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Dyeing Properties, UV Protection, and Deodorization of Silk Fabric Using Hot Water Extract of *Ecklonia cava*

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Abstract

To explore the potential use of *Ecklonia cava* as a natural dye for textiles, silk fabric was dyed with *Ecklonia cava* extracted by hot water under varied conditions, including temperature, duration, dye concentration, mordanting, and pH adjustment. The fabric was also evaluated for fastness, sun-protective property, and deodorization. *Ecklonia cava* extract was estimated by FT-IR to have polyphenol as a main functional colorant in plants, while the existence of phlorotannins through the UV-spectrum method was also confirmed. The fabric was optimized for maximum dye uptake at a temperature of 80°C for a duration of 50 minutes along all dye concentrations. The dyed fabric showed a hue of Yellow Red under all dyeing conditions while additional color tones, such as grayish and dark, were generated through mordanting and pH adjustment. Both good sun-protective properties and a positive deodorization rate were also recorded, with more than 20% (owf) *Ecklonia cava* extract on silk fabric. These results imply that *Ecklonia cava* has great potential to be used as an eco-friendly natural dye and in fashion goods with skin-health functions made of silk.

Key words: Silk, Natural dyeing, *Ecklonia cava*, Ultraviolet protection factor, Deodorization

I. Introduction

Ecklonia cava is a large brown algae that grows 5-20 m underwater and is helpful in maintaining the diversity of marine organisms by providing unique habitats. Sea water temperatures typically range between 12-25°C, and, in South Korea, *Ecklonia cava* is distributed in areas where the sea temperature is relatively high, such as around Jeju Island, off the southern coast, and the islands of Ulleungdo and Dokdo, which sit off the eastern cost of South Korea, the south coast of China, and the central coast of Japan. The survival environment of *Ecklonia cava* is changing due to the increase in sea water temperature caused by coastal pollution and climate change (Jo et al., 2016), as well as the environment in the distribution area or seasonal temperature, especially sea water temperature, which has influenced the morphometric characteristics of *Ecklonia cava* (Serisawa et al., 2002).

Jeju Island produces a massive 300,000 tons of *Ecklonia cava* every year, which is used in a wide range of areas, including food raw material, animal feed, fertilizer, and medicine (Li et al., 2008). There is currently a significant interest in producing effective antioxidants using *Ecklonia cava* to deal with oxidative stress

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in the human body. Phlorotannins are bioactive derivatives in *Ecklonia cava* that have polymerized phloroglucinol, and its various advantages in terms of biologic activity are known to the public, thus receiving attention (Li et al., 2009). The advantages have been confirmed through phlorotannin studies on antioxidant function (Kang et al., 2004), cardiovascular protection function (Kang et al., 2003), antiviral effect (Ahn et al., 2004), and the potential effects of alleviating Alzheimer's disease (Choi et al., 2015). A previous study, which investigated the physiological use of hot water extracts from *Ecklonia cava* (Cho & Choi, 2010), analyzed and confirmed antioxidative properties, dinitrate scavenging, and alcohol metabolism efficiency.

Research on the biological properties of brown algae, including *Ecklonia cava*, has already been actively conducted in the fields of food and medicine, but research on its dyeing properties using natural dyes that are friendly to the human body has been lacking. Natural dyeing, which is environment-friendly and has natural color characteristics, is drawing attention from the textile industry (Yi & Choi, 2009). So far, dyeing properties have been frequently investigated using land plants, such as polygoum tinctoria (Kim, 2010), sappan wood, gardenia seeds, and gallnut (Park & Yoon, 2010), as natural dyes. Many advantages regarding this approach have been discovered, such as antibacterial qualities and antialkalinity, but color research using marine resources as natural dyes has been lacking. The superior antibacterial and color properties of silk fabrics dyed using extracts from brown algae undaria pinnatifida as natural dyes have been confirmed (Kim & Jeon, 2014a). Dyeing properties for silk, wool, and cotton fabrics with extracts from Sargassum thunbergii, Hizikia fusiformis, and Sargassum horner were examined (Bak, 2010). The silk was dyed, while various colors were expressed using a marine resource Laminaria japonica (Kim & Jeon, 2014b) with some metal mordants, in which excellent anti-microbial activity was exhibited. In general, a variety of se plant have been attempted as natural dye resources for textiles and they seemed to have a potential to be functional dyes for skin health and to have ecological benefit.

