

Analysis of the Effect of Mordants on the Degradation of Alizarin in Silk Dyed with Natural Madder Dye

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Received December 11, 2018; Accepted February 21, 2019

Abstract

This research investigated the effect of mordants on the degradation of madder dye in silk when silk was treated by the H₂O₂/UV condition as a laboratory simulation of burial induced degradation. Alum, iron, and alum/iron composite mordanting methods were applied to silk before dyeing with madder dye. Dye extracted from silk was examined using HPLC-DAD-MS analysis. The abundance of the chromatogram peak at 8.88 min retention time was used as the concentration of alizarin pigment in silk. K/S values, CIE L*a*b* values; in addition, Munsell HVC values were obtained using a spectrophotometer. The findings indicated that alizarin degraded most severely in silk mordanted by alum/iron composite mordanting than alum mordanting or iron mordanting. Mordanting with alum alone provided a relatively lower dye fixation at the point of dyeing; however, it provided a better survival of alizarin after 12 hours of degradation treatment.

Key words: Madder, Mordant, Silk, Burial, Degradation

I. Introduction

Color fading is one of the most visibly recognizable problems in museum textiles (Padfield & Landi, 1966). Fading is more severe especially if the textiles were recovered through the excavations of ancient burials (Ahn et al., 2015). In order to protect the excavated textiles from further deterioration of dyes, it is necessary to examine the degradation of dyes which were used to dye these textiles. Previous literatures which dealt with dyes related to museum textiles suggested that the degree of fading might be related to the type of mordant used in dyeing the particular piece of textile (Ahn et al., 2015; Crews, 1982).

In a study which examined the 17th century excavated textiles of Korea, the findings indicated that there

was some relationship between the amount of pigments surviving in the excavated textiles and the type of mordant which was used to dye the fabric (Ahn et al., 2012). In a study by Crews (1982) who investigated the influence of mordant on the lightfastness of yellow natural dyes, change of color was prominent in wool mordanted with tin and alum whereas little change of color occurred in wool mordanted with copper, iron, and chrome (Crews, 1982). Based on the previous literatures, it is proposed that mordants might have influence on the survival or degradation of dye in burial textiles. And thus the degree of color remaining in an excavated textile may be related to the type of mordant which was used in dyeing the particular piece of textile.

This research was aimed to investigate the effect of mordants on the degradation of madder dye, after treating the dyed silk with H₂O₂/UV condition as a laboratory simulation of burial induced degradation. Alum mordanting, iron mordanting, and alum/iron com-

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본 논문은 인천대학교 2017년도 자체연구비 지원에 의하여 연구되었음.

posite mordanting methods were considered in this study. H₂O₂/UV condition which was used in the prior research as a way to simulate burial induced degradation was utilized in this research to artificially degrade the dye in the silk dyed with natural madder. A high performance liquid chromatography equipped with a diode array detector and a mass selective detector (HPLC-DAD-MS) was used to investigate the amount of dye surviving in the silk after degrading the silk in H₂O₂/UV condition.

II. Review of Literature

1. Madder Dye Plant and Its Pigment, Alizarin

Madder is one of the most representative mordant dye which was widely used in the past (Ford et al., 2015). Two most common species of madder are *Rubia tinctorum* L. and *Rubia cordifolia* L. (Ford et al., 2015; Sisubalan et al., 2015). *Rubia tinctorum* L. is often called the ‘Dyers’ madder’ and its historical usage as red dye has been reported in many different literatures (Ford et al., 2015). *Rubia cordifolia* L. is often called the ‘Indian madder’ or ‘Chinese madder’ and its usage in the past also occurs in many different literature sources (Bhatt & Kushwah, 2013; Sisubalan et al., 2015). Pigments of madder are found in the hairy roots of madder plant (Ford et al., 2015).

It is known that the most abundant pigment of madder is alizarin (1,2-dihydroxyanthraquinone, C₁₄H₈O₄, molar mass: 240.21 g · mol⁻¹) which belongs to the chemical family of anthraquinone (“Alizarin”, 2018; Ford et al., 2017). Ford et al. (2017) examined the amount of alizarin, purpurin, and major anthraquinone glycosides in the dyebaths of different *Rubia tinctorum* varieties from Iran, Turkey, and England. The amount of alizarin glycoside and alizarin showed the highest content among 7 coloring compounds the authors examined (Ford et al., 2017). In all 3 samples, alizarin showed higher content than purpurin by difference of 2.6-11.7% (Ford et al., 2017).

Sisubalan et al. (2015) investigated the amount of alizarin and purpurin in 7 different root samples of *Rubia cordifolia* L. from Tamil Nadu. Except for one sample, the amount of alizarin was higher than that of

purpurin, showing 8.70-32.40% and 0.59-33.40% of the dry roots for alizarin and purpurin, respectively (Sisubalan et al., 2015). In one sample which showed higher purpurin content than alizarin, the difference between the amount of two pigments was only by 1% (Sisubalan et al., 2015). The findings of preview literature indicate that the major and the most abundant pigment of madder is alizarin, regardless of whether the madder species is *Rubia tinctorum* or *Rubia cordifolia*.

Alizarin pigment requires mordant to be fixed in the fiber and the pigment produces textiles with different color depending on the type of mordants (Ford et al., 2015, 2017; Zarkogianni et al., 2009). When dyed with alum mordanting, alizarin forms ‘fiber-metal-dye’ chelate which provides a strong dye fixation to fibers (Ahn et al., 2015; Khan et al., 2012).

2. Records of Madder Dyeing in Historical Textiles

According to Park et al. (2007), the word ‘Chunhong’ represented the dark red color of Joseon dynasty which was produced by dyeing the fabric with madder dye and alum mordant. Yean (2015) examined the historical references 『Gyuhap Chongseo』 (Yi, 1809/1975), 『Imwonkyungjaeji』 (Seo, as cited in Lee, 2010), and *Sangbang jeongnye* and said that our ancestors used safflower, sappanwood, and madder as red dye. And especially, purple gromwell and madder were used together to produce *simbisek*, the dark red color (Yean, 2015).

In a study which examined the degradation behaviors of 7 different coloring compounds using the high performance liquid chromatography diode array mass spectroscopy analysis (HPLC-DAD-MS), Ahn et al. (2015) reported that alizarin dyed on silk was much more resistant to degradation than alizarin dissolved in dye solution. Zarkogianni et al. (2009) identified and quantified the amount of alizarin in old textiles from western Macedonia, Greece using the reversed phase high performance liquid chromatography (HPLC) analysis. Abdel-Kareem et al. (2010) identified madder dye in a rare tunic from the Coptic Museum using the HPLC equipped with a photo diode array (HPLC-PDA).

