Research Paper>

## Dyeability of Fabrics by Malt-fermented Materials and Mineral Water Mordanting -Effect of Mordanting with Hwangsu(mineral water) of Yeongcheon, Korea-

## Youngmi Park

Department of Clothing and Fashion, Yeungnam University, Gyeongsan, Korea

(Received: November 30, 2012 / Revised: December 12, 2012 / Accepted: December 22, 2012)

**Abstract:** This study examined the dyeing characteristics of five oriental herbs, namely *Gardenia jasminoides*, *Sophora japonica L., Rheum coreanum, Rhus javanica L., Ginkgo biloba L.*, on fabrics with traditional fermentation using malt. And the properties of Hwangsu (mineral water) of Yeongcheon (Korea)as a mordant in the post-treatment of textile were evaluated. The dyeability and fastness of cotton fabric and silk to light and washing as well as different fermentation periods and temperatures were investigated, and the following results were obtained. The dyeability of the fermented and non-fermented material did not show a significant difference. Fabrics mordanted with Hwangsu generally exhibited a reddish color due to the presence of iron. The dyeing of cotton fabric and silk by fermentation and Hwangsu mordanting were found to be effective on *Rhus javanica L.* and *Rheum coreanum*. These results were confirmed through fastness to light 3 of cotton on *Rheum coreanum* and 3-4 of silk on *Rhus javanica L.*, respectively. The washing fastness of both fabrics dyed with fermented *Rhus javanica L.* and *Rheum coreanum* was improved, showing higher K/S value after washing than before washing.

Keywords: fermentation dyeing, mineral water, Hwangsu(mineral water), malt, Yeongcheon(Korea)

## 1. Introduction

The utility of environment-friendly products and changes in customers' views compared to synthetically dyed products are expected to lead the future perspective on product development in a positive direction but most studies including papers on the environment<sup>1-7</sup>) or patents<sup>8-11</sup> have failed to overcome the ultimate drawback of the weak color fastness insufficient dyeability that the customer demands.

This study evaluated a fundamental solution of the problems and tested the 5 most frequently used materials in natural coloring. The 5 materials were extracted using fermentation and non-fermentation methods and compared to determine if there were any differences in color uniformity and fastness.

Fermentation dyeing was the first attempt to link the properties generated by the work of microorganismsused frequently in industries other than the textile industry with the denaturation of materials and its effect on the change in colors to adapt the process to the textile industry. Fermentation dyeing should consider the possible changes to the pigments during the dyeing process, and the dyed products need to be compared with those dyed with non-fermentation materials to determine the difference in color change.

Traditional dyeing and general natural dyeing can be considered the same in that both use materials available in nature but have different processes of extracting the materials. That is, the natural dyeing in this study refers to a dye process using dyes extracted hydro thermally at high temperatures, and traditional dyeing refers to the extracting process of first fermenting the materials using malt and then extracting the pigment at room temperature. Malt is a starter culture made by fostering mold possessing alcoholproducing enzymes on grains, and has been used most widely in the process of fermenting dyes.

This study used Hwangsu, a famous mineral water from Yeongcheonsi, Gyeongsangbukdo, as natural mordant to replace the chemical mordant that is blamed for environmental pollution. Hwangsu was regarded as precious medicinal spring water in earlier times, but is currently unsuitable for drinking because of the

<sup>&</sup>lt;sup>†</sup>Corresponding author: Youngmi Park (ymp9397@yu.ac.kr) Tel.: +82-53-810-2791 Fax.: +82-53-810-4687 ©2012 KSDF 1229-0033/2012-12/270-280

harmful effects of its heavy-metal content on human health. This study first confirmed the existence of mordant ingredient through composition analysis and then selected it as a mordant.

This study analyzed the color difference and fastness of fabrics dyed using existing dyeing methods, which is known as natural dyeing, and the dyeing method suggested by this paper, i.e. using the dyes extracted after fermentation through natural starter culture malt, and evaluated the various dyeing results using traditional fermentation dyeing. This study did not use any of synthetic mordants, such as iron, copper, aluminum etc., but used Hwangsu, which is ground mineral water, as a natural mordant to evaluate the results of dyeing, and provide ground for practical applications to product manufacturing. These results are expected to assist in the development of dyes, improvements in dyeing methods and applications to products, and provide a source in the process of environment-friendly natural dyeing products.