As for dyeing textiles with *Ecklonia cava*, a previous study in which dyed cotton fabric using boiled extract of *Ecklonia cava* grown along the Jeju coast (Sarmandakh et al., 2017), reported excellent antibacterial properties. In the previous study (Sarmandakh et al., 2017), cotton showed Yellow Red of shade by dyeing with boiled extract of *Ecklonia cava* and it gave effectiveness of repeated dyeing on dye fastness. Another previous study (Sarmandakh et al., 2018) has also attempted combination dyeing by adding *Ecklonia cava* to a main dye stuff, persimmon fruit powder in order to improve the stiff tactility associated with dye of immature persimmon. However *Ecklonia cava* has not been yet attempted as an ecological dye stuff for other textiles such as silk, nylon, and other fibers.

Accordingly, the present study investigates dyeing properties of *Ecklonia cava* on silk focusing on dyeing optimization for time and temperature, the fastness (rubbing fastness, perspiration fastness, dry cleaning fastness, and color fastness to light), UV protection properties, and deodorization of silk fabrics dyed using *Ecklonia cava*. The significance of this marine resource is that while it can both be used for natural dyeing and can protect the environment, it can also be created as a high value-added commercial product. The findings will represent significant basic data regarding natural dyes.

Therefore, the present study will explore the possibility of a valuable marine resource *Ecklonia cava* as a natural dyeing material by suggesting optimal dyeing conditions for silk fabric in consideration of the temperature and time with *Ecklonia cava* powder dye obtained by hot water extraction followed by lyophilizing, identifying the adjustment of mordanting properties and the pH level, and investigating functions, such as color fastness, UV protection properties, and deodorization.

II. Experimental

1. Materials

For the experiment, commercially available dried

Ecklonia cava (Chongm, Korea) was purchased. *Ecklonia cava* of 1.5 kg was soaked in 30 liters of distilled water, and it was extracted twice at 75°C for six hours using a low temperature extractor (COSMOS-660, Korea). The extracted solution was concentrated to 50% and then powderized by lyophilization (Ilshin-biobase, Lyoph-Pride, Korea). The final yield rate of the dye powder was calculated to be 13.98%. The fabric sample used for dyeing was 100% silk habutae, and its characteristics are presented in <Table 1>. For pH dyeing, the first grade reagents of citric acid ($C_6H_8O_7$, Sigma-Aldrich, cat. no. 40-061288-01) and Sodium hydroxide (NaOH, DAEJUNGcat. no. 28-08 704-01) were used. Ammonium sulfate ($AlNH_4(SO_4)_2 \cdot 12H_2O$, JUNSEI, cat. no. 28-00690-01), Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, DAEJUNG, cat. no. 28-01506-01), and Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, JUNSEI, cat. no. 28-06131-01) with the first grade reagents were added to post mordanting as mordants.

2. Dyeing Methods

The fabric samples were dyed using an IR automatic dyeing machine (Perfect 24, Korea Science Co., Korea). The conditions were set to combinations of 60°C and 80°C for temperature, and 30 and 50 minutes for duration at 1:200 bath ratio. The dyeing bath concentration were set to 20%, 40%, 60%, 80%, 100%, 200%, 300%, 400%, 500%, and 600% depending on the weight of the fiber (owf hereinafter).

The fabrics were dyed by adjusting the pH levels of dye solution from 2 to 12 using the first-grade reagents of 1M citric acid and NaOH. Post mordanting was done with a 3% mordant solution at a bath ratio of 1:50 for 20 minutes at 40°C using Al, Cu, and Fe as mordants. After dyeing, it was washed with water and air dried.

3. FT-IR Characterization

The FT-IR spectra of the extracted dye were obtained using the KBr method, and peaks in the range of 650-4,000 cm^{-1} were measured using an infrared spectrophotometer (FT-IR spectroscopy, Perkin Elmer, USA). This was done in order to determine whether the components contained in powder dye were hot water extracts from *Ecklonia cava*.

4. UV/visible Spectra Characterization

UV-responses of *Ecklonia cava* powder collected by hot water extraction were measured using an UV/visible spectrophotometer (UV-1800, Shimadzu, Japan) region spans the wavelength range from 200 to 800 nanometers (nm).

