of silk yarns with green walnut husk extract for the first time. Application of the erbium(III) complexes in the natural dyeing of silk yarns is impressive because rare-earth metals as coordination centers possess a higher coordination number and a greater size than *d*-block transition metals. Therefore, erbium(III) coordinates to more functional groups within the ligands, dye molecules, and

yarn, increasing the color yield of the dyed samples. Also, coordination of the different ligands to the metal center produces a wide range of colors due to the various electronic transitions, which can overlap with the electronic transitions of dye, resulting in the extension of the shade range in the dyeing of natural fibers. The dyeing process was also investigated in different conditions, and the effective dyeing parameters were carefully optimized.

EXPERIMENTAL

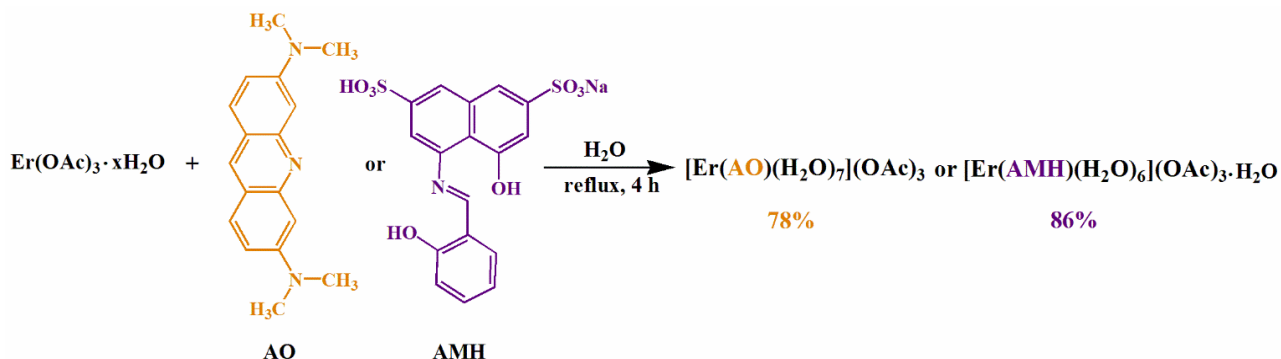
Chemicals and Materials

The commercially bleached silk yarns were obtained from the Grand Bazaar of Isfahan (Iran). Powder of green walnut husk was obtained from the Isfahan Medicinal Plants Market (Iran). Acridine orange hydrochloride hydrate (3,6-bis(dimethylamino)acridine hydrochloride), azomethine-H monosodium salt hydrate (4-hydroxy-5-(2-hydroxybenzylideneamino)-naphthalene-2,7-disulfonic acid monosodium salt hydrate), glacial acetic acid, sodium carbonate, and stannous chloride were purchased from Merck Company. Erbium(III) acetate hydrate and aluminum potassium sulfate dodecahydrate (potassium alum) were purchased from Sigma-Aldrich Company.

General Procedure for the Synthesis of Erbium(III) Complexes

A solution of acridine orange (AO) (0.117 g, 0.390 mmol) or azomethine-H monosodium salt hydrate (NaAMH) (0.173 g, 0.390 mmol) in 30 ml of distilled water was added to a solution of erbium(III) acetate (0.134 g, 0.390 mmol) in 12 ml of distilled water into a round-bottom flask equipped with a magnetic stirring bar. The resulting solution was refluxed for 4 h, filtered and then evaporated to dryness under high vacuum to give the precipitate of the target complex, $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ or $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3 \cdot \text{H}_2\text{O}$ (yield: 78% (0.221 g, 0.30 mmol) and 86% (0.311 g, 0.34 mmol), respectively) (Scheme 1). The synthesized erbium(III) complexes were characterized by elemental analysis and spectroscopic techniques.

$[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$, IR data (KBr pellet): ν (strong bands) = 1349 (C-N); 1460 and 1590 (C=C); and 1638 (C=N) cm^{-1} . Found: C, 37.24; H, 5.68; N, 5.64%;



Scheme 1. Synthesis route to erbium(III) complexes

molecular formula $\text{C}_{23}\text{H}_{42}\text{O}_{13}\text{N}_3\text{Er}$ (MW = 735.94 g mol⁻¹) requires C, 37.53; H, 5.76; N, 5.71%. UV-Vis data λ_{max} (water) 266 nm and molar extinction coefficient ϵ_{max} 3.1×10^4 mol⁻¹ dm³ cm⁻¹; λ_{max} (water) 490 nm and molar extinction coefficient ϵ_{max} 3.3×10^4 mol⁻¹ dm³ cm⁻¹.

[Er(AMH)(H₂O)₆](OAc)₃·H₂O, IR data (KBr pellet): ν (strong bands) = 1220 (C-O); 1171 and 1384 (S=O); 1458 and 1610 (C=C); and 1638 (C=N) cm⁻¹. Found: C, 29.95; H, 3.79; N, 1.49%; molecular formula $\text{C}_{23}\text{H}_{35}\text{O}_{21}\text{S}_2\text{NNaEr}$ (MW = 915.89 g mol⁻¹) requires C, 30.16; H, 3.85; N, 1.53%. UV-Vis data λ_{max} (water) 232 nm and molar extinction coefficient ϵ_{max} 2.4×10^4 mol⁻¹ dm³ cm⁻¹.

Dyestuff Extraction

The extraction process was carried out in an aqueous medium using different ratios of material (M) to liquor (L) (M:L). The extraction baths were prepared by the addition of 1, 3, 5, 10, 15, 20 and 25 g of the walnut husk powder to 200 ml of distilled water, and the isolation of the colorant was performed by stirring and heating at 90 °C for 90 min. At the end of each extraction process, the mixture was cooled to reach ambient temperature and then filtered. The obtained filtrate was diluted four times with distilled water, and the resulting solution was then used for the dyeing of silk.

Dyeing and Mordanting Method

Prior to the dyeing process, the silk yarns were immersed in a bath containing 4 g l⁻¹ non-ionic detergent solution at 40 °C for 30 min and then rinsed carefully with distilled water. The dyeing process was carried out using an

M:L ratio of 1:40. In addition, the dyeing process was performed under different conditions to investigate the effective parameters. Therefore, the separate dyeing baths containing various amounts of the dye powder at different pH levels (3, 5, 7, 9 and 11), different dyeing times (10-120 min), and different dyeing temperatures (50-90 °C) were used.