## 2. Experiment

#### 2.1 Materials

The materials used in this study were 5 kinds of oriental herbs, *Gardenia jasminoides* (Gardenia), *Sophora japonica L.* (Sophora), *Rheum coreanum* (Rheum), *Rhus javanica L.* (Rhus), *Ginkgo biloba L.* (Ginkgo), which were purchased from Omniherb.Co., Ltd. Korea. Hwangsu mineral water from mineral water spring located in Gokyungmeon, Yeongheonsi, Gyeongsangbukdo was used as the natural mordant. Cotton fabric and silk were purchased from Seomun Traditional Market in Daegu, and the malt and starch syrup were provided by Songhakgokja located in Gwangju, Korea. The density of plain cotton  $(100g/m^2, 0.25mm)$  and satin silk  $(42g/m^2, 0.11mm)$  was  $73 \times 74/inch^2$  and  $160 \times 98/inch^2$ , respectively.

# 2.2 Fermentation by malt of a natural dye and extraction

## 2.2.1 Composition ratio of fermentation

Malt and starch syrup are used mainly for the fermentation of materials.

Table 1 lists the composition ratio of fermentation of each material.

## 2.2.2 Fermentation conditions

For fermentation dyeing, the material, water, malt and starch syrup were mixed and left to ferment at given temperature. Table 2 lists the fermentation periods and temperature/humidity conditions. The fermented dyes were collected and extracted on a weekly basis.

## 2.3 Analysis of Hwangsu as a natural mordant

To check the composition of Hwangsu, two specimens were collected once every month in 2012. Water quality analysis was conducted by first separating the cation and anion specimens for analysis, and then analyzing for the solid matter, organic matter, anion and conductivity (water temperature 12.9°C) using a Ion Chromatography (Dionex IC 25, Scientific Support, Inc., US).

Table 1. Mixing ratio of the dyeing materials used

Dyeing Materials	Mixing Ratio
Gardenia jasminoides, Sophora japonica L., Rheum	Each Materials : Nuruk : starch syrup = 500g : 25g : 25g
coreanum, Rhus javanica L., Ginkgo biloba L.	Each Matchais . Nuruk . statch syrup – 500g . 25g . 25g

Table 2. Fermentation conditions of the dyeing materials

Times	Temperature	Humidity	рН	Date
1	21.0°C	15%	5.6	10 days
2	23.0°C	14%	6.5	24 days
3	23.0°C	14%	6.2	59 days

The metal content was analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, OPTIMA 3000, Perkin-Elmer, US).

## 2.4 Dyeing and mordanting

Dyeing was performed using the most widely used batch dyeing regardless of the extraction conditions of colorants. For general coloring, the material and water was mixed in a 20L coloring container, the temperature was increased to 70°C and immersed fabrics, dyed for 20 min with stir, and then washed. For mordanting, 2L of Hwangsu and 2L of ionized water were mixed and increased temperature up to 23°C and reacted for 10min with maintaining pH 2.6. After fermentation, the liquid was then filtered to obtain the dye, washed, mordanted at and then washed several times. Table 3 lists the specific conditions for fermentation and non-fermentation dyeing.

## 2.5 Color shade of the surface and reproducibility of colors

The color shade of the dyed fabric was measured using Color eye-3100 (Gretag Macbeth, US) to determine the brightness of the color L\*. The chromaticity is represented by a\*, b\*, h, and the C values.

The viewing conditions were set to the D65 illuminant/10°standard observer system in 400 - 800 nm. The *K/S* value was calculated using Kubelka- Munk after measuring the surface reflectanceat the maximum absorption wave.

 $K/S = (1-R)^2/2R$ , where R refers to the decimal fractions of the reflectance, K is coefficient of light absorption, and S is scattering coefficient for dyed fabrics at  $\lambda$ max, respectively.

## 2.6 Observation of surface structure through change of surface colors

The change in surface color of the fabric after dyeing was observed with the naked eye, and pictures were then taken to compare the colors.

## 2.7 Prevention of dyeing stain

This paper made a direct judgment by a naked eye observation because there is no official standard to judge the prevention of dyeing stain. Any unlevel dyeing of the fermentation colored cotton fabric and silk was assessed by the naked eye.