5. Dye Uptake Measurement

The K/S values were obtained in the absorption wavelength range of 360-740$_\lambda$ by using a colorimeter (CM-2500d, Japan) on the surface of the sample and SpectraMagic NX PC software. The surface reflectance (R) within the absorption wavelength range was measured, while the K/S value of each wavelength within the absorption wavelength was calculated based on Kubelka-Munk equation (Eq. 1).

$$K/S = (1 - R_\lambda)^2/2R_\lambda \quad \cdots\cdots \text{Eq. 1.}$$

K: Coefficient of absorption
S: Coefficient of scattering
R: Reflected light at wavelength

6. Color Characteristics

Under D65 light source, the values of L*, a*, b*, C*

Table 1. Characteristics of fabric specimen

Fiber	Weave	Weight (g/m^2)	Thickness (mm)	Fabric count (warp × weft/in^2)
Silk 100%	Plain	76	0.24	142 × 142

of CIE at a 10° viewing angle using the colorimeter (CM-2500d, Japan), and they were converted to Musell H V/C by SpectraMagic NX PC software. By the principle of calculating color difference in <Eq. 2> , ΔE* was obtained for each dyed fabric. Using Practical Color Coordinate System (PCCS), tone were determined as well.

$$\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2} \quad \cdots\cdots \text{Eq. 2.}$$

7. Color Fastness Measurement

The rubbing fastness of dyed silk fabric was evaluated according to KS K 0650-1:2017 (Korean Agency for Technology and Standards [KATS], 2017) using the crock-meter in both wet and dry conditions, while the color fastness to perspiration was evaluated depending on KS K ISO 105-E04:2013 (KATS, 2019a) for four hours under 37 ± 2°C. The color fastness to dry cleaning was evaluated according to KS K ISO 105-D01: 2010 (KATS, 2021b), and the color fastness to light was performed based on KS K ISO 105-B02:2014 (KATS, 2021a) Xenon arc.

8. UV Protection Properties

The measurement regarding the UV protection properties of silk fabric dyed with hot water extracts from *Ecklonia cava* was done according to KS K 0850:2019 (KATS, 2019b) using UV transmittance Analyzer (Labsphere Co., USA), with Xenon Arc as the light source, while the UV protection properties was presented in percentages by dividing the light source into UV-A (315-400 nm) and UV-B (290-315 nm) based on 315 nm UV light. The UV protection rates were calculated according to the following <Eq. 3>–<Eq. 4>.

$$\text{UV transmittance (\%)} = (T/B) \times 100 \quad \cdots\cdots \text{Eq. 3.}$$

$$\text{UV protection (\%)} = 100 - \text{UV transmittance (\%)} \quad \cdots\cdots \text{Eq. 4.}$$

T: UV transmittance through the fabric sample
B: UV transmittance without the fabric

9. Deodorization

The dyed silk fabric was prepared in a 10 cm × 10 cm size, based on the gas detector tube method. The deodorization rate was measured four times at 30 minute intervals (30, 60, 90, and 120 minutes) by placing the sample in a 1L container at a temperature of 20°C with 65% humidity, injecting a 500μg/mL concentration of ammonia (NH_3). The deodorization rate was calculated using the following <Eq. 5>.

$$\text{Deodorization rate (\%)} = (A-B)/A \times 100 \quad \cdots\cdots \text{Eq. 5.}$$

A: Gas concentration of blank
B: Gas concentration of sample

III. Results

1. FT-IR Characteristics of Hot Water extract of *Ecklonia Cava*

The results of the FT-IR spectra analysis regarding the characteristics of the hot water extracted *Ecklonia cava* dye were presented in <Fig. 1>. Peaks were observed at 3,229 cm^{-1}, 1,606 cm^{-1}, 1,412 cm^{-1}, 1,030 cm^{-1}, and 1,247 cm^{-1}. The results were consistent with the findings of Venkatesan et al. (2016), who observed that the characteristics of AgNPs synthesized using *Ecklonia cava* involved reducing and capping agents, rather than traditional chemical synthesis method. The peak at 3,229 cm^{-1} indicates the appearance of polyphenol or polysaccharide -OH, while the peak at 1,606 cm^{-1} represents the -NH bending vibration of amine or amide groups. The peak at 1,412 cm^{-1} is assumed as generated by the C-N stretching vibration of amine or amide groups. The $1{,}247^{-1}$ and 1,030 cm^{-1} absorption band signifies the stretching vibration of -C-O or C-O-C (Badmaanyambuu et al., 2018).