The dyed yarns were treated with different concentrations of the mordant (*i.e.* two erbium(III) complexes at 2, 5, 7 and 10% owf, owf = on the weight of fiber (yarn)) under different mordanting methods to enhance the color fastness and to improve the colorimetric properties.

During the post-mordanting process, the silk yarns dyed at 90 °C for 50 min were treated with the mordant solution at 60 °C for 50 min. During the meta-mordanting process, the silk yarns were dyed in a bath containing the dye and the mordant using an M:L ratio of 1:40 at 90 °C for 50 min. During the pre-mordanting process, at first, the silk yarns were treated with the mordant solution at an M:L ratio of 1:40 at 60 °C for 50 min, and the treated yarns were then dyed at 90 °C for 50 min. Finally, the dyed yarns obtained from each experiment were rinsed with distilled water and air-dried in the shadow.

Comparison of the Erbium(III) Complexes with the Pure Metal Salts as the Mordant

The mordant efficiency of the synthesized erbium(III) complexes, [Er(AO)(H₂O)₇](OAc)₃ and [Er(AMH)(H₂O)₆](OAc)₃, was compared with the pure metal salts in the natural dyeing of silk. For this purpose, the

silk yarns dyed in optimal conditions were post-mordanted at various concentrations of the pure metal salts, including erbium(III) acetate, stannous chloride, and aluminum potassium sulfate (2%, 5%, 7% and 10% owf), using an M:L ratio of 1:40 at 60 °C for 50 min.

Spectroscopic Measurements

The UV-Vis spectra of the aqueous solutions of the green walnut husk extract and erbium(III) complexes ($[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$) were recorded by a JASCO 7580 UV-Vis double-beam spectrophotometer. The FT-IR spectra of the erbium(III) complexes were recorded using an FT-IR JASCO 680-PLUS spectrophotometer.

Measurement of the Colorimetric Properties of the Dyed Silk Yarns

The color characteristics, including L^* (lightness-darkness), a^* (redness-greenness), and b^* (yellowness-blueness) of the dyed silk yarns, were evaluated using a Datacolor Spectraflash 600 (illuminant D65/10° observer). The reflectance spectra (400-700 nm) of the dyed yarns were also measured. Three parameters, including L^* , a^* and b^* , were used to calculate the color difference (ΔE^*) between the various mordanted samples and the blank sample (without the mordant) according to Equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Furthermore, the reflectance value (R) of the dyed samples at the λ_{max} was used to calculate the K/S value (the absorption coefficient (K)-to-scattering coefficient (S) *ratio*), which indicates the color strength of the dyed yarns. The K/S value was calculated using Equation (2) (Kubelka-Munk equation).

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

Color Fastness Studies of the Dyed Silk Yarns

The color fastness to washing for the dyed samples was performed according to ISO 105-C06:2010 (A1S) as the standard test method. The dyed samples were immersed in 4 g l⁻¹ non-ionic detergent solution at 40 °C for 30 min by

an AHIBA 1000 Polymath apparatus (Data Color, Switzerland). The color variation of the samples and staining on the adjacent white fabrics (silk and cotton) were evaluated using grey scales. Furthermore, the light fastness of the dyed silk yarns was assessed by the following procedure. The dyed yarn samples were tightly wrapped around the cardboard and placed in a SUNTEST apparatus. Then, one-half of each sample was covered with an aluminum foil to avoid light exposure, and the other half was exposed to the artificial light (xenon lamp) for 80 h. The light fastness of the dyed samples was evaluated according to the color difference between the light-exposed and light-protected areas of the samples using grey scales.

RESULTS AND DISCUSSION

UV-Vis and FT-IR Spectroscopic Studies

As indicated in Fig. 1, the electronic spectrum of the aqueous extract of the green walnut husk reveals two absorption bands at 228 and 268 nm, which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the carbonyl groups of juglone, respectively [17].

The UV-Vis spectra of the erbium(III) complexes are displayed in Fig. 2. The absorption spectrum of the acridine orange complex, $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$, reveals a weak absorption band at 234 nm as well as two intense absorption bands at 266 and 490 nm, which are related to the intra-ligand $\pi \rightarrow \pi^*$ transitions of the coordinating acridine orange ligand (Fig. 2a). These absorption bands are slightly perturbed by the coordination to erbium(III) compared to those of the free acridine orange molecule [18]. The spectrum of the azomethine-H complex, $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$, exhibits an absorption band in the UV region at 232 nm, due to the intramolecular $\pi \rightarrow \pi^*$ transitions. This spectrum also reveals a lower-energy broad absorption band around 300-400 nm in the visible region, which is assigned to the ligand-centered $\pi \rightarrow \pi^*$ transition involving the π electrons of the azomethine group in the coordinating AMH chromophore. (Fig. 2b) [19].

Moreover, the absorption bands of Er(III) that originate from the intra-configurational $f \rightarrow f$ electronic transitions were investigated for an aqueous solution of $\text{Er}(\text{OAc})_3$ (Fig. 2c). The sharp absorption bands in the UV-Vis region at 220, 360, 378, 408, 450, 490, 522, 544 and 654 nm, are

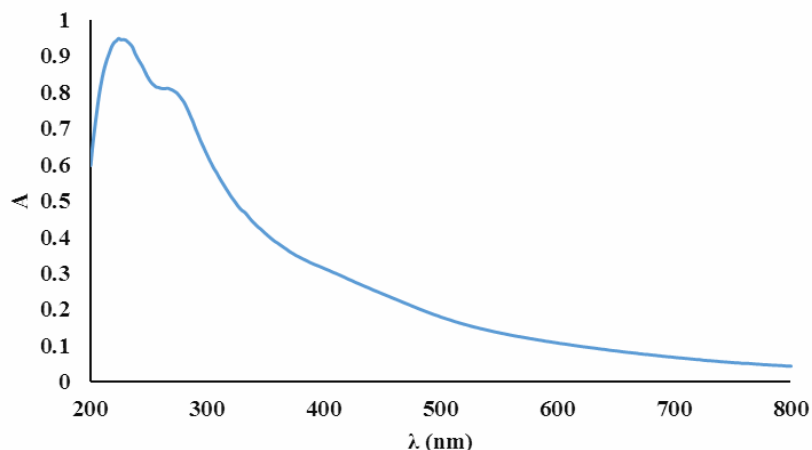


Fig. 1. Electronic absorption spectrum of the aqueous solution of the green walnut husk extract.