#### 2.8 Color fastness to light and washing

To measure the durability of the fabric after dyeing, the fastness to light was evaluated using Blue-wool scale after 20 hrs exposure to a Xenon-arc (ATLAS Ci-4000, Atlas Co. Ltd. US) light in compliance with KS K ISO 105-B02: 2010. The fastness to washing was measured after washing using LAUNDER-O-METER (DONG YANG, MODEL: D7-0850) in compliance with KS K IOS 105-C06. Subsequently, the L\*, a\*, b\* and the *K/S* value was calculated using a color-difference meter (Macbeth color-Eye 3100).

## 3. Results and Discussion

## 3.1 Property of Hwangsu

Table 4 lists the analysis results of Hwangsu of Gogyung, Yeongcheon, which can't drink anymore and was collected twice within a certain period of time. The iron content was highest (414.9 mg/L), followed in order by aluminum (88.9 mg/L) and manganese (4.9 mg/L, water temperature at 12.9°C).

Dyeing Conditions									
Fabrics	Weight	Dyestuff	Water	Temperature	Time	Bath ratio			
Cotton	19g	1.5L	3L	70°C	20 min	1:60			
Silk	13g	1L	2L	70°C	20 min	1:60			
		]	Mordant Condition	ns					
Sample	Weight	Water	Temperature	Time	рН	Bath ratio			
Hwangsu	2L	2L	23°C	10 min	2.6	1:100			

Table 3. Dyeing and mordant conditions

Analysis Item		Results	
Electric Conductivity (µs/cm)		4.41	
Metal Content	Fe	Al	Mn
(mg/L)	414.9	88.9	4.9
Solid Matter	TDS	FDS	VDS
(mg/L)	2,416±10	2,051±23	364±13
Solid Matter After Ion Removal	TDS	Inorganic Acid (FDS)	Humic Acid (VDS)
(mg/L)	29.0±1.4	3.0±1.4	26.0±2.8
Organic Matter (Humic acid)	TOC	COD	
(mg/L)	2.5	9.4	
Anion Ion	F, NO <sub>2</sub> , Br, NO <sub>3</sub> , PO <sub>4</sub> <sup>3-</sup>	Cl	$SO_4^{2-}$
(mg/L)	ND	15.5	1,970

Table 4. Assay of mineral water Hwangsu

T; Total, D; Dissolved, S; Solution, F; Fixed, V; Volatile, ND; No Detect

The figures were slightly higher than those of the 2008 analysis conducted by the Gyeongsangbukdo Research Institute of Public Health & Environment (iron, aluminum and manganese content were 156, 24, 3.2 respectively). On the other hand, when the oxidation of iron and dissolved form was considered, the analysis results of different analysis times and from different institutes showed that inorganic matter was contained at the level that could be ignored, regardless of the surroundings. That is, the analysis or organic and inorganic matter in Hwangsu confirmed that the amount was not large enough to affect dyeing. In addition, the other organic and inorganic matter except for those mentioned above were not the main factors causing a change in dveing property. The level of sulfate ions combined with iron and aluminum ions were similar: 1441 mg/L on the 2008 analysis, 1137 mg/L 3 years later on 2011 September 19th and 1970 mg/L one month after on October 4th  $2011^{12}$ 

On the other hand, the level of organic matter except for the heavy metal ions exhibited an almost 50% (575: 461 mg/L) ratio to inorganic matter, but its effect on dyeing or mordanting did not appear to be large. The pH of hydrogen ions was 2.5 on the 2008 analysis and 2.6 on October 2011, suggesting that it was a strong acidic aqueous solution. Therefore, the fact that no color differences appeared when each metal ion was dissolved but only appeared when Hwangsu was used as a mordant, exhibiting bright reddish color, confirmed that it could have been largely affected by the metal components in Hwangsu, i.e. iron, aluminum, copper.

## 3.2 Color shade of fermented Gardenia jasminoides

The effort of a superior synthetic fabric to counteract the organic properties of natural fabric focused on the form and hygroscopic properties together with improved coloration. In particular, the coloration improvement of PET, which is considered highly economical for cloth and used widely, has attracted considerable interest, and studies on cotton fabric, which lacks coloration in natural dyeing, have been conducted steadily. In this study, the materials were extracted by first fermenting various colorants with malt microorganisms. The fermentation dyed test cotton fabric and silk, post-treated the test fabrics with the natural mordant-Hwangsu.