2. UV/visible Spectra Characteristics of Hot Water Extracts from *Ecklonia cava*

In <Fig. 2> the characteristics of the UV/visible

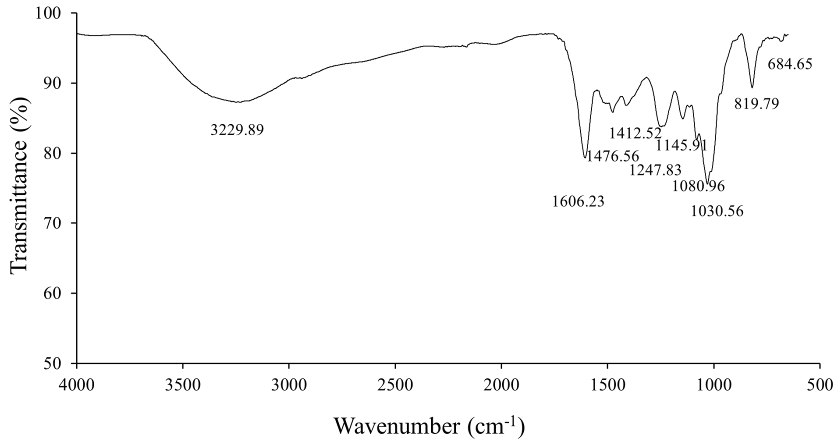


Fig. 1. FT-IR spectrum of hot water extract from *Ecklonia cava*.

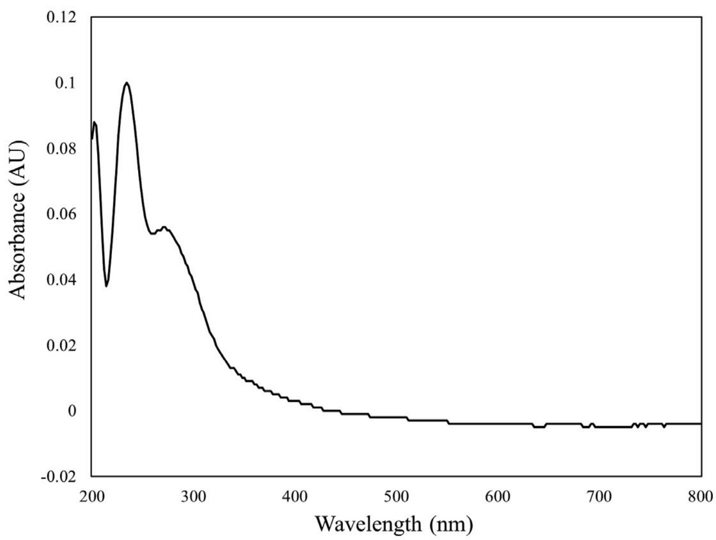


Fig. 2. Ultraviolet-visible spectra of hot water extract from *Ecklonia cava*.

spectra of hot water extract of *Ecklonia cava* dye powder with a concentration of 0.0125%wt in distilled water were shown. The maximum wavelengths were seen at 234 nm and 272 nm. The maximum absorption wavelength of the natural phenols was seen at 220-285 nm, as shown in a previous study (Venkatesan et al., 2016). Ahn et al. (2004) stated that the main component of *Ecklonia cava* is phlorotannins. Accordingly, the present study confirmed that natural polyphenols is the main component found in hot water extract *Ecklonia cava* powder. 0.0125%

3. Optimum Dyeing Conditions

In order to investigate the optimum dyeing conditions of hot water extracts from *Ecklonia cava* for silk fabric, the fabric was dyed under various duration and temperatures. The silk fabric was dyed with both lower and higher concentrations, than 100% concentration. The dye uptake K/S values given in <Fig. 3>

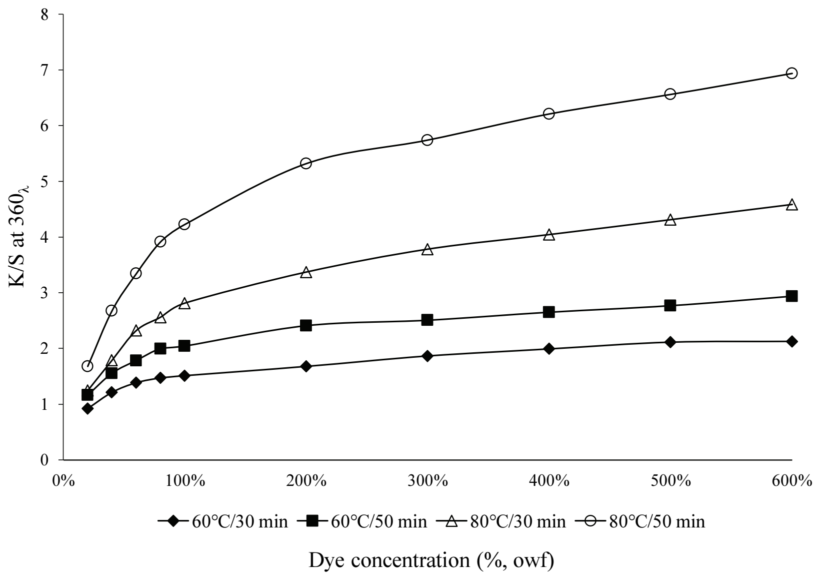


Fig. 3. Effect of dyeing conditions (dye concentration, temperature, time) on dye uptake.

