



Analysis of the Degradation of Dye in the Silk Dyed with Natural Dye-Mordant Combination

Cheunsoon Ahn*, Longchun Li, Incheon National University, Korea
Xia Zeng and S. Kay Obendorf, Cornell University, USA

Keywords: Natural dye, degradation, identification, burial

Textiles excavated from burial grounds exhibit higher degree of color fading than any other textile heritages in the museum collections. The degree of color fading would be greater if there is smaller number of intact dye molecules surviving within the textiles. Most dyeing practices of the past incorporated the use of mordants either before or after applying the dye to the fiber. In order to understand the color fading phenomena of the textile heritages, it is necessary to examine the degradation of dyes in the textiles in relation to the past dyeing practices which incorporated different dye-mordant combination. While earlier studies such as Crews (1982) and Crews (1987) provide useful information on the light fastness of museum textiles for conservation and display, it is still unanswered whether different mordants are responsible for the different degree of color fading in the textiles excavated from the burial grounds.

The purpose of this research was to investigate the effect of different mordants on the degradation of dye in the silk dyed with five standard dyes, alizarin, purpurin, berberine, palmatine, and indigotin after treating the dyed silk with H₂O₂/UV treatment. H₂O₂/UV treatment was used to simulate the burial degradation of textiles based on the fact that underground soil is rich in H₂O₂ due to the excretion of oxidases by various micro-organisms (Martinez et al., 2005) and also by the accumulation of rainwater (Petigara et al., 2002). H₂O₂ would accumulate in the textiles during burial and when the textile meets the UV light during excavation, the H₂O₂ would react with the UV light, initiating the degradation of dye.

Berberine chloride form (berberine in the following) (97%), palmatine chloride hydrate (palmatine in the following), alizarin, purpurin (90%), and indigotin (95%, synthetic) purchased from Sigma-Aldrich were used as the standard dyes. Aluminum potassium sulfate [AlK(SO₄)₂·12H₂O], iron sulfate (FeSO₄·7H₂O), copper sulfate (CuSO₄), and tannic acid of Chinese natural gall nut (C₇₆H₅₂O₄₆) were used as mordants. Hydrogen peroxide (30%) was used in the degradation process. Methyl alcohol (HPLC grade) and HCl (38%) were used to extract the dye from the silk samples. Dimethyl sulfoxide (DMSO, LC grade) was used to prepare the standard dye for calibration. Acetonitrile (HPLC grade), HPLC water, and formic acid (88%, ACS grade) were used in the HPLC analysis. Silk used for dyeing was the Standard Adjacent Fabrics for Colorfastness (KS K0905) 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).

A 0.5 g/L each of aluminum potassium sulfate, iron sulfate, copper sulfate, and tannic acid were used to mordant a 24 cm x 24 cm sized silk (2.96g) for 60 min at 60°C with 1:100 liquor ratio. Mordanted silk was dyed with each standard dye using a 2 % o.w.f. dye concentration in water with 1:00 liquor ratio. Dyeing was carried out for 60 min at 60°. Each sample was cut into 4 cm x 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 for each degradation time. The vials were placed under a 8 Watt 365 nm UV lamp (UVL-28, Upland, CA). 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 instrumental protocols of the HPLC-DAD-MS analysis of this research followed the method used in Ahn et al. (2015).

All samples showed a dramatic decrease in pigment concentration within 30 minutes of H₂O₂/UV treatment with the greatest change occurring in the silk dyed with alizarin/copper followed by alizarin/alum and alizarin/iron dye/mordant combinations. Berberine and palmatine dyed with tannin mordant showed a higher resistance to degradation than any other mordant combination. The high resistance of berberine/tannin and palmatine/tannin to degradation was notable especially since the degradation of samples such as berberine and palmatine with iron and copper mordants was severe enough to lose most of their pigments during the first 30 minutes of treatment. Indigotin combined with copper mordant exhibited an extremely high dye concentration in the control and the degraded samples. The concentration of dye in the indigotin/copper mordant sample before treating with H₂O₂/UV degradation was 0.99 mg/mL which was about 4.7 times higher than alizarin/iron mordant sample and about 20 times higher than indigotin dyed with other mordants. Such high concentration of indigotin in the copper mordanted sample was due to the formation of indigotin-Cu(II) chelate within the silk fiber and this subject will be discussed below.

References

- Ahn, C., Zeng, X., & Obendorf, S. K. (2015), HPLC-DAD-MS analysis of major natural dyes with the application of H₂O₂/UV treatment as a way to simulate burial degradation of textiles. *Textile Research Journal*, 84(3), 238-250.
- Crews, P. C. (1982). The influence of mordant on the lightfastness of yellow natural dyes. *Journal of the American Institute for Conservation*, 21, 43-58.
- Crews, P. C. (1987). The fading rates of some natural dyes. *Studies in Conservation*, 32(2), 65-72.
- Martinez, A. T., Speranza, M., Ruiz-Duenas, F. J., Ferreira, P., Camarero, P., Guillen, F., Martinez, M. J., Gutierrez, A., & del Rio, J. C. (2005). Biodegradation of linocellulosics: Microbial, chemical, and enzymatic aspects of the fungal attack of lignin. *International Microbiology*, 8(3), 195-204.
- Petigara, B. R., Blough, N. V., & Mignerey, A. C. (2002). Mechanism of hydrogen peroxide decomposition in soil. *Environmental Science & Technology*, 36(4), 639-645.