After dyeing, the coloration of the fabric was measured by the K/S value from computer color matching system (CCM, X-Rite 8200, USA).

Gardenia is one of the most famous oriental materials capable of dyeing yellow. As shown in Table 5, both cotton fabric and silk were dyed acceptably with the fermentation dye. Mordanting of Hwangsu did not produce a difference in cotton and silk.

Sample	Туре	Days	L*	a*	b*	С	h	R	K/S
	Received	0	83.81	-0.35	0.59	0.69	120.38	61.96	0.12
	Non mondont	10	76.85	3.64	37.91	38.09	84.52	20.90	1.49
Cotton	Non-mordant	24	80.12	-0.01	21.73	21.73	90.02	43.06	0.58
	Unionega	10	74.81	4.58	37.82	38.09	83.10	19.61	1.65
	Hwangsu	24	78.51	0.70	21.41	21.43	88.13	34.52	0.62
	Received	0	81.60	-0.02	3.83	3.83	90.24	49.78	0.25
	Non-mordant	10	64.27	-6.07	30.67	31.27	101.2	13.81	2.69
Silk	Non-mordant	24	68.12	-3.46	20.06	20.36	99.78	24.55	1.16
	Uwonggu	10	62.60	-4.91	27.56	28.00	100.1	13.94	2.66
	Hwangsu	24	65.20	-2.75	19.37	19.56	98.08	18.08	1.86

Table 5. Color characteristics of cotton and silk dyed with fermented Gardenia with and without Hwangsu after a fermentation period of 10 and 24 days

Table 6. Color characteristics of cotton and silk dyed with fermented Sophora with and without Hwangsu at fermentation times of 10 and 24 days

Sample	Туре	Days	L*	a*	b*	С	h	R	K/S
	Received	0	83.81	-0.35	0.59	0.69	120.38	61.96	0.12
-	Non-mordant	10	81.72	-5.44	17.35	18.18	107.42	14.55	2.51
Cotton	Non-mordant	24	80.21	-5.44	18.39	19.17	106.47	13.55	2.76
-	11	10	66.63	0.13	12.54	12.55	89.40	21.91	1.39
	Hwangsu	24	65.11	-0.59	12.89	12.90	92.64	21.67	1.42
	Received	0	81.60	-0.02	3.83	3.83	90.24	49.78	0.25
-	Non-mordant	10	77.33	-3.63	19.70	20.03	100.43	8.11	5.21
Silk	Non-mordant	24	75.62	-3.47	23.94	24.19	98.25	5.92	7.48
	11	10	57.06	-1.03	22.60	22.63	92.60	8.22	5.12
	Hwangsu	24	52.76	-0.86	24.93	24.94	91.98	6.20	7.10

On the other hand, as the fermentation period in increased, the a\* value for cotton fabric with fermented dyeing and non-mordanting and that with fermented dyeing and Hwangsu mordanting increased compared to the non-fermentation dyed fabric. For silk, all the values were smaller than those of the non-fermentation dyed fabric. In addition, the K/S value of cotton fabric, whose fermentation period was 24 days after the first fermentation, decreased by more than 50%, and the K/S value of silk was lower than that observed in the beginning.

On the other hand, the K/S value of the two fabrics showed the better result 10 days after fermentation, when compared with the received sample. The reason for this is illustrated by the b\* value, which is the representative color of Gardenia. The b\* value of 0.59 prior to fermentation peaked to more than 30 when extracted and dyed 10 days after fermentation, and it decreased there after.

## 3.3 Dyeability of fermented Sophora japonica L,

As shown in Table 6, Sophora like other fermented materials exhibited a better result for silk that the fermentation greatly increased the dyeability after 10 days compared to non-fermentation. In terms of the fermentation period between 10 and 24 days, dyeability of cotton did not show much change with time. On the other hand, the K/S value of silk show a tendency to rise as increasing of the fermentation time.