assigned to the $f \rightarrow f$ electronic transitions from the ground state $^4I_{15/2}$ to the excited states $^2I_{13/2}$, ($^4G_{9/2}$, $^2G_{7/2}$), $^4G_{11/2}$, ($^2H_{9/2}$, $^2G_{9/2}$, $^4F_{9/2}$), ($^4F_{5/2}$, $^4F_{3/2}$), $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ [20,21]. The $f \rightarrow f$ transitions in erbium(III) are sharp and narrow because its $4f$ orbitals are shielded by fully filled $5s$ and $5p$ subshells, and consequently, its electron cloud is not influenced by the crystal field. However, the absorption bands of lanthanides are weak because the $f \rightarrow f$ transitions are Laporte forbidden and are unable to be identified in the absorption spectra of their complexes [22].

The FT-IR spectrum of $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ presents an absorption band at 1638 cm^{-1} which is related to the $\text{C}=\text{N}$ stretching vibration of the pyridine ring. While compared to the free AO ligand, this band appears at a lower frequency with less intensity, which indicates the complex formation and the involvement of the pyridine ring nitrogen in the coordination to Er(III). In addition, there are three strong bands at 1590 , 1460 and 1349 cm^{-1} that are assigned to $\nu(\text{C}=\text{C})$ vibrations of the aromatic rings, and $\nu(\text{C}-\text{N})$ vibration of the aromatic amine, respectively [23].

The FT-IR spectrum of $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ reveals two strong bands at 1384 and 1171 cm^{-1} that are assigned to the asymmetric and symmetric of $\nu(\text{S}=\text{O})$, respectively. Additional predominant bands for this complex are related to the $\nu(\text{C}=\text{N})$ vibration of the imine group at 1637 cm^{-1} , and the $\nu(\text{C}=\text{C})$ vibrations of the aromatic rings around $1400\text{-}1600 \text{ cm}^{-1}$. The appearance of an absorption band at 1220 cm^{-1} is due to the stretching

vibration of C-O bonds of the phenolic hydroxyl groups. Furthermore, the infrared spectrum of the free AMH ligand presents several strong bands around $750\text{-}1000 \text{ cm}^{-1}$ due to the $\nu(\text{S}-\text{O})$ vibrations, which appear at a very low intensity in the complex spectrum, confirming the coordination of Er(III) by the sulfonate group of the ligand. Another predominant band for this complex is associated with the $\nu(\text{Er}-\text{O})$ vibration around $500\text{-}550 \text{ cm}^{-1}$, which demonstrates the complex formation between erbium(III) and AMH.

Effect of the Different Dyeing Parameters

Effect of the mordanting method. Figure 3 reveals the influence of the various mordanting methods on the dye uptake and color strength. The results revealed that the post-mordanting method results in a more significant color strength than the other two methods, pre- and meta-mordanting, due to the extra mordant ability in the formation of the complex with the dye and yarn in this method [16]. In addition, the simultaneous mordanting gave the lowest color strength. Hence, the post-mordanting method was utilized as the most desirable dyeing method in this study.

Effect of pH. Figure 4 displays the color strength of the dyed silk yarns in a variety of pH values. The highest color strength was observed at $\text{pH} = 3$ due to the structural features of juglone (the main colorant in the green walnut husk) and silk. There is a pH-dependent equilibrium between two different forms of juglone molecule in an