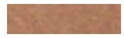
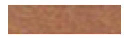
showed that the values at 60°C for 30 minutes increased at the slowest rate in the range from 20 to 100% as lower dye concentrations. Similar dye uptakes were observed both at 20% concentration at 60°C for 50 minutes and at 80°C for 30 minute. However, with the increase in dye concentration, the K/S values under 80°C for 30 minutes increased faster. The effects of the temperature and time on dye uptake were clearer with the increase in *Ecklonia cava* concentration. Overall, the highest dye uptake was observed at 80°C for 50 minutes of dyeing at lower concentrations. The K/S values at higher concentrations ranging from 100% to 600% are also shown in <Fig. 3>. Smaller increases in K/S values were observed similarly to each other at 60°C for 30 minute and at 60°C for 50 minute. In the case of the 80°C for 50 minute condition, however, the dye uptake more rapidly increased than in the other conditions. Consequently, the optimum dyeing conditions of the silk fabric were determined to be at 80°C for 50 minutes when all the conditions at low and high concentrations were comprehensively examined. The optimum dyeing condition of temperature and duration found in this study is the same as that reported by Sarmandakh et al. (2017), who dyed cotton fabric with a boiled extract of *Ecklonia cava*.

4. Color Characteristics

The colorimetric characteristics of the surface of dyed silk fabric under the 80°C, 50 minute condition, which was the optimum dyeing condition, at 20-600%, were presented in <Table 2>. The values of a* and b*, which represent the redness and yellowness of CIE color values, respectively, were found to increase with an increase in the concentration of the dye solution. While Sarmandakh et al.'s (2017) study showed YR (Yellow Red) colors on cotton fabrics dyed with extract by steaming *Ecklonia cava* only at much higher concentrations of 500% and 700%, the present study did YR color series at all concentrations. Consequently, silk fabrics were thought to develop YR color series, even at lower concentrations, compared to cotton fabrics.

In addition, the values of both CIE L* and Munsell V, which signifies brightness, decreased, with colors tending to darken as the concentration of dye bath

Table 2. Color characteristics of silk fabric depending on dye concentrations

Dye concentration (%, owf)	CIE				Munsell			PCCS tone	ΔE*	Visual color
	L*	a*	b*	C*	H	V	C			
20	70.79	7.10	15.70	17.23	7.5YR	6.97	2.86	light	32.44	
40	64.84	8.83	17.93	19.99	7.2YR	6.38	3.36	soft	38.59	
60	62.14	9.68	19.07	21.38	7.1YR	6.11	3.61		41.52	
80	60.21	10.31	19.67	22.21	6.9YR	5.92	3.77	dull	43.50	
100	59.39	10.59	20.06	22.68	6.8YR	5.84	3.85		44.43	
200	57.06	11.5	21.22	24.14	6.7YR	5.61	4.09		47.12	
300	56.41	11.86	21.73	24.76	6.6YR	5.55	4.19	deep	48.01	
400	55.55	12.04	21.94	25.03	6.6YR	5.46	4.23		48.85	
500	55.03	12.25	22.23	25.38	6.6YR	5.41	4.29		49.46	
600	54.48	12.41	22.32	25.54	6.5YR	5.36	4.32		49.99	

YR: Yellow Red

increased. In addition, CIE C* signifying the saturation, increased, with the colorfulness rising. Accordingly, PCCS tone was also expressed from the bright and thin tone to the dark and deep tone. Although the saturation increased with an increase in the concentration of the dye solution, it was still in the low saturation, as the Munsell C values did not go over five. Since the brightness value ranged between 5.36 and 6.97, this can be described as a medium brightness. Consequently, reddish and yellowish colors become stronger with an increase in the concentration of the dye solution, resulting in the tendency of increasing the saturation while decreasing the brightness. All of the dyed silk fabrics were of a medium brightness, low saturation, and belonged to YR series, while the tone changed from light to deep.

Now, with the optimized dyeing condition revealed above, that is, under the 80°C, 50 minute condition, mordanting and pH adjustment as well as UV protection and deodorization were evaluated for, 20%, 40%, 80%, and 300% because they were the lowest concentrations for each PCCS tone (light, soft, dull, deep). On the other hands, color fastness evaluation was performed additionally for some dye concentrations if they showed identical tone to higher dye concentrations by employing mordants such as Al, Cu, and Fe.