In particular, for cotton, the K/S value was declined about twice by mordanting with Hwangsu than nonmordanting, whereas the silk did not show a much difference with mordant. The reddish value of the two fabrics decreased slightly and the yellowish increased with time owing to the effect of iron in Hwangsu.

## 3.4 Dyeability of fermented Rheum coreanum

Traditionally, Rheum dye is generally used with a

strong alkali mordant. Such as calcium hydroxide. Table 7 presents the results of fermentation coloring of Rheum. As the K/S value was increased continuously after 24 days fermentation, a longer fermentation period would produce a good result by fermentation. For Hwangsu, an elevated K/S value was exhibited on cotton when the mordant was not used.

A significantly higher value was observed for silk compared to that of the non-fermented material but the use of a mordant did not increase the coloration significantly. This is due to the property of Rheum mentioned earlier, in that an alkali mordant works better than the strongly acidic Hwangsu.

## 3.5 Dyeability of fermented Rhus javanica L.

Rhus is the gall of a sumac that contains more than 50% of tannin, and it is common to perform

combination dyeing with low fastness materials because it exhibits higher fastness than other materials. Cotton fabric dyed with fermented Rhus exhibited a low K/Svalue, as shown in Table 8, meaning poor fermentation dyeability. Because the K/S value of Rhus is far lower than the other materials, the fermentation effect is not large.

For silk dyeing, mordanting with Hwangsu was found to be more effective. The dyeing result of silk after fermentation favored short tern fermentation (within 10 days) just like *Gardenia jasminoides*.

## 3.6 Dyeability of fermented Ginkgo biloba L,

The used Ginkgo leaves were green. So the content of chlorophyll was very high and then change of color to brown by heating is also easy. It means that the coloration to green was hardly dyed with or without

 Table 7. Color characteristics of cotton and silk dyed with fermented Rheum with and without Hwangsu at fermentation times of 10 and 24 days

Sample	Туре	Days	L*	a*	b*	С	h	R	K/S
	Received	0	83.81	-0.35	0.59	0.69	120.38	61.96	0.12
-	N	10	75.44	3.75	17.19	17.59	77.69	31.99	0.72
Cotton	Non-mordant	24	75.21	1.78	18.09	18.18	84.38	32.11	0.72
-	I I	10	61.36	0.71	7.02	7.05	84.24	22.03	1.38
	Hwangsu	24	60.66	0.97	6.85	6.92	81.94	23.06	1.28
	Received	0	81.60	-0.02	3.83	3.83	90.24	49.78	0.25
-	N	10	70.52	0.83	35.08	35.09	88.65	14.35	2.56
Silk	Non-mordant	24	75.21	1.78	18.09	18.18	84.38	11.90	3.26
-	I I	10	56.44	-1.89	19.56	19.65	95.51	12.11	3.19
	Hwangsu	24	75.70	2.41	11.73	11.98	78.39	10.97	3.61

Table 8. Color characteristics of cotton and silk dyed with fermented Rhus with and without Hwangsu at fermentation times of 10 and 24 days

Sample	Туре	Days	L*	a*	b*	С	h	R	K/S
	Received	0	83.81	-0.35	0.59	0.69	120.38	61.96	0.12
	NT 1.4	10	83.12	-0.79	3.86	3.95	101.60	50.58	0.24
Cotton	Non-mordant	24	82.31	-1.00	4.73	4.84	101.94	46.68	0.31
	TT	10	49.15	1.85	-2.95	3.49	302.11	47.70	0.29
	Hwangsu	24	59.87	1.47	0.68	1.62	24.97	25.73	1.07
	Received	0	81.60	-0.02	3.83	3.83	90.24	49.78	0.25
		10	77.84	0.00	9.15	9.15	90.03	34.44	0.62
Silk	Non-mordant	24	77.40	-0.02	11.07	11.07	90.09	30.97	0.76
	TT	10	51.17	1.79	-2.54	3.11	305.19	18.87	1.74
	Hwangsu	24	55.59	1.67	-0.47	1.74	344.25	15.66	1.44

the use of a mordant or fermentation. That is, when the pigment component, chlorophyll, turns brown, it is denatured and loses its original properties, resulting in a low chemical reaction between molecules. As shown in Table 9, both cotton fabric and silk exhibited low dyeability, and the K/S value was similar to that of non-fermented dye.