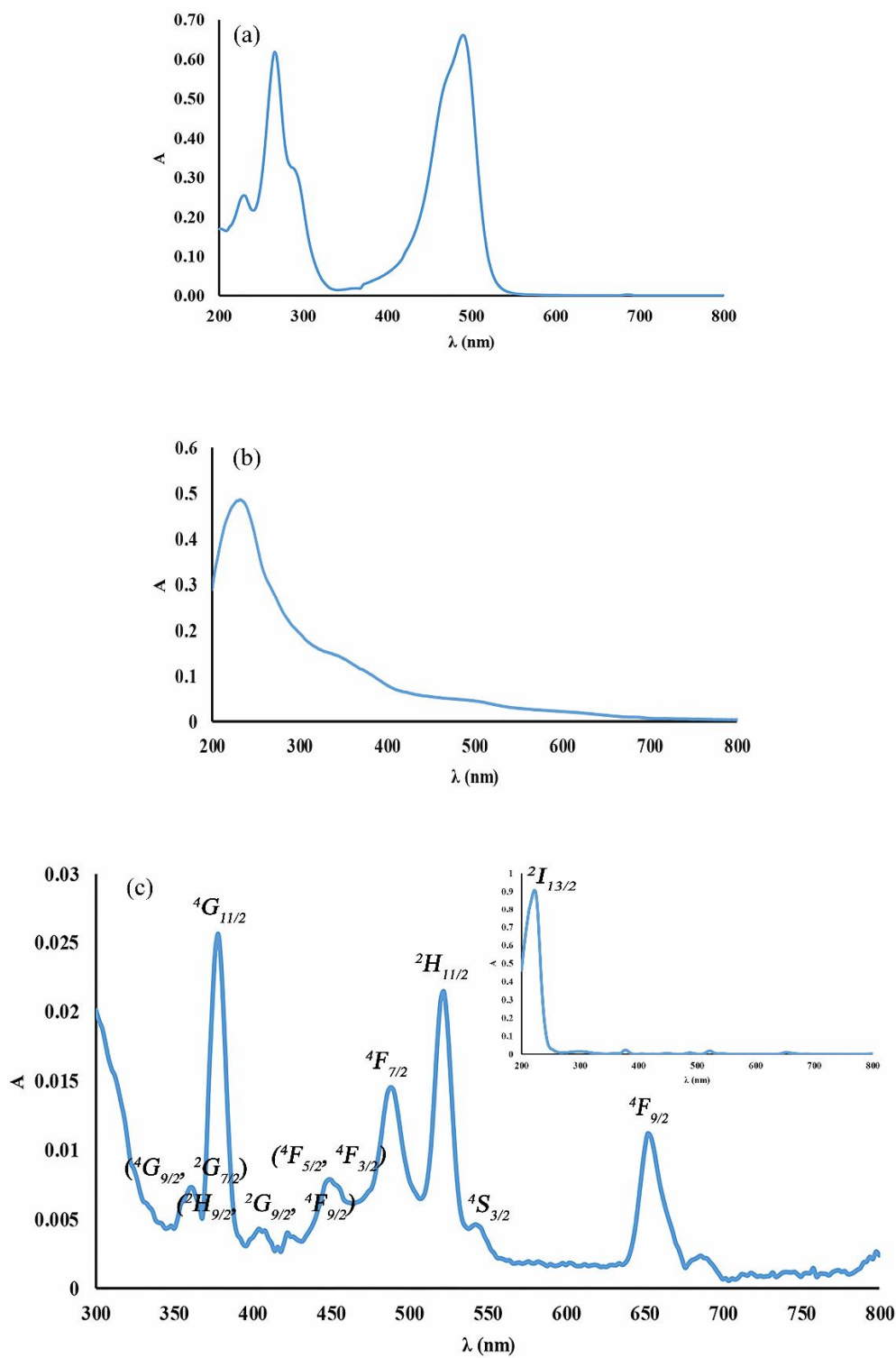


Fig. 2. Electronic absorption spectra of the aqueous solutions of (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ (2×10^{-5} M), (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (2×10^{-5} M), and (c) $\text{Er}(\text{OAc})_3$ (0.01 M).

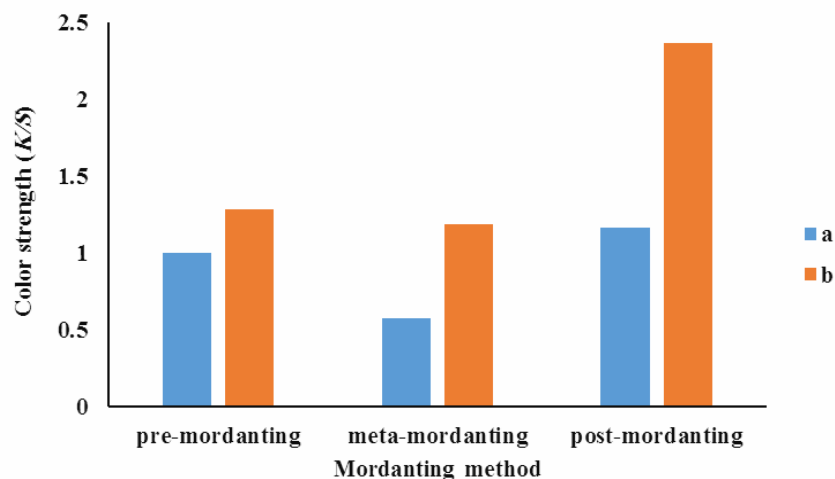


Fig. 3. Effect of various mordanting methods on the K/S value of the dyed samples which mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: dye conc. = 10 g/200 ml, complex conc. = 5% owf, M:L ratio = 1:40, pH = 5, temp. = 90 °C, and time = 50 min).

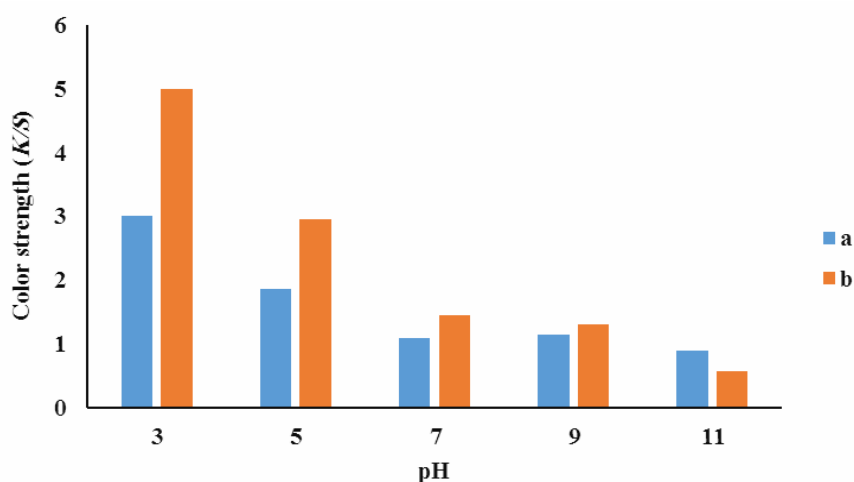
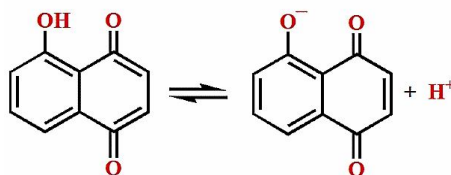


Fig. 4. Effect of various pH values on the K/S value of the dyed samples which post-mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: dye conc. = 10 g/200 ml, complex conc. = 5% owf, M:L ratio = 1:40, temp. = 90 °C, and time = 50 min).

aqueous solution (Scheme 2).

Since juglone has a pK_a of 3.65 and the isoelectric pH of the silk is about 3.8-4, only 18% of the juglone molecules are in the ionized form at pH = 3. In an acidic condition, the terminal amino groups in the silk structure are protonated. Therefore, the ionic interactions are created between these

functional groups and the ionized species of the colorant. These interactions shift the equilibrium to the right in Scheme 2, resulting in a higher color strength for the dyed yarns [24,25]. In an alkaline condition, although juglone is entirely ionized, raising the number of amino (NH_2) and carboxylate (COO^-) groups result in electrostatic repulsion