3. Mordant

Mordant is a substance such as metal salt that allows chemical bonding between the dye and the fiber so that the dye can be fixed to the fiber to produce color and fastness (Perkin & Everest, 1918; Samanta & Konar, 2011). Records of past dyeing processes indicate that a variety of natural resources were used as mordants, and the most representative sources were naturally occurring minerals and lye (Chu & Nam, 1997; Perkin & Everest, 1918).

Records of traditional dyeing methods indicate that iron fragments were immersed in water with wheat juice, sugar cane, or vinegar, which was then aged for one to two days before being used as mordant (Chu, 2005). Nam (2000) explained that the composition of iron liquor obtained in this manner was similar to ferrous sulfate. In traditional dyeing processes, lye was prepared by filtering the water obtained by burning bean pod, stalks of indigo, or similar materials (Chu & Nam, 1997; Lee, 2010; Yi, 1809/1975). It is said that lye obtained in this manner is composed of potassium, sodium, aluminum, and iron ions (Chu & Nam, 1997). Therefore, when lye was used as mordant, it is presumable that different metal ions from lye water would provide a concerted effect of metal-fiber-dye chelation.

Following the traditional methods, alum mordanting and iron mordanting became the most generally used mordanting processes in modern natural dyeing (Nam, 2000). Since alum refers to aluminum potassium sulfate with the chemical formula $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ("Alum", 2018), this chemical compound is often used as the medium for alum mordanting (Doty et al., 2016). And since iron refers to iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), this chemical compound is often used as the medium for iron mordanting in modern natural dyeing (Seo et al., 2011). Actual use of aluminum potassium sulfate and iron sulfate in madder dyeing process has been reported in previous literatures such as Ahn and Obendorf (2004), Ford et al. (2017), Hofenk de Graaff et al. (2004), or Zhang and Laursen (2005).

4. Laboratory Simulation of Burial Degradation

White-rot fungus has been widely recommended

for cleaning the dye wastewater released from textile dyehouse (Hossain et al., 2016). Decolorizing effect of white-rot fungus on dye wastewater comes from the fact that many types of white-rot fungi emit peroxidase enzymes from their body to the environment (Falade et al., 2017; Vasina et al., 2017). The decolorizing principle of peroxidase enzyme is similar to the decolorizing effect of Advanced Oxidation Process using hydrogen peroxide and ultraviolet radiation (Hissaindee et al., 2013). Decolorization occurs through the oxidative degradation of dye by hydroxyl radical ($\cdot\text{OH}$) produced from peroxidase enzyme or H_2O_2 in Advanced Oxidation Process (Amin et al., 2008; Karimi et al., 2010).

A large number of soil micro-organisms emit peroxidase enzymes into soil (Bach et al., 2013; Tian & Shi, 2014). And atmospheric conditions such as rain produce hydrogen peroxide within soil (Petigara et al., 2002). Considering the above review of literature, it is possible that the color fading of burial textiles within the long-term burial environment was induced, in part, by the decolorization of peroxidase produced from soil micro-organisms and hydrogen peroxide released into soil (Ahn & Obendorf, 2004; Ahn et al., 2012). In light of this proposal, this research utilized the $\text{H}_2\text{O}_2/\text{UV}$ treatment to simulate the burial induced degradation of dyed textiles in the laboratory. $\text{H}_2\text{O}_2/\text{UV}$ treatment was used in the previous literatures to examine the degradation behavior of the pigment compounds of some of natural plant dyes (Ahn & Obendorf, 2004; Ahn et al., 2012; Ahn et al., 2015).

III. Experimental

1. Materials

Madder powder dye was purchased from Lyn Art (Korea). Alizarin was purchased from Sigma-Aldrich. Aluminum potassium sulfate [$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] was purchased from Dae Jung Chemicals & Metals Co. (Siheung, Korea), iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from Wako Pure Chemical Industries (Osaka, Japan). Hydrogen peroxide (30%) and HCl (38%) were purchased from Junsei Chemical Co. (Tokyo, Japan). Methyl alcohol (HPLC grade) was purchased from J. T. Baker

(Center Valley, PA). Dimethyl sulfoxide (DMSO, LC grade) was purchased from Macron Fine Chemicals (Center Valley, PA). Acetonitrile (HPLC grade) and HPLC water were purchased from Fisher Scientific. Formic acid (88%, ACS grade) was purchased from Macron Fine Chemicals. Silk used for dyeing was the Standard Adjacent Fabrics for Colour fastness Test of KS K 0905 (Korean Agency for Technology and Standards [KATS], 2015) purchased from KATRI (Seoul, Korea). Each HPLC sample was filtered using a glass fiber enhanced 0.45 μm True™ nylon syringe filter by Alltech Associates. Water used for dyeing was distilled using a water purification system by Human Power (Human Corporation, Korea).

2. Methods

1) Dyeing of Silk with Madder Dye

A 5 g/L of madder powder was extracted with distilled water at 80°C for 60 minutes and used as the madder dye liquor. A 0.5 g/L each of aluminum potassium sulfate and iron sulfate were separately used to mordant a 24 cm \times 24 cm sized silk (2.96 g) for 60 min at 60°C with 1:100 liquor ratio. For the sample of Alum/Iron mordanting, two above procedures were carried out consecutively. Mordanted silk was dyed with madder dye liquor at 60°C for 60 minutes with 1:100 liquor ratio.

2) Preparation of Standard Alizarin Solution

Standard solution of alizarin was made by dissolving 0.01 g of alizarin standard in 100 mL of DMSO. Alizarin standard solution was used to obtain the HPLC-DAD-MS fingerprint data for alizarin in madder dye and alizarin in the dyed silk.

3) Degradation of Dyed Silk with H₂O₂/UV Treatment

Total degradation time applied was up to 12 hours. The dyed silk was cut into 4 cm \times 5 cm sized samples and a stock solution of 9:1 v/v H₂O:H₂O₂ solution was prepared. A 20 mL of the stock solution and a piece of silk sample were put into a clear glass vial (borosilicate threaded glass vial, O.D. 25 mm \times H 95 mm, Fisher Scientific) for each degradation time. The vials

were placed under a 8 Watt 365 nm UV lamp (UVL-28, Upland, CA) so that the surface of the lamp housing tightly covered the rim of each vial and that the light was radiating vertically from top of the vial. The distance between the surface of the lamp and the upper surface of liquid in the vial was 4 cm according to this set up. At the end of each degradation time, silk sample was taken out, rinsed and dried between the layers of Kimwipes®.