## 3.7 Fastness to light and surface color

Table 10 shows the result of the fastness to light and the observation of structural formation through the change in surface color. The surface color was estimated before light-fastness testing. A naked eye observation of the color changes after dyeing confirmed the difference indicated by the dyeing number of times and fermentation period. Generally, the color became darker with increasing the number of dyeing times. This was attributed to the physicochemical treatment by contact, which is a property of natural dyeing, as the number of dyeing times was increased. The surface color by fermentation dyeing of various

fermentation periods and the effect of the mordant was observed.

Actually, the fabrics after natural dyeing, when the grade of light fastness over 3 is can be say reasonable for use, meanwhile, the grade lower than 1 needs definitely mordant or more treatment for improving the fastness. From Table 10, the cotton by different mordants used exhibited high light fastness as grade 3.

On the other hand, for silk, the result appeared to be good by the surface observation, but the fastness to light after 20 h exhibited a lower grade 1-2 than before. This was not caused by the fermentation period, but was attributed to the problem between the chemical affinity site and the functional group of the specimen. The temperature and pH in the fermentation process of the dye are believed to be the largest factor, and highlights the need for further studies on varying the fermentation temperature and pH.

Through the fastness of light, it is considered that the Gardenia would better not ferment than 10 days over fermentation. When exposed to light after nonmordanting and the Hwangsu-mordant, both cotton and silk exhibited moderate grade 1-2. Gardenia also calls for further studies on pre-mordanting, and on the dyeing conditions, such as the types of dye (origin, freshness), temperature of dyeing, time etc.

Sophora dyed fabrics exhibited slightly better results with non-fermentation than fermentation, and the alkaline mordant was found to be more effective for mordanting.

The Sophora dyed cotton which fermentation period is 10 days exhibited a relatively high fastness grade 3 and then still maintained a good grade after 24 days fermentation. Similar to dyeability, it exhibited a very satisfied fastness with 4 for silk under non-mordanting. The light fastness of Sophora is better without mordant than with mordant, hence additional experiments on varying the fermentation conditions are required.

Sample	Туре	Days	L*	a*	b*	С	h	R	K/S
	Received	0	83.81	-0.35	0.59	0.69	120.38	61.96	0.12
	Non-mordant	10	82.44	-1.12	3.69	3.85	106.89	46.07	0.32
Cotton	Inon-mordani	24	83.30	-0.39	1.65	1.70	103.36	58.49	0.15
	Umanagu	10	81.03	-0.45	9.59	9.6	92.71	37.96	0.51
	Hwangsu	24	81.13	-0.34	7.88	7.89	92.48	41.32	0.42
	Received	0	81.60	-0.02	3.83	3.83	90.24	49.78	0.25
	Non montout	10	80.09	-0.45	6.04	6.06	94.24	37.93	0.51
Silk	Non-mordant	24	79.39	0.17	6.68	6.68	88.5	41.48	0.41
	Umanagu	10	73.32	0.95	11.71	11.75	85.34	25.70	1.07
	Hwangsu	24	75.56	1.56	9.21	9.35	80.39	32.09	0.72

Table 9. Color characteristics of cotton and silk dyed with fermented Ginkgo leaf with and without Hwangsu at fermentation times of 10 and 24 days

Fermented Plants	Days*	Fabric	Mordant	Grade**	Surface Color***	Stain or spot
Candonia ineminoidos	10	Cotton	Non	1-2		No
Gardenia jasminoides	10	Silk	Hwangsu	1-2		No
		Cotton	Hwangsu	3		No
	10	0:11-	Non	4		No
Sanhaun impanian I		Silk	Hwangsu	1-2		No
Sophora japonica L.		Cotton	Hwangsu	3		A little
	24	Silk	Non	2		No
		Slik	Hwangsu	2		No
		Cotton	Hwangsu	3		No
	10	Silk	Non	3		No
DI			Hwangsu	2		No
Rheum coreanum		Cotton	Hwangsu	3		A little
	24	0:11-	Non	1-2		No
		Silk	Hwangsu	1-2		No
	24	Silk	Non	3-4		No
Rhus javanica L.	24	Silk	Hwangsu	2-3		No
	10	0.11	Hwangsu	1-2		No
Ginkgo biloba L.	24	Silk	Hwangsu	1-2		No

Table 10. The fastness of light and surface color of cotton and silk by fermentation dyeing depends on mordant

\*; fermentation time, \*\*; light fastness, \*\*\*; washed color after dyeing but before washing fastness

The dyeability of cotton with Rheum when the mordant treated with Hwangsu resulted in grade 3 fastness.