Scheme 2. pH-dependent ionization of juglone in water

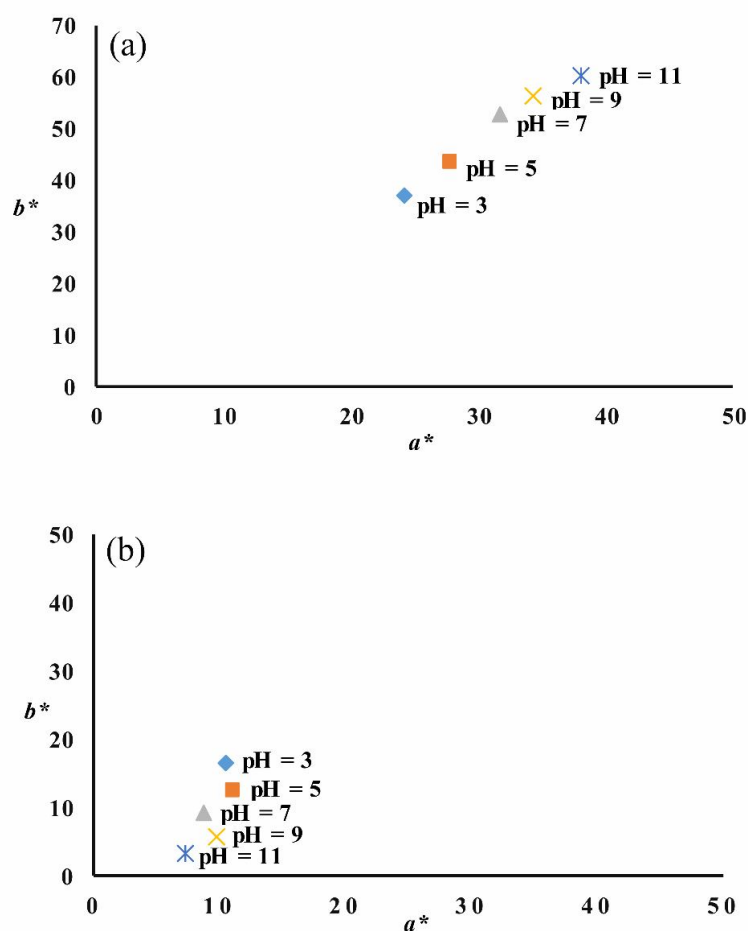


Fig. 5. a^*/b^* plot of the post-mordanted silk yarns with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ at various pH values of the dyeing bath (dyeing conditions: dye conc. = 10 g/200 ml, complex conc. = 5% owf, M:L ratio = 1:40, temp. = 90 °C, and time = 50 min).

between the protein yarns and the anionic colorant, which reduces the dye uptake [26]. Therefore, the highest and lowest color strengths were obtained at a pH of 3 and 11 for the dyed samples, respectively.

Figure 5 displays the colorimetric parameters of the

dyed yarns, which post-mordanted with two erbium(III) complexes at different pH values of the dyeing bath. For the post-mordanted samples with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$, the a^* and b^* values are gradually increased with an increasing pH value of the dyeing bath. The color of these samples is

shifted from red-brown in an acidic pH range to bright orange in an alkaline condition. The post-mordanting of the yarns with $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ resulted in lower a^* and b^* values compared to the above samples. The samples treated with $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ showed an increase in the b^* value by decreasing the pH of the bath from 11 to 3, while the a^* value remained almost unchanged. In this case, the color of the samples was dark and light brown in acidic and basic conditions, respectively.

Effect of the quantity of dye. The effect of the dye concentration on the color strength of the dyed silk yarns, which were post-mordanted with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ complexes, is displayed in Fig. 6. As indicated, the K/S value of the samples is increased by raising the quantity of the walnut husk powder and reached the constant amount in the dye concentration of 15 g/200 ml. This is due to the fact that a more significant amount of dye yields a higher dye concentration so that the extraction medium is gradually saturated with the colorant, and an equilibrium state is finally provided. Furthermore, the surface of the silk yarns is increasingly saturated with a high colorant concentration. Finally, a balance is created between the dye on the yarns and the dye in the dyestuff solution [27]. Therefore, according to the obtained results, 15 g of walnut husk powder in 200 ml of distilled water was selected as the dye's optimal concentration. The color of post-mordanted silk yarns with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ complexes was bright orange and light brown in low colorant concentrations, respectively, and was reddish-brown and dark brown in high colorant concentrations, respectively.

Effect of the dyeing temperature. The temperature effect was also examined in the dyeing process. As displayed in Fig. 7, the color strength of the dyed samples is risen at higher temperatures, because the kinetic energy of the colorant molecules and the expansion of the yarns increase at higher temperatures, resulting in diffusion of the dye into the yarns [28,29]. Consequently, the dye uptake of the dyed silk yarns is increased at higher temperatures due to an increase in the dyeing process rate. Therefore, the dyeing process was carried out at 90 °C as the optimal temperature. It is worth mentioning that the higher temperatures, near the boiling point of water, are not recommended for the dyeing of silk [30].

Effect of the dyeing time. Figure 8 displays the influence of dyeing time on the K/S value of the dyed samples. As indicated, an increase in the dyeing duration leads to an increase in the dye uptake of the samples until the further extension of the dyeing time cannot significantly change the K/S value, revealing that the dye exhaustion in the dyeing bath achieves an equilibrium after 50 min. Hence, the time interval of 50 min was used as the optimal dyeing time.

Effect of the mordant concentration. Figure 9 displays the color strength values of the dyed yarns using different concentrations of two erbium(III) complexes as the mordants. As shown in Fig. 9, the color strength value of the samples is increased by raising the concentration of each complex to 5%, and subsequently reaches a constant value due to saturation of the surface of the silk yarns.

Comparison of the Erbium(III) Complexes with Pure Metal Salts as the Mordant

For comparison, the pure metal salts, including erbium(III) acetate, aluminum potassium sulfate, and stannous chloride, were utilized as the mordant in the natural dyeing of the silk yarns under the same dyeing conditions, and the obtained results were compared to those obtained using the erbium(III) complexes. The color strength value of the dyed silk yarns, which post-mordanted with various concentrations of these salts, is displayed in Fig. 10. The concentration related to the highest color strength value was selected as an optimum concentration for each mordant. Thus, the optimal concentration of erbium(III) acetate, aluminum potassium sulfate, and stannous chloride was 10%, 10% and 5% owf, respectively. The results revealed that the use of erbium(III) acetate as the mordant leads to higher color strength values in comparison to other metal salts (aluminum potassium sulfate and stannous chloride). Since the possible coordination number of lanthanides is higher than that of *d*-block metals, they can bind to additional dye molecules and consequently enhance the color yield for the dyed samples.