4) Extraction of Dye from Degraded Silk

Approximately 0.5 cm \times 0.5 cm sample of each degraded silk specimen was placed in a small beaker with 0.4 mL of mixed solution of HCl/methanol/water (2:1:1 v/v/v). The beaker was placed in 100-110°C oven until liquid was completely dried. An aliquot of 1.5 mL of DMSO was added to beaker for the final extraction process. The DMSO extract was filtered and analyzed using the HPLC-DAD-MS.

3. HPLC-DAD-MS Analysis

1) Chromatographic Conditions

An Agilent 1200 series binary HPLC-DAD-MS system (Foster City, CA) equipped with a diode-array detector (DAD) and a mass selective detector (MSD) consisting of a single quadrupole mass analyzer was used for sample analysis. The mass detector was operated in the SIM (selective ion monitoring mode) and SCAN mode using the atmospheric pressure chemical ionization (APCI) source in the positive mode to detect the chromophoric compounds. LC separation was achieved by Agilent ZORBAX SB-C18 column (length 50 mm \times I.D. 2.1 mm, particle size 1.8 μm). The gradient elution applied in the analysis using solvent A (acetonitrile) and solvent B (1% formic acid in water) was: 0-5.70 min, 90-20% B; 5.70-10.00 min, 20-61% B, 10.00-15.00 min, 61% B. The flow rate was 1.00 mL/min, and the injection volume was 20 μL . Detection wavelength for the DAD was set for 265, 255, 288, 606, 542 nm. The column temperature of the MSD was 25°C and the ionization source was operated with drying gas flow 11.5-13.0 L/min, drying gas (N₂) temperature 300-350°C, vaporizer temperature 250°C, nebulizer pressure 60 psi, capillary

voltage of 5 kV in positive ion mode, charge voltage 1.3-2.0 kV, fragmentor voltage 95 V, and mass range m/z 200-400. The SIM program was ran with group 1 0-8.00 min m/z 336, 338, 352, 354; group 2 8.00-9.50 min m/z 241, group 3 9.50-10.70 257, m/z 263, and group 4 10.70 m/z 263.

2) Analysis of Relative Concentration of Dyes

An ion chromatogram was generated for ion m/z 241 in the mass spectra obtained from the APCI positive ion SIM mode. Based on the R_t range of alizarin compound, the relative area (abundance, mAU) of the major peak was obtained using the integration results of the Agilent Chem Station (Agilent Technologies, 2001-2006). This abundance was used as the relative concentration of alizarin compound.

4. Color Measurement

Color strengths of non-degraded silk samples were examined by way of the K/S value calculated based on the reflectance value (% R) at λ_{\max} of dyed silk. The measurement was taken using a JS-555 spectrophotometer (Color Techno System, Japan) under D_{65} illuminant and 10° standard observer at three spots and the average data were reported.

IV. Results and Discussion

1. Result of Madder Dyeing on Silk

This study investigated the effect of alum mordanting, iron mordanting, and alum/iron composite mordanting on silk dyed with natural madder dye in regard to the degradation of alizarin pigment when dyed silk was treated in H_2O_2/UV condition. As an initial step, silk was dyed with madder using three different mordanting procedures.

K/S value is used in textile science and industry as a parameter which describes the color strength of the dyed fabric (Sadi & Hossain, 2017) or in other terms the buildup or fixation of dye on textiles (Ahmed et al., 2006). The result of color strength or dye fixation represented by the K/S value is shown in <Table 1>. The highest K/S value was obtained from the silk dyed with madder by alum/iron composite mordanting which was done by premordanting the silk by alum mordant and then by iron mordant. The lowest K/S value was obtain from the silk mordanted with alum mordant only. The spectral distribution of the K/S values show that the λ_{\max} , the wavelength of maximum absorbance, was different for three silk samples (Fig. 1). From alum mordanting to alum/iron mordanting, the λ_{\max} shifted towards the higher wavelength, indicating that the color changed to a redder tone as the mordanting method changed to iron mordanting and then to alum/iron mordanting. Such change in color was observed in the color measurement data of the 3 silk samples.

Measurement of Munsell hue (V) indicated that alum/iron mordanted silk showed a red purple (RP) hue whereas both alum mordanted and iron mordanted silk showed a yellow red (YR) hue (Table 1), (Fig. 2). Iron mordanted silk showed a slightly redder hue (5.493YR) than the alum mordanted silk (9.902 YR) and this tendency was also examined by the b^* value which showed a significantly higher b^* value the in alum mordanted silk (37.197) than in the iron mordanted silk (9.930).

The results of the present study was quite different from Lim and Jang (2013) who reported that when silk was dyed with madder using different mordants, the silk showed 7.7R (R: red) to 8.3R hue by alum mordanting ($AlK(SO_4)_2 \cdot 12H_2O$) and 3.7YR to 3.8YR hue by iron mordanting. The alum mordanted silk of this study showed a YR color whereas Lim and Jang

Table 1. Result of madder dyeing on silk using different types of mordant

| Dyed sample | λ_{\max} (nm) | %R | K/S | L* | a* | b* | ΔE | H | V | C |
|----------------------|-----------------------|--------|-------|--------|--------|--------|------------|---------|-------|-------|
| No dyeing | 400 | 77.470 | 0.033 | 93.199 | -0.188 | 1.446 | 0.000 | 0.000 | 9.215 | 0.000 |
| Alum mordanting | 420 | 13.012 | 2.908 | 68.195 | 11.868 | 37.197 | 45.263 | 9.902YR | 6.653 | 6.330 |
| Iron mordanting | 460 | 9.882 | 4.109 | 44.909 | 10.012 | 9.930 | 50.080 | 5.493YR | 4.355 | 2.396 |
| Alum/Iron mordanting | 480 | 6.215 | 7.076 | 32.318 | 8.261 | -3.006 | 61.626 | 5.542RP | 3.148 | 1.143 |