5. Effects of Mordanting and pH on Dyeing Properties

In order to examine the effects of mordanting and pH, post mordanting and pH adjustment were carried out at the lowest concentrations for each PCCS tone (light, soft, dull, deep), that is, 20%, 40%, 80%, and 300% respectively. The K/S values of the dyed silk fabric mordanted with Al, Cu, and Fe using the post mordanting method were presented in <Fig. 4>. In the post-mordanting method, the dye is adsorbed onto the fiber, followed by the formation of an insoluble complex with metal ions such as Al, Cu, and Fe (Deo & Desai, 1999). The dye uptake K/S value of the fabric mordanted with Fe was the highest, and the mordanting effect appeared to improve with an increase in the concentration of the dye solution. Furthermore, the dye uptake K/S value of the fabric mordanted with Cu tended to increase as well, but this increase was smaller than that of Fe-mordanting. The K/S value of the

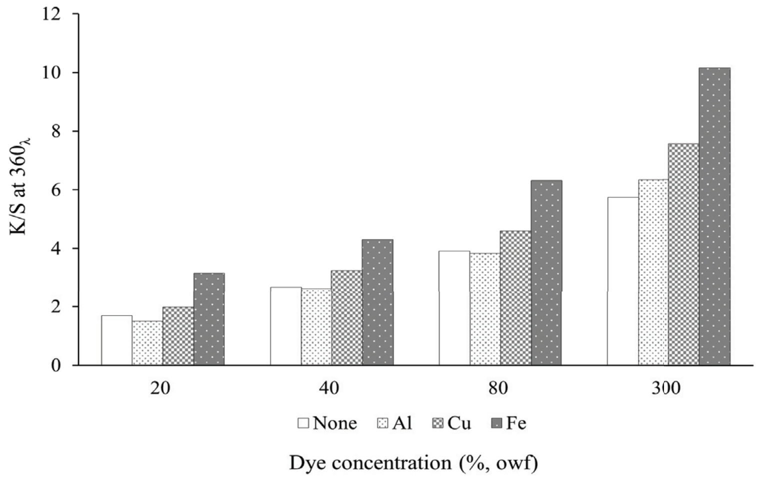


Fig. 4. Effect of post-mordanting on dye uptake depending on dye concentrations.

fabric mordanted with Al was lower than that which was unmordanted in a low concentration of dye solution (20-80%), but it was a little higher when the concentration was 300%. Overall, however, the improvement in the post mordanting K/S value was lower than that of Cu and Fe. These results may be due to the greater complex-forming ability of Fe and Cu ions with the dye molecules than that of Al. In summary, post mordanting with Cu and Fe affected the K/S values of fabrics dyed with hot water extracts from *Ecklonia cava*, and the effects were more prominent when the concentration of dye solution was high. In particular, post mordanting with Fe was found to significantly increase the K/S value of the dyed silk fabric, which is supported by some of natural dyeing researches on mordanting effects including one about undaria pinnatifida as a natural dye (Kim & Jeon, 2014a) as well as a research on natural dyeing on silk fabric (Sa et al., 2013).

The color characteristics of the post mordanted silk fabric are presented in <Table 3>. As mentioned earlier, the CIE a*, b*, and C* values, as well as the Munsell C value, become larger as the concentration of the dye solution increased for all post mordanting, while both the CIE L* value and Munsell V value tended to decrease. Furthermore, all mordanting agents (Al, Cu, and Fe) developed YR color series without any change in hue even after mordanting, which is not identical to the results by previous studies dealing with other sea plants which reported that Cu mordanting has caused hue change to greenish (Kim & Jeon, 2014a, 2014b).

Generally such color changes by mordanting were most remarkable in Fe post mordanting as expected in <Fig. 4> above. Precisely these changes are consistent with the increase in K/S values after mordanting, with an increase in the concentration of the dye solution, as shown in <Fig. 4>. A careful examination of the PCCS tone revealed that lighter tones changed todarker or more saturated tones with an increase in the concentration of the dye solution. Changes in tone from light to light grayish were observed after Cu and Fe mordanting at a 20% of dye concentration, while changes in tone from soft to grayish were observed when mordanted with Fe at 40%, a dye solution concentration. However, no change in the color tone of the dyed silk fabric by post mordanting was observed in the 80% of dye concentration. Lastly, the tone of the dyed silk fabric changed from deep to dark after mordanting with Fe under a 300%. Overall, ΔE*, which is the color difference between mordanted and unmordanted fabrics, was found to be largest for Fe, followed by Cu and Al.