Furthermore, Table 1 shows the effect of the various mordants on the color strength value (K/S) and colorimetric properties (*viz.*, L^* , a^* and b^*) of the dyed silk yarns with the aqueous extract of green walnut husk. As indicated in

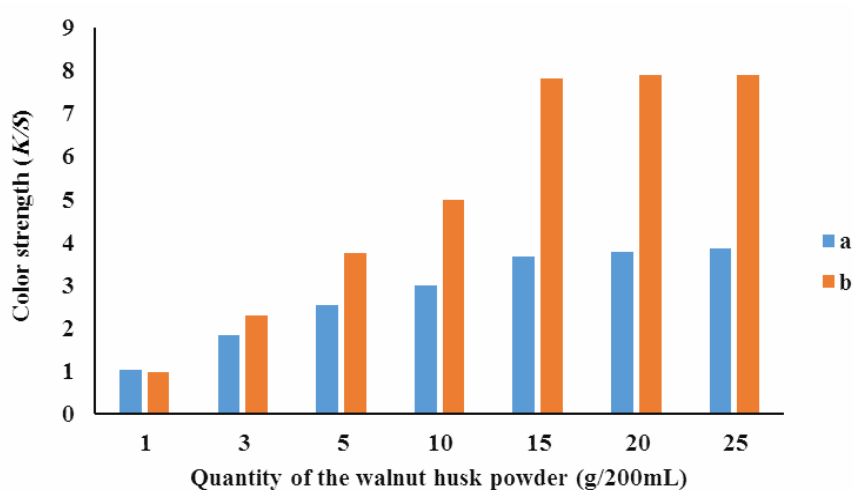


Fig. 6. Effect of quantity of the dye material (g/200 ml of distilled water) on the K/S value of the dyed samples which were post-mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: complex conc. = 5% owf, M:L ratio = 1:40, pH = 3, temp. = 90 °C, and time = 50 min).

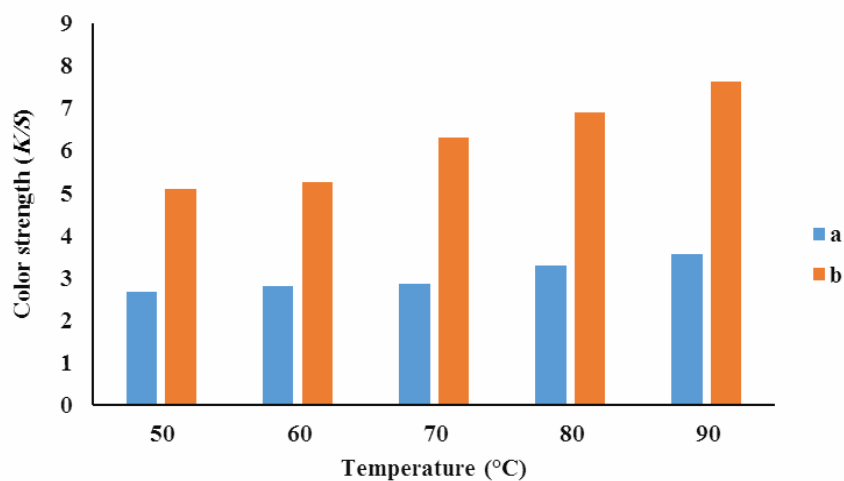


Fig. 7. Effect of dyeing temperature on the K/S value of the dyed samples which were post-mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: dye conc. = 15 g/200 ml, complex conc. = 5% owf, M:L ratio = 1:40, pH = 3, and time = 50 min).

Table 1, when $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ was utilized as the mordant, the obtained mordanted samples exhibit the highest color strength value.

A comparison of ΔE^* values in Table 1 reveals that the highest color difference is related to the mordanted samples with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$. Furthermore, as indicated in

Table 1, the order of the color difference value for the other mordants is as follows: $\text{Er}(\text{OAc})_3 > [\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3 > \text{AlK}(\text{SO}_4)_2 > \text{SnCl}_2$. According to the colorimetric data (a^*/b^* plot), which is displayed in Fig. 11, the color of the mordanted dyed yarns with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ shifts from brown to reddish brown.

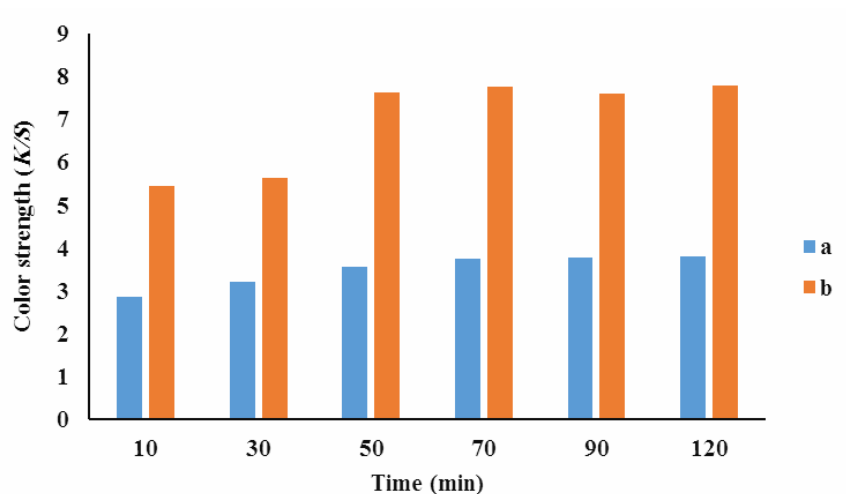


Fig. 8. Effect of dyeing time on the K/S value of the dyed samples which were post-mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: dye conc. = 15 g/200 ml, complex conc. = 5% owf, M:L ratio = 1:40, pH = 3, and temp. = 90 °C).