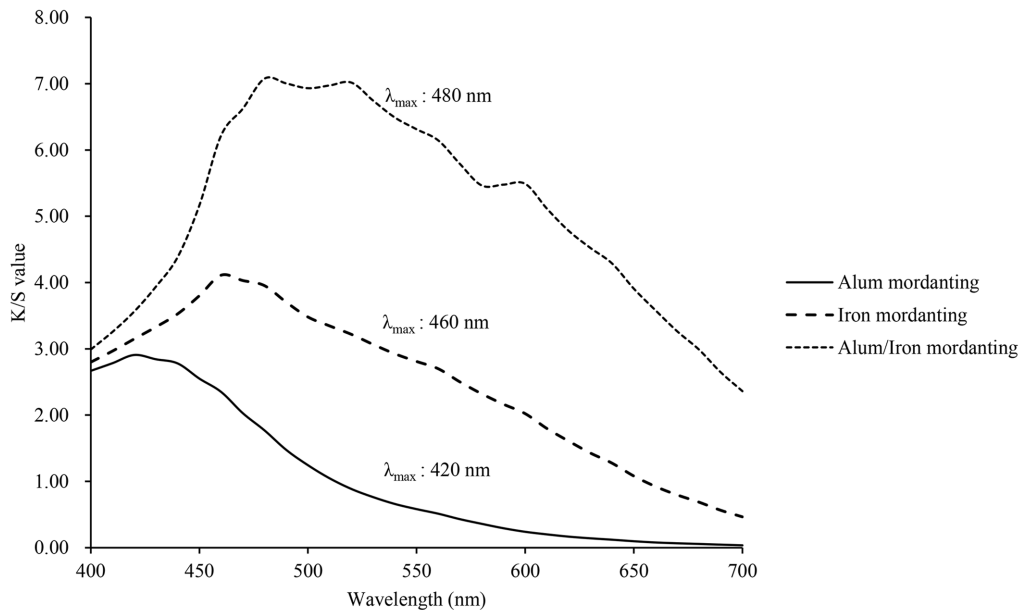


Fig. 1. Spectral distribution of K/S values from the color measurement of three silk samples dyed with madder dyeing.

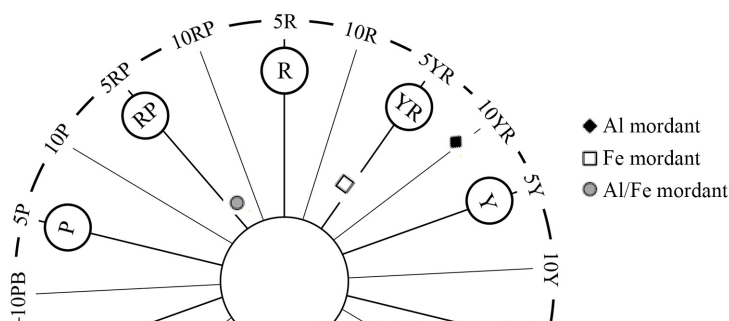


Fig. 2. Munsell color of madder dyed silk based on hue and chroma values.

(2013) resulted in R range of colors. The iron mordanted silk of this study showed higher YR value than those of Lim and Jang (2013). Difference in the results is probably due to the fact that Lim and Jang (2013) removed the yellow dye components from madder before the actual dyeing whereas such pretreatment was not applied in this research.

Overall, results of color measurement of present study indicate that the color of dyed silk became redder in the order of alum < iron < alum/iron mordanting

and that the color different (ΔE) was also in the order of alum < iron < alum/iron mordanting.

2. Analysis of Standard Dyes

High performance liquid chromatography diode array detector mass spectroscopy (HPLC-DAD-MS) analysis was conducted on alizarin standard dye to obtain the fingerprint data for detecting and quantifying alizarin compound in the silk dyed with madder.

HPLC chromatogram, UV spectrum, and the mass spectrum by HPLC-DAD-MS analysis are shown in <Fig. 3>.

Major peak of alizarin sample was observed in the HPLC chromatogram at retention time of 8.88 min. When DAD UV-Vis spectrum of the peak was analyzed, the peak showed maximum UV-Vis absorbance at 250 nm, 277 nm, and 428 nm. When mass spectrometry analysis (MS) was conducted, the mass of peak at 8.88 min showed m/z 241, which was identical to the mass of alizarin compounds. The 8.88 min retention time, 250 nm, 277 nm, and 428 nm maximum absorbance wavelengths, and mass spectrum of m/z 241 were used as the fingerprint data for identifying alizarin in madder dye and the madder dyed silk.

3. Analysis of Madder Dye Solution

The results of HPLC-DAD-MS analysis of madder dye prepared in DMSO solution is shown in <Fig. 4>. Major peak at 8.88 min retention time was observed in the HPLC chromatogram. The DAD UV-Vis spectrum indicated three maximum absorbance peaks at 248 nm, 277 nm, and 428 nm. MS spectra indicated a major ion at m/z 241, confirming the presence of aliz-

arin in madder dye solution. Using the data integration of the SIM mode (selected ion monitoring mode), the concentration of alizarin represented by the relative area of the peak at 8.88 min was calculated to be 1291.3 mAU (Table 2).

4. Analysis of Dyed Silk: Before Degradation Treatment

Silk sample was immersed in a mixed solution of HCl/methanol/water (2:1:1 v/v/v) to hydrolyze and extract the dye from the sample. The results of HPLC-DAD-MS analysis of the extract from the silk dyed by alum mordanting is shown in <Fig. 5>. By the retention time (8.88 min) of HPLC chromatogram, maximum UV-Vis absorbances (248 nm, 277nm, and 428 nm) obtained by DAD analysis, and the molecular ion (m/z 241) obtained from the MS analysis, it was confirmed that the major pigment compound present in the silk dyed with madder dye was alizarin. The presence of alizarin pigment was also confirmed in the silk dyed by iron mordanting and alum/iron mordanting based on the data represented in <Fig. 6>-<Fig. 7>.

Using the data integration of SIM mode, the concentration of alizarin in silk samples represented by