Dyeing according to pH was carried out at the dyeing concentrations of 20%, 40%, 80%, and 300%,

Table 3. Color characteristics of silk fabric depending on dye concentrations and mordant types

Dye concentrations (%, owf)	Mordant	CIE				Munsell			PCCS tone	ΔE*
		L*	a*	b*	C*	H	V	C		
20	None	70.79	7.10	15.70	17.23	7.5YR	6.97	2.86	light	-
	Al	73.49	6.06	15.52	16.66	8.1YR	7.25	2.71		0.45
	Cu	69.59	5.10	16.41	17.19	9.4YR	6.85	2.67		3.64
	Fe	65.29	4.55	13.73	14.46	9.1YR	6.41	2.26	light grayish	7.82
40	None	64.84	8.83	17.93	19.99	7.2YR	6.38	3.36	soft	-
	Al	66.26	7.84	17.92	19.56	7.8YR	6.52	3.22		0.49
	Cu	63.14	6.97	18.45	19.72	8.8YR	6.20	3.16		3.25
	Fe	59.63	5.22	14.79	15.69	9.1YR	5.84	2.47	grayish	8.46
80	None	60.21	10.31	19.67	22.21	6.9YR	5.92	3.77	dull	-
	Al	61.39	9.29	19.75	21.82	7.6YR	6.03	3.64		0.71
	Cu	58.33	8.28	19.74	21.41	8.4YR	5.73	3.47		3.16
	Fe	53.66	5.95	15.69	16.78	9.1YR	5.25	2.66		9.30
300	None	56.41	11.86	21.73	24.76	6.6YR	5.55	4.19	deep	-
	Al	56.01	11.18	22.62	25.23	7.5YR	5.51	4.19		1.21
	Cu	52.29	9.88	21.56	23.71	8.1YR	5.13	3.86		3.84
	Fe	45.71	6.42	15.82	17.07	9.0YR	4.48	2.65	dark	12.76

ΔE* is color difference values from unmordanted fabric (None).
YR: Yellow Red

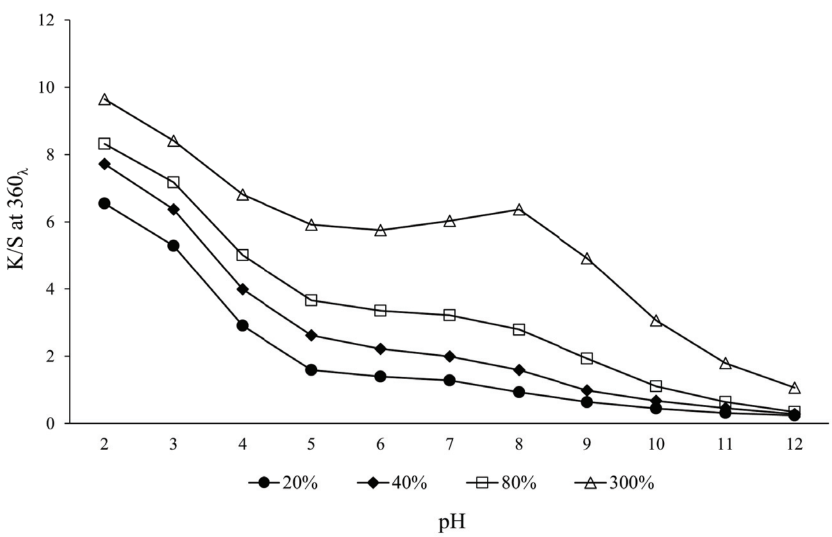


Fig. 5. Effect of pH adjustment on dye uptake depending on dye concentrations.

which were selected for each tone as the optimal dyeing condition at 80°C for 50 minutes. The K/S values of the dyed fabrics are presented in <Fig. 5>. Since the unadjusted pH value of the dye solution (that is, hot water extracted from *Ecklonia cava*) was between 5.72 and 6.13, the results were examined based on the results of dyeing at pH 6. The results showed that the higher the pH, the lower the K/S values, while the lower the pH, the higher the K/S value.

According to Bai (2008), in the case of silk fabrics, the amino group (-NH_3) among acid dye solutions comes to have cationic properties due to dissociative phenomenon, while *Ecklonia cava* extract forms anions by the dissociation of sugar due to hydrolysis, which makes ionic bonding stronger, resulting in greater dye uptake. On the other hand, dye uptake appears to decrease due to an increase in alkalinity of dye solution, which increases the anionic properties of the fabric, making ionic boding with *Ecklonia cava* extract difficult (Lee & Ko, 2010). Since the dye uptake of hot water extracts from *Ecklonia cava* is strongest under acidic conditions when dyeing protein fibers, such as silk fabric, it is considered to be an appropriate acidic dye for protein fibers in the majority of natural dyes (Lee & Ko, 2010).