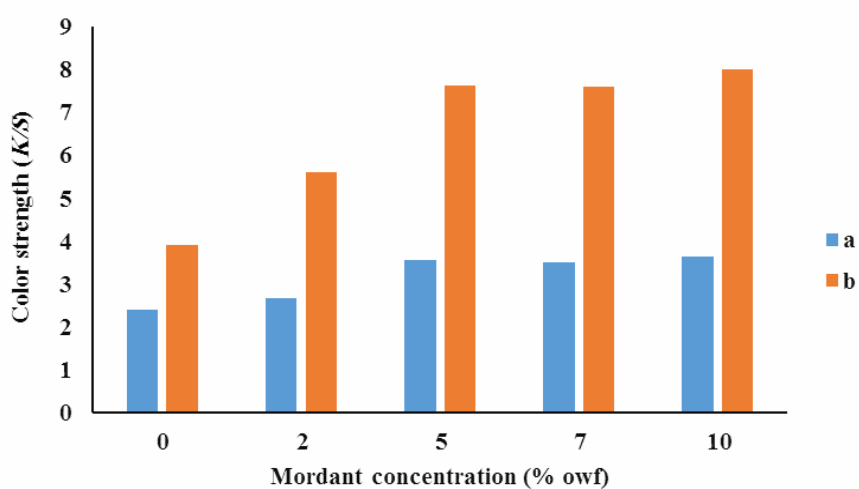


Fig. 9. Effect of mordant concentration (% owf) on the K/S value of the dyed samples which were post-mordanted with (a) $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ and (b) $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ (dyeing conditions: dye conc. = 15 g/200 ml, M:L ratio = 1:40, pH = 3, temp. = 90 °C, and time = 50 min).

Figure 11 also displays that the treatment of the dyed samples with $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ provides a significant shift toward yellow and red coordinates with high a^* and b^* values, while the post-mordanting of the dyed samples with the other mordants leads to slight alterations in the red-yellow zone of color spectrum.

In general, the overlapping between the absorption spectra of the dye and the mordant (e.g., Er(III) complex), as well as the formation of a new complex between the dye and the mordant intensify the color of the yarns and result in a significant increase in the color strength value and occasionally a notable color difference (ΔE^*). Scheme 3

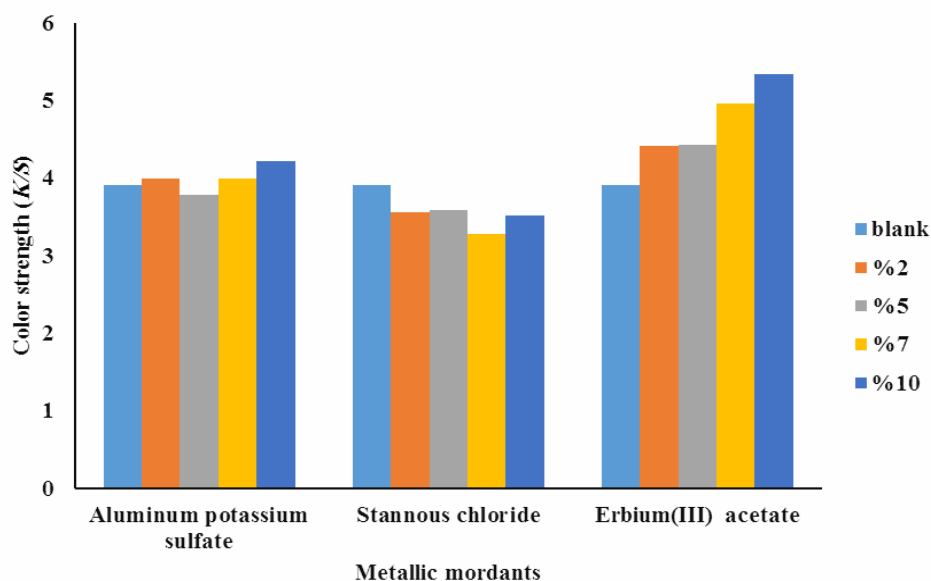








Fig. 10. Effect of mordant concentration (% owf) on the K/S value of the dyed samples which were post-mordanted with the pure metal salts, including erbium(III) acetate, stannous chloride, and aluminum potassium sulfate (dyeing conditions: dye conc. = 15 g/200 ml, M:L ratio = 1:40, pH = 3, temp. = 90 °C, and time = 50 min).

Table 1. Colorimetric Properties (L^* , a^* , b^* and K/S) and Color Difference of the Unmordanted and Mordanted Dyed Silk Yarns

Type of mordant	Mordant conc. (% owf)	K/S ($\lambda_{\max} = 520$ nm)	L^*	a^*	b^*	ΔE^*	Color
Without mordant	-	3.91	43.23	8.79	21.76	-	
$[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$	5	3.56 ^a	36.41	23.23	33.93	20.08	
$[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$	5	7.62	37.28	9.97	15.56	8.67	
$\text{Er}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$	10	5.34	37.46	7.73	14.77	9.13	
$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	10	4.22	41.36	8.00	18.45	3.88	
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	5	3.58	44.29	8.32	22.13	1.22	

^a $\lambda_{\max} = 570$ nm.