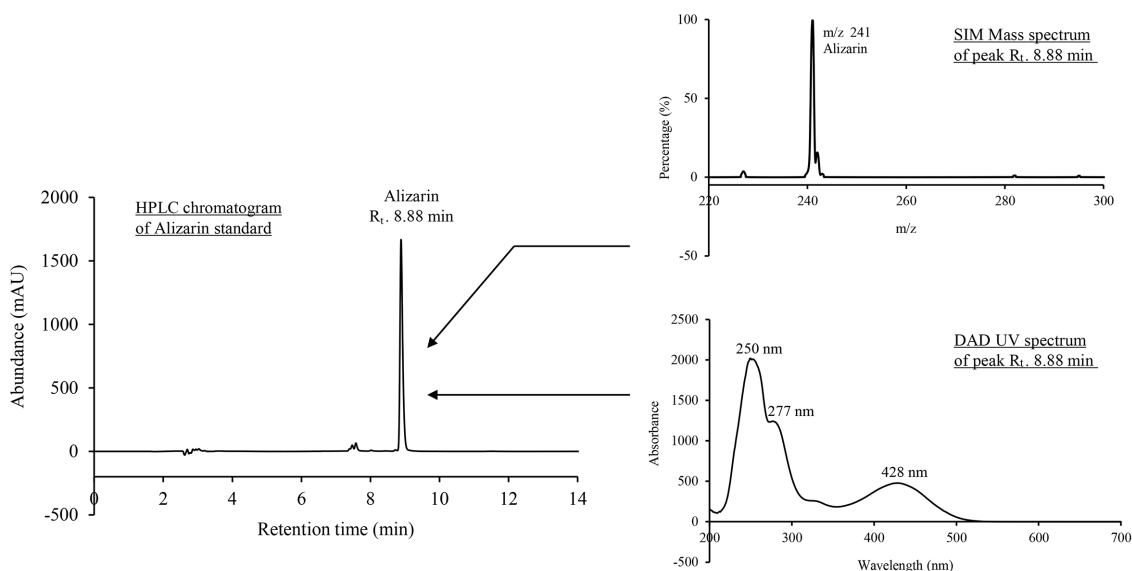


Fig. 3. Result of HPLC-DAD-MS analysis of alizarin standard.

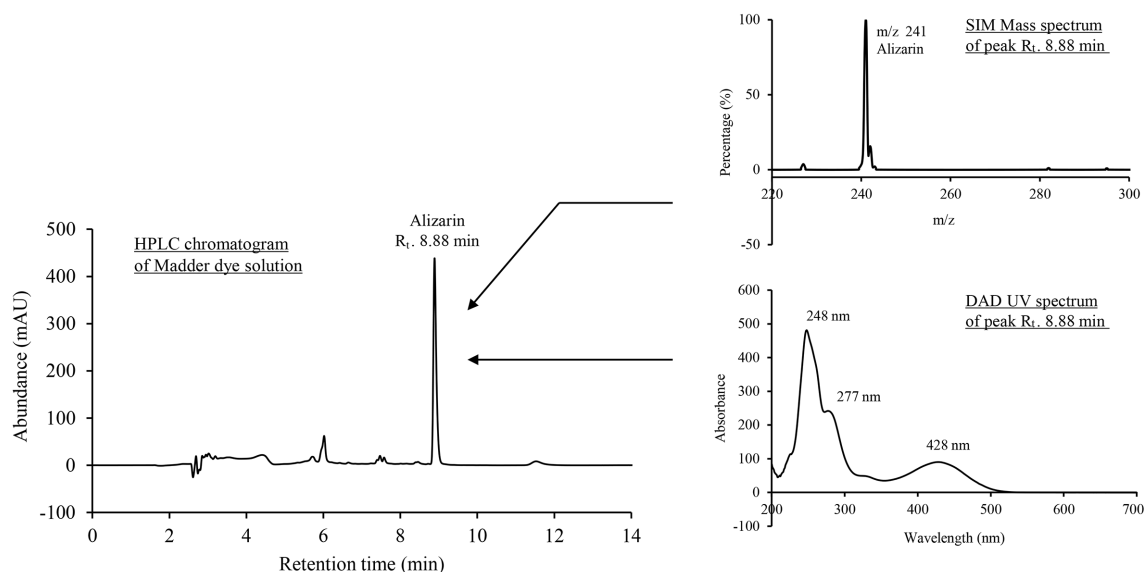


Fig. 4. Result of HPLC-DAD-MS analysis of madder dye solution.

Table 2. Concentration of alizarin in madder dye solution (DMSO medium) represented by the relative area of the HPLC chromatogram

| Sample | Retention time (min) | Wavelength λ_{\max} (nm) | Major ion (m/z) | Abundance (mAU) |
|---------------------|----------------------|----------------------------------|-----------------|-----------------|
| Madder dye solution | 8.88 | 428 | 241 | 1291.3 |

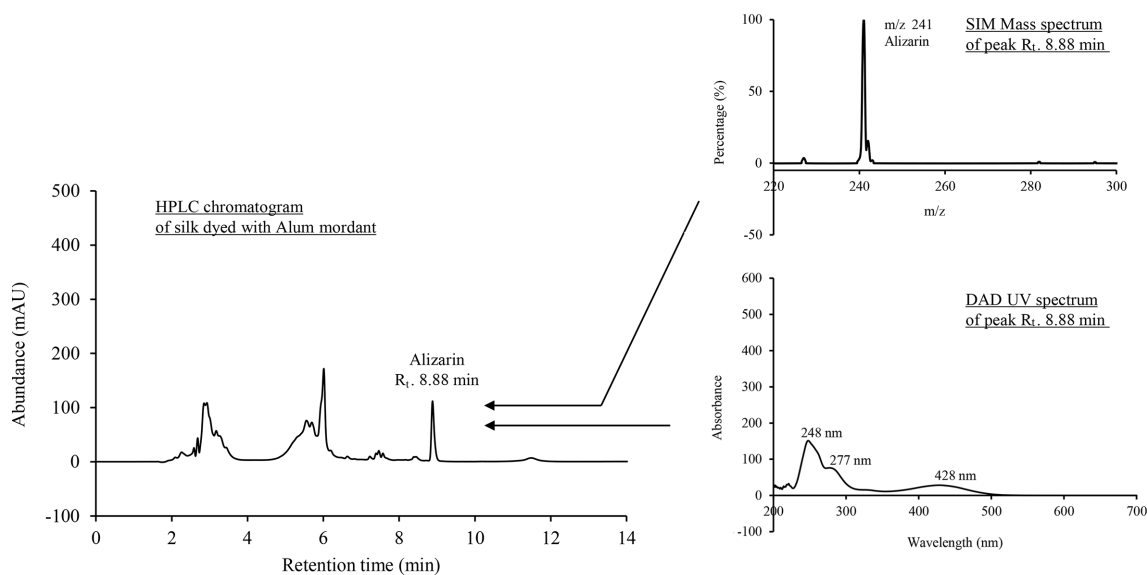


Fig. 5. Result of HPLC-DAD-MS analysis of dye extracted from the silk dyed with madder by alum mordanting.