The durability of cotton did not decrease even with a prolonged fermentation time, but silk demonstrated weaker fastness to light because it was left to ferment longer. This suggests that even if the outcome of dyeing appears dark enough to the appearance eye, like after Hwangsu mordant, the actual evaluation can differ, and data to prove the durability result for natural dyeing must be presented. Although the fastness to light for Rheum was very good (> grade 3), its original yellow color was not realized through Hwangsu mordant, which indicated that the coloration function as a natural dye is far from good. Although the K/S value after dyeing with Rhus was quite low, it showed higher than grade 3 of light fastness for non-mordant and Hwangsu mordant.

Especially, Rhus exhibited better coloration of nonfermentation than mordanted samples after 24 days. The coloration of cotton could not be identified by the naked eye. Therefore, only the fastness of silk was analyzed, which exhibited superior durability of higher than grade 3, even which is quite different from the naked eye observation.

An analysis of Ginkgo showed slightly better dyeability for silk than cotton. On the other hand, the fastness to light after 10 and 24 days was similar at a low grade 1-2.

As described above, the use of a mordant can im-

prove the dyeability, but fundamental fading by light can diminish the fastness due to the heavy metals contained in the mordants, whereas a perfect chelate bond would sustain the dyed color and retain durability. Therefore, the reaction mechanism of dyes by fermentation should be researched continuously.

## 3.8 Dyeing stain

Generally, it is considered that the dyeing stains are made when the dye spreads rapidly to the surface of the fabric due to the hygroscopic property of the fabric, adhesive property of the dye component to the fabric and hydrophilicity of the dye etc. When dyeing stains were checked with appearance eye, few cases exhibited stains. Table 11 shows the incidence of dyeing stain in cotton showing good dyeability by the naked eye in case of Rheum and fermented Sophora, whereas cotton dyed with Gardenia, Rhus and Ginkgo could not found the stain. Silk did not exhibit any stain for any of the materials. These materials can be refined or combination dyed to realize the indigenous color of natural dyeing.

#### 3.9 Fastness to washing

The fastness to washing was evaluated using a K/S value before and after washing which means not washing after dyeing but fastness washing. The (a) and (b) in Figure 1 shows the K/S value of cotton with and without Hwangsu and (c) and (d) also represent the K/S value of silk with and without Hwangsu, respectively.

For the cotton dyed with Gardenia without Hwangsu (a), the K/S value after washing was decreased by about 50% but a small decrease was discernible when with Hwangsu (b).

Nevertheless, the difference was not significant. Silk produced a good dyeing outcome for all the fermented materials, and its strong fastness to washing resulted in a much larger increase. In particular, silk dyed with Rhus exhibited a remarkable increase both for the case of without (c) and with Hwangsu mordant (d), showing high from 1.7 to 10.4. These results probably seems when the dye molecules after fermentation were rearrangement by washing, the weak bonded molecules were broken and secession, on the

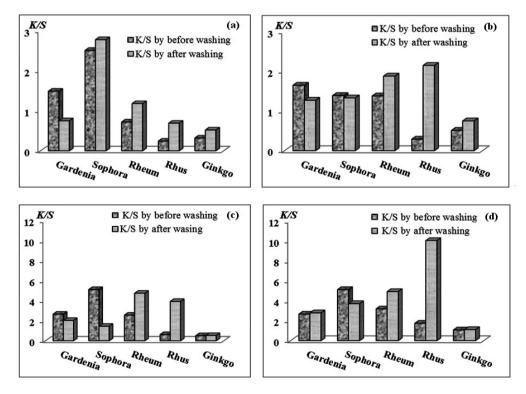


Figure 1. Fastness of washing based on the K/S value of cotton without (a) and with (b) and silk without (c) and with (d) Hwangsu after 10 days of fermentation.

other hand, fermented fully enough molecules were bonded with fabrics stably.