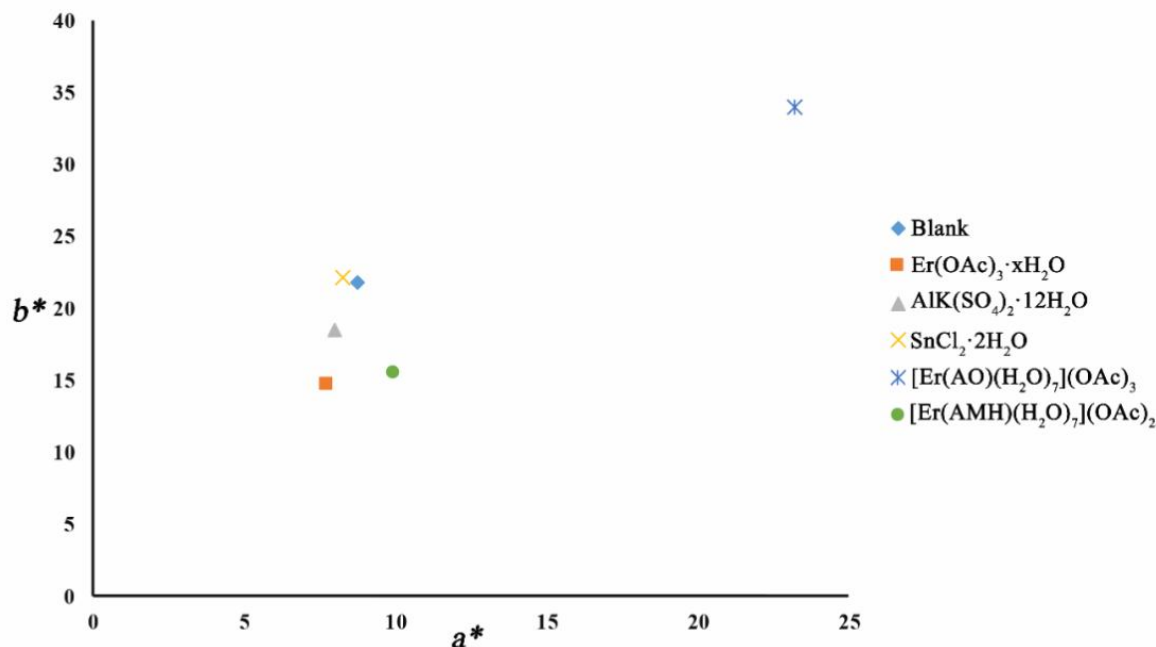
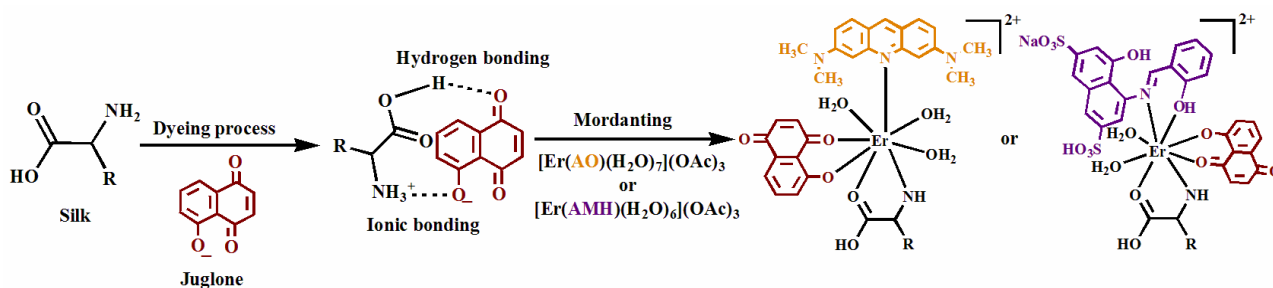


Fig. 11. Colorimetric data (a^*/b^* plot) of the dyed silk yarns which were post-mordanted with the various mordants.



Scheme 3. Schematic representation of the dye-mordant-silk interaction

shows the proposed interaction between the dye, silk yarn and erbium(III) complexes as the mordant, which increases the color strength value and creates a color difference.

Ultimately, the results indicated that the dyed silk yarns treated with $[\text{Er}(\text{AMH})(\text{H}_2\text{O})_6](\text{OAc})_3$ and $[\text{Er}(\text{AO})(\text{H}_2\text{O})_7](\text{OAc})_3$ complexes provide a higher color strength value and greater color difference in comparison with the samples mordanted with pure metal salts. Therefore, the synthesized erbium(III) complexes can be successfully applied to achieve a wide range of colors in the

natural dyeing process.

Evaluation of the Color Fastness Properties

The color fastness of the unmordanted and mordanted samples to washing and light was investigated, and the results are presented in Table 2. It was observed that the washing fastness of all samples is acceptable to great. Moreover, all samples exhibited little or no color staining on the adjacent white fabrics (silk and cotton). This is due to the removal of the physically absorbed colors from the dyed

Table 2. Color Fastness Properties of Unmordanted and Mordanted Dyed Silk Yarns

Type of mordant	Washing fastness			Light fastness
	Color change	Color stain		
		Silk	Cotton	
without mordant	3	3	4	5
[Er(AO)(H ₂ O) ₇](OAc) ₃	5	3	4	5
[Er(AMH)(H ₂ O) ₆](OAc) ₃	5	5	5	5
Er(OAc) ₃ ·xH ₂ O	4	3	4	5
AlK(SO ₄) ₂ ·12H ₂ O	4	3	4	5
SnCl ₂ ·2H ₂ O	3	4	4	5

silk yarns during washing. In addition, all samples exhibited an adequate light fastness rating of 5 on the grey scale. As shown in Table 2, the mordanting process of the dyed silk yarns has a significant effect on their color fastness properties. It is worth mentioning that some factors, such as the dye chemical structure, yarn properties, type of bonding between the dyestuff and yarns, and the colorant concentration used in the dyeing process, are effective on the color fastness characteristics of the dyed samples. It has been reported that walnut husks contain several phenolic compounds in addition to juglone. The phenolic hydroxyl groups of these compounds can form crosslinks with the dyestuff and yarns and improve the color fixation [10,14,31].

CONCLUSIONS

In this work, two new erbium(III) complexes, [Er(AO)(H₂O)₇](OAc)₃ and [Er(AMH)(H₂O)₆](OAc)₃, were prepared and fully characterized by elemental analysis and spectroscopic techniques. The Er(III) complexes were utilized as the mordants in the natural dyeing of the silk yarns with the green walnut husk extract. The dyeing conditions were optimized, and the optimal conditions include a dye concentration of 15 g in 200 ml of distilled water, the mordant concentration of 5% owf, pH = 3, dyeing temperature of 90 °C, and dyeing interval of 50 min.

Furthermore, the post-mordanting method was selected as the most suitable mordant technique from the three different mordanting methods. The dyed samples post-mordanted with the erbium(III) complexes were compared to those post-mordanted with the pure metal salts in terms of the color difference (ΔE^*) and color strength (K/S). The results revealed that the mordanted samples with [Er(AMH)(H₂O)₆](OAc)₃ and [Er(AO)(H₂O)₇](OAc)₃ complexes provide a higher color strength value and a more significant color difference, respectively, than those mordanted with the pure metal salts. In addition, all samples exhibited excellent color fastness to light and washing. Generally, the use of natural dyes combined with lanthanide complexes is an efficient strategy to reach a wide range of colors in the natural dyeing process, which makes natural colorants more attractive.

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