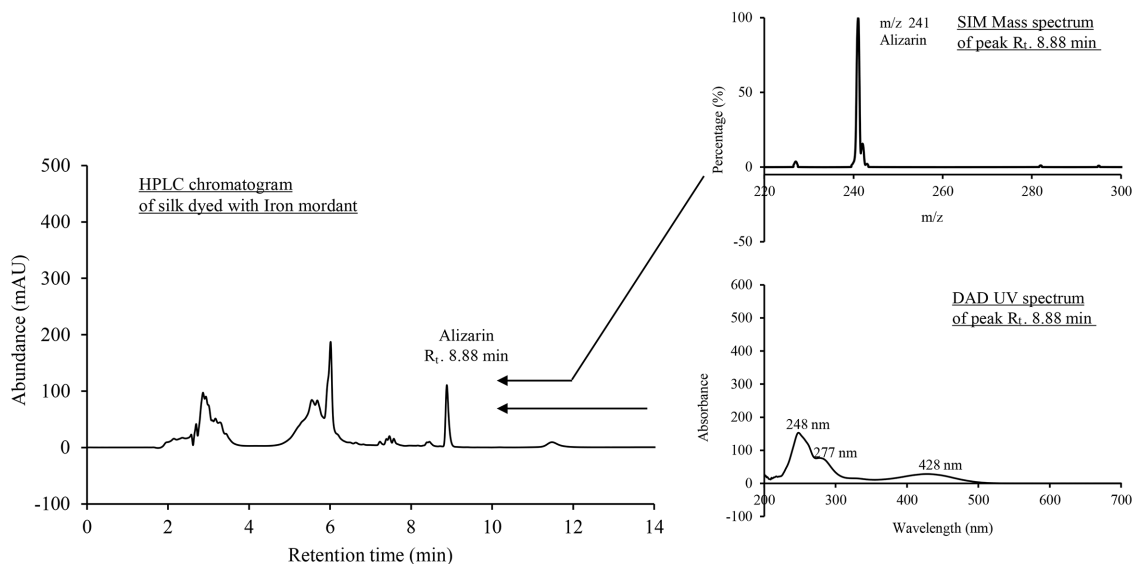


Fig. 6. Result of HPLC-DAD-MS analysis of dye extracted from the silk dyed with madder by iron mordanting.

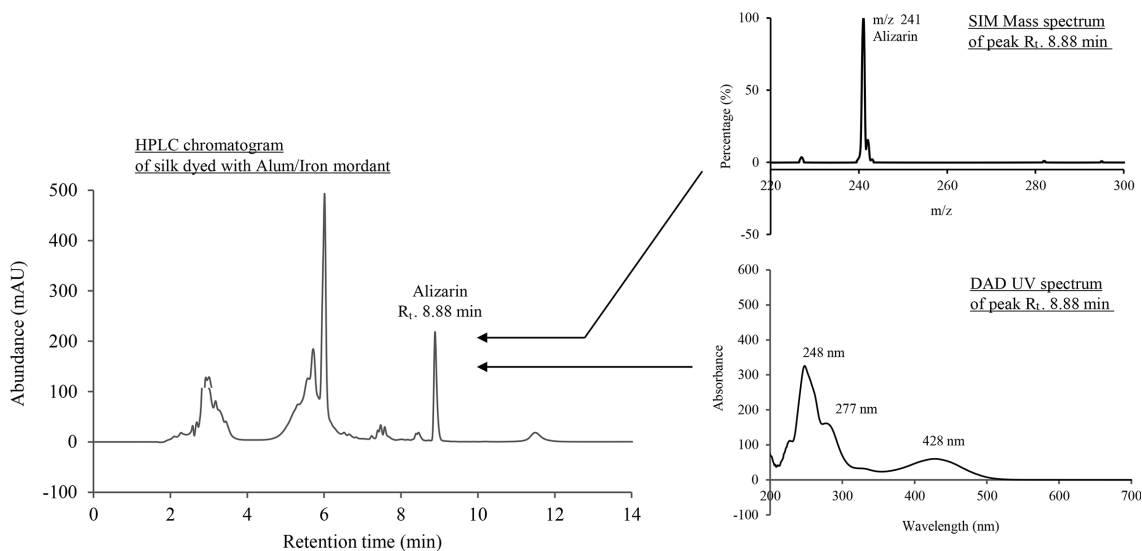


Fig. 7. Result of HPLC-DAD-MS analysis of dye extracted from the silk dyed with madder by both alum and iron mordanting.

the relative areas of the peak at 8.88 min was calculated. The results showed 554.35 mAU for alum mordanted silk, and 579.25 for both iron mordanted silk and alum/iron mordanted silk samples (Table 3). Therefore, the concentration of alizarin in the iron mord-

anted silk and alum/iron mordanted silk were higher than that of the alum mordanted silk. This result suggests that mordanting of silk with iron mordant provides better fixation of alizarin than mordanting with alum mordant alone. However, the quantitative results

Table 3. Relative amount of alizarin in the silk dyed with madder dye represented by the abundance of HPLC chromatogram: Sample before the H₂O₂/UV treatment

| Silk sample | Retention time (min) | Wavelength λ_{\max} (min) | Major ion (m/z) | Abundance (mAU) |
|----------------------|----------------------|-----------------------------------|-----------------|-----------------|
| Alum mordanting | 8.88 | 428 | 241 | 554.35 |
| Iron mordanting | 8.88 | 428 | 241 | 579.25 |
| Alum/Iron mordanting | 8.88 | 428 | 241 | 579.25 |

of HPLC-DAD-MS only partly agrees with the results of K/S values in <Table 1> which indicated that the K/S value of alum/iron mordanted silk (7.076) was much higher than the silk mordanted with iron mordant only (4.109).

Ahmed et al. (2006) explained that the K/S values of the dyed sample provided good linear function of dye concentration when the samples had pale depth of shade. However, when a large amount of dye was fixed on the sample therefore giving a darker shade, the K/S value significantly deviated from the actual dye concentration (Ahmed et al., 2006). Sadi and Hossain (2017) explained that the higher the depth of shade, the lower the % reflectance value measured by the spectrophotometer.

It is probable that the discrepancy between the K/S value and the concentration of dye represented by the abundance of the peak in HPLC chromatogram is due to the high depth of shade of the dyed sample. According to <Table 1> the percent reflectance values of the three silk samples were in the range of 6.215-13.012. Considering that the percent reflectance value of an undyed silk was 77.470, these are significantly low values. And the values suggest that a high amount of dye was absorbed in each pieces of silk.