Gardenia and Sophora tend to show lower durability by fermentation, whereas Rheum and Rhus were more effective when fermented. As for Ginkgo, the K/Svalue was sustained or increased through fermentation but dyeing after fermentation was not effective considering that the dyeing outcome was barely identifiable. The most effective dye when using Hwangsu was Rhus, as illustrated by the increased fastness to washing and light through fermentation.

## 4. Conclusion

The aim of this study was to improve the natural dyeing method, which has too weak fastness to light. Fermented materials were collected for a certain period of time according to their biological reaction, and post-treated with natural mineral water obtained from Yeongcheon. Iron in water is used widely as chemical mordant. This study is significant in which it used materials nature. The study result showed that the mineral water was composed of iron, followed in order by aluminum and manganese. Consequently, the surface color of cotton fabric and silk, first dyed and then mordanted, exhibited a reddish color unique to the iron component. In addition, the some case of fabrics had improved fastness to light, which cannot be acquired from most natural dyeing processes. In particular, Rhus and Rheum showed increased durability, even after washing. Research is needed to check the properties of fermentation dyeing under different conditions in the fermentation process, such as temperature and humidity, and the fermentation properties to light per material etc. The problems with environmental pollution and work environment can be solved by replacing existing pre- and post-treatment using chemicals with natural mordants. The possibility of using the Hwangsu of Gogyung in Yeongcheon as a mordant will foster the rapid development of a regional specialized business. Natural dyeing as a traditional dyeing method is expected to play an important role in standardizing fermentation processes by optimizing the fermentation conditions and commercializing traditional culture.

## Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant number 212-C-000-194).

## References

- A. Shams-Nateri, Reusing Wastewater of Madder Natural Dye for Wool Dyeing, J. of Cleaner Production, 19(6–7), 775(2011).
- P. S. Vankar, R. Shanker and A. Verma, Enzymatic Natural Dyeing of Cotton and Silk Fabrics without Metal Mordants, *J. of Cleaner Production*, **15**(15), 1441(2007).
- E. S. Im and H. S. Lee, A Study on Function of Natural Dyeing with Cotton Fabrics Using *Jeju* scoria, Textile Coloration and Finishing(J. Korean Soc. Dye. and Finish.), 23(3), 179(2011).
- M. W. Huh, Dyeability and Functionality of Cotton Fabrics Treated with Persimmon Juice, *Textile Coloration and Finishing(J. Korean Soc. Dye. and Finish.)*, 23(4), 241(2011).
- F. A. Nagia and R. S. R. EL-Mohamedy, Dyeing of Wool with Natural Anthraquinone Dyes from Fusarium Oxysporum, *Dyes and Pigments*, **75**(3), 550(2007).
- Y. M. Park, K. Koo, S. S. Kim and J. D. Choe, Improving the Colorfastness of Poly(ethylene terephthalate) Fabrics with the Natural Dye of *Caesalpinia sappan L*. Wood Extract and the Effect of Chitosan and Low-temperature Plasma, *J. of Applied Polymer Science*, **109**(1), 160(2008).
- P. Nigam, G. Armour, I. M. Banat, D. Singh and R. Marchant, Physical Removal of Textile Dyes from Effluents and Solid-state Fermentation of Dyeadsorbed Agricultural Residues, *Bioresource Technology*, 72(3), 219(2000).
- P. Velmurugan, S. K. Kannan, V. Balachandar, P. Lakshmanaperumalsamy, J. C. Chae and B. T. Oh, Natural Pigment Extraction from Five Filamentous Fungi for Industrial Applications and Dyeing of Leather, *Carbohydrate Polymers*, **79**(2), 262(2010).
- 9. B. H. Park, I. J. Lee, M. H. Jang and J. U. Lee,

US Pat. 2010-278888(2010).

- 10. D. K. Sakamoto, Japan Pat. 2011-10237341(2011).
- 11. A. M. Baid, M. Arun, US Pat. 07485158(2004).
- C. O. Choo and J. K. Lee, Geochemistry and Mineralogical Characteristics of Precipitate formed at Some Mineral Water Springs in Gyeongbuk Province, Korea, J. Miner. Soc. Korea, 22(2), 139 (2009).