5. Analysis of Silk after H₂O₂/UV Treatment

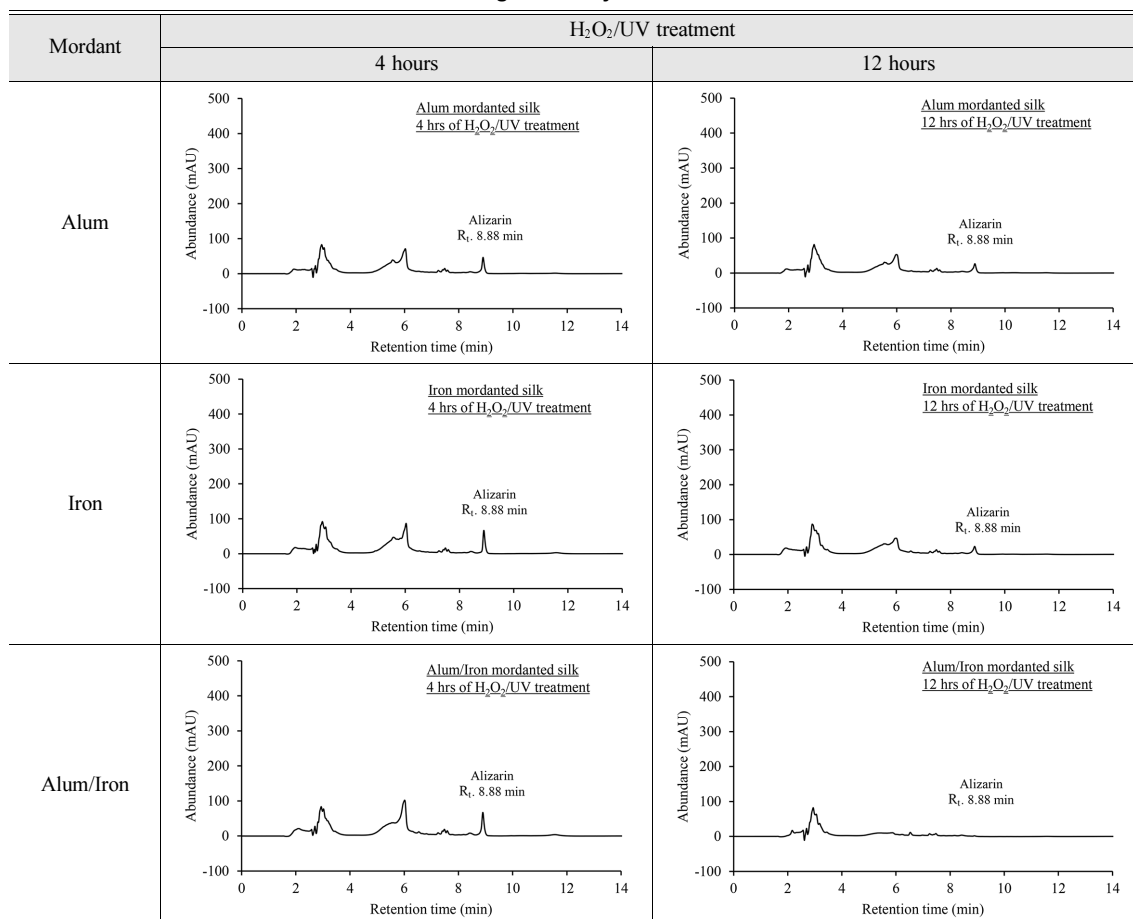
Dyed silk samples were treated with the H₂O₂/UV treatment for up to 12 hours and the results of HPLC-DAD-MS analysis on the 4 hours and 12 hours degraded samples are shown in <Table 4>. Chromatograms within <Table 4> indicate that the peak of alizarin at 8.88 min retention time are decreasing its intensities as degradation progressed up to 12 hours. The peak of 8.88 min was too weak or not present in alum/iron mordant sample after 12 hours of treatment.

<Table 5> shows the amount of alizarin in dyed silk represented by the abundance of the peaks at retention time 8.88 min in HPLC chromatograms. The graphical presentation of data is shown in <Fig. 8>. While iron mordanting provided a high amount of dye fixation on the silk at the point of dyeing, alizarin degraded at a faster rate when iron coexisted with madder dye inside the silk fiber.

Alizarin pigment in madder is attracted to silk protein by weak chemical force such as hydrogen bonding and van der Waals force (Tímár-Balázs & Eastop, 2012). Alizarin is water soluble and has small molecular size (molar mass: 240.21 g · mol⁻¹). Due to weak bonding between alizarin/fiber and also due to small molecular size, alizarin can escape easily from the pores of fiber during and after the dyeing process when the silk is dyed without mordanting. Water soluble small molecule with low chemical bond to fiber makes it easy to leak from fiber in an aqueous medium.

When silk is dyed with madder by mordanting, the metal ion such as aluminum (Al³⁺) or iron (Fe²⁺) forms 'fiber-metal-dye' chelation through coordinate bonding (Ahn et al., 2015; "Chelation", 2018; Khan et al., 2012). Alizarin molecules also form 'dye-metal-dye' chelation among themselves forming a larger dye aggregates within the fiber (Ahn et al., 2014; Ahn et al., 2015; "Chelation", 2018; Khan et al., 2012). The stronger chemical bond with fiber and the larger aggregates of alizarin pigment allow the dye to be attracted and trapped within the pores of fiber, providing a better fastness and better resistance to degradation (Ahn et al., 2014; Ahn et al., 2015; Khan et al., 2012).

Repon et al. (2016) reported that the strength of coordinate bond formed in 'fiber-metal-dye' chelation was higher in iron mordanting than in alum mordanting. Ahmed and Darwish (2012) said that the dyeing results of madder dyeing on silk improved with using

Table 4. HPLC-DAD-MS chromatograms of dyed silk treated with H₂O₂/UV condition**Table 5. Amount of alizarin in madder dyed silk after H₂O₂/UV treatment, represented by the abundance (mAU) calculated from the relative area of the peak at 8.88 min retention time**

| H ₂ O ₂ /UV treatment (hr) | Alum mordanting | | Iron mordanting | | Alum/Iron mordanting | |
|--|-----------------|--------------------------|-----------------|--------------------------|----------------------|--------------------------|
| | Abundance (mAU) | Amount relative to A (%) | Abundance (mAU) | Amount relative to B (%) | Abundance (mAU) | Amount relative to C (%) |
| 0 | 554.35 | 100.00 | 579.25 | 100.00 | 929.50 | 100.00 |
| 0.5 | 237.90 | 45.13 | 239.45 | 43.52 | 449.80 | 49.60 |
| 1 | 213.05 | 40.82 | 281.80 | 50.56 | 410.70 | 45.50 |
| 2 | 214.00 | 40.99 | 225.25 | 41.16 | 395.80 | 43.93 |
| 4 | 179.80 | 35.06 | 244.05 | 44.29 | 271.10 | 30.83 |
| 7 | 167.40 | 32.91 | 174.60 | 32.74 | 130.20 | 16.03 |
| 12 | 137.10 | 27.66 | 132.30 | 25.71 | 58.80 | 8.53 |

iron II sulphate as mordant as well as using iron III chloride and copper sulphate as mordants. Findings of the previous literatures as above support the high

K/S values <Table 1> and the high abundance of HPLC chromatograms <Table 5> of iron mordanted silk over alum mordanted silk in the present investigation.

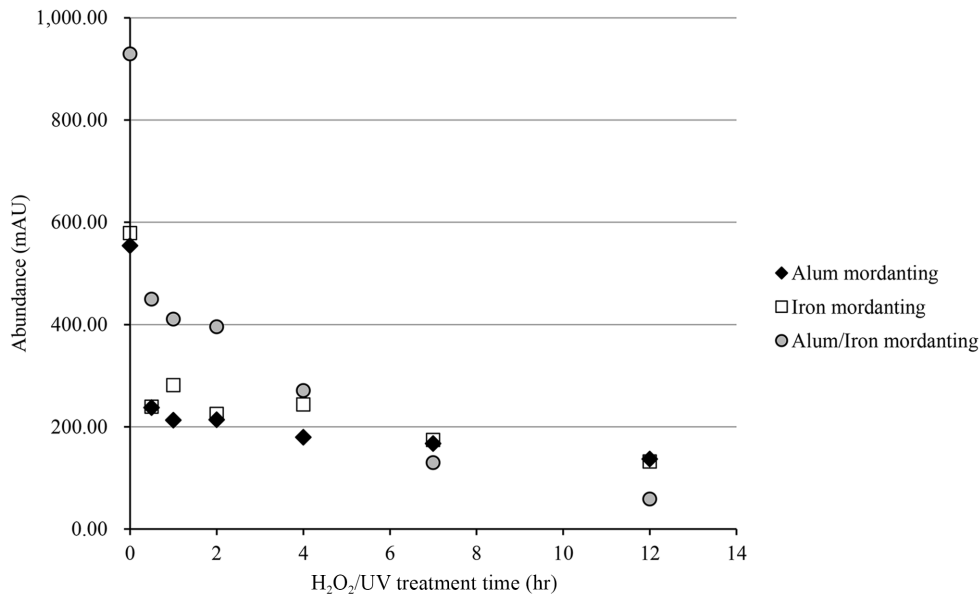


Fig. 8. Change in the amount of alizarin in madder dyed silk after H₂O₂/UV treatment, amount represented by the abundance of the peak at 8.88 min in HPLC chromatograms.

However, the present data suggested that after a long-term degradation in the burial environment, which was simulated by the H₂O₂/UV treatment, mordants influenced the degradation of alizarin pigment of madder, and the degradation was more severe in silk mordanted by iron mordant. Some previous literatures dealt with the burial degradation of natural dyed silk using different mordants, but nonetheless their results did not agree with the results of the present study.

For example, Needles et al. (1986) examined the burial induced changes in the color of natural dyed wool and silk by burying the dyed fabric samples 2.5 cm under sandy loam soil for up to 14 days. Between aluminum potassium sulfate and iron sulfate, iron sulfate mordant showed lower degree of color change than aluminum potassium sulfate (Needles et al., 1986). Yatagai et al. (2001) examined the light induced degradation and color fading of silk fabrics dyed with natural pigment/mordant combination using standard Xenon Fade-Meter (300-700 nm) for up to 40-400 hours. The results indicated that lower color change was observed in silk mordanted with FeSO₄ than in silk mordanted with KAl(SO₄)₂ in both curcumin dyed

and hematoxylin dyed silk samples (Yatagai et al., 2001).

The results of Needles et al. (1986) and Yatagai et al. (2001) agree with the early stage of degradation of this study, up to 4 hours or 7 hours of H₂O₂/UV treatment shown in <Table 5> and <Fig. 8>. However, their results do not agree with present findings when the dyed silk was treated with H₂O₂/UV treatment for more than 7 hours.

H₂O₂/UV treatment used in this study was an accelerated degradation treatment which induced a rapid chemical hydrolysis of dyes (Ahn et al., 2014; Ahn et al., 2015). The treatment was utilized with the purpose of simulating an extensively long-term burial environment. Considering that the H₂O₂/UV treatment was a much severer degradation treatment than the soil burial of Needles et al. (1986) or the light radiation of Yatagai et al. (2001), it is highly likely that with an extensively long-term burial in the burial environment, alizarin is more prone to degradation when the silk is dyed with madder using iron as the source of mordant. Mordanting with alum alone, although it provided a relatively lower dye fixation at the point of dyeing,

may provide a better surviving environment for madder dye within the silk fiber after a long period of burial in the burial environment.

V. Conclusions

This research investigated the effect of mordants on the degradation of madder dye after the madder dyed silk was treated with the H₂O₂/UV treatment. H₂O₂/UV treatment was utilized to simulate the long-term degradation within the soil burial environment. The followings are the findings of the present investigation.

1. Madder dyed silk premordanted by alum/iron composite mordanting showed higher K/S value and higher color difference (ΔE) than the silk mordanted by alum mordanting or iron mordanting. The K/S values and ΔE values were in the order of alum < iron < alum/iron mordanting.

2. Color of silk premordanted with alum showed yellow red hue, and the color shifted to redder YR hue and then to RP hue as the silk mordanting changed to iron mordanting and then to alum/ iron composite mordanting.

3. Presence of alizarin pigment was confirmed in madder dye and in madder dyed silk by 8.88 min retention time of HPLC chromatogram, λ_{\max} at 248 nm, 277 nm, and 428 nm of DAD analysis, and molecular ion m/z 241 of MS analysis.

4. Before the degradation treatment, the concentration of alizarin pigment deduced from the abundance of the peak at 8.88 min of HPLC chromatogram was higher in iron mordanted silk and in alum/iron mordanted silk than that of alum mordanted silk.

5. When madder dyed silk was treated with H₂O₂/UV condition, after 4 hours of treatment the order of remaining alizarin in silk was alum < iron < alum/iron mordanting. However, after 12 hours of treatment the order of remaining alizarin changed to alum/iron < iron < alum mordanting.

The results of present investigation suggest that when madder dyed silk undergoes a short-term degradation in burial environment, the silk dyed with iron mordanting or alum/iron composite mordanting may show a better survival of madder dye, therefore showing

the trace of reddish yellow color. However, when the madder dyed silk undergoes a long-term degradation in burial environment, the silk dyed with alum mordanting may show a better survival of madder dye, therefore showing the trace of yellowish color rather than the reddish yellow color.

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