The results of color characteristics by dyeing at pH 2 to pH 12 at 80°C for 50 minutes at 20%, 40%, 80%, and 300% were presented in <Table 4>. When the dye solution is acidic, all of the colors were expressed in YR. As the alkalinity of the dye solution increased, the color changed from YR to Y, and other adjacent colors, which means yellowness increased. The brightness increased while the saturation decreased, which resulted in fainter and weaker tones by PCCS. On the contrary, the acidity of the dye solution became strong, which resulted in all the colors being expressed in YR, while the brightness tended to decrease and the saturation tended to increase. Precisely, the soft tones produced at the dye concentrations of 20% and 40% were dull tones under a high acidic condition, while the dull tones at 80% and 300% changed to deep tones when the acidity of the dye solution became stronger.

Table 4. Color characteristics of silk fabric depending on pH

pH value	Dye concentrations (%, owf)															
	20%				40%				80%				300%			
	H	V	C	Tone	H	V	C	Tone	H	V	C	Tone	H	V	C	Tone
2	7.4YR	5.56	4.42	dull	7.2YR	5.32	4.53	dull	7.1YR	5.22	4.69	deep	7.3YR	5.13	4.81	deep
3	7.5YR	5.74	4.05	dull	7.2YR	5.49	4.28	dull	7.0YR	5.35	4.49	deep	7.3YR	5.28	4.73	deep
4	7.4YR	6.33	3.48	soft	7.3YR	5.97	3.87	dull	7.0YR	5.69	4.13	dull	7.2YR	5.47	4.52	deep
5	7.6YR	7.08	2.88	light grayish	7.5YR	6.47	3.40	soft	7.3YR	6.04	3.79	dull	7.0YR	5.57	4.30	deep
6	7.9YR	7.28	2.67	light grayish	7.7YR	6.72	3.19	soft	7.4YR	6.17	3.63	dull	6.9YR	5.60	4.16	dull
7	8.1YR	7.43	2.52	light grayish	7.9YR	6.89	3.04	soft	7.6YR	6.31	3.47	dull	6.8YR	5.58	4.08	dull
8	8.5YR	7.82	2.09	light grayish	8.1YR	7.20	2.74	soft	7.8YR	6.58	3.27	soft	6.9YR	5.61	4.06	dull
9	9.0YR	8.27	1.55	pale	9.0YR	7.87	2.17	light grayish	8.7YR	7.14	2.93	soft	8.1YR	6.05	3.88	dull
10	9.5YR	8.65	0.96	pale	10.0YR	8.32	1.63	light grayish	0.1Y	7.90	2.43	light grayish	9.4YR	6.78	3.70	soft
11	8.9YR	8.96	0.33	pale	0.5Y	8.70	0.99	light grayish	0.8Y	8.41	1.63	light grayish	9.7YR	7.37	3.20	soft

YR: Yellow Red, Y: Yellow

6. Color Fastness

The color fastness of each for a total of eight tones was evaluated by equally selecting the dyeing conditions: 1) dye concentrations without additives to each tone of dyed silk fabric; and 2) dye concentrations with additives, which is lower than anyone showing identical tone by additives. The results were presented in <Table 5>. The rubbing fastness under humid and dry conditions was found to be excellent, mostly at grade 4 or higher. As for the perspiration fastness in terms of changes in color due to acidic sweat, the grade of silk fabric dyed at 20% under pH 4 was the lowest showing 2-3 grade; silk fabrics dyed with Fe mordanting at 300% and those by Al mordanting or pH 3 at 80% were middle grades of 3-4; and the rest were all grades 4 or higher, which were all good fastness. In terms of changes in color due to alkaline sweat, the grades of silk fabric dyed at 20% and pH 4 were 2-3; the grades of silk fabrics with Fe mordanting at 300% and those with Al mordanting or under pH 3 were 3-4; and the rest were all grades 4 or higher. As for the contamination of silk and cotton by acidic and alkaline sweat, the grades were grade 4 or higher, which are all excellent. In terms of the results of dry cleaning fastness, color changes and the contamination of silk and cotton were all excellent, with grade 4 or higher. Regarding color fastness to light, grades 3 or higher were scored for dyeing using a 20% dye concentration at pH 8 and pH 10; the rest were grades 3 or lower. In terms of 20% dyeing, the color fastness to light of dyed silk fabric that had no additives was grades 2-3, but the grades improved to 3-4 after dyeing at pH 8 and pH 10. The fastness was again grades 2-3 when the fabric was dyed at pH 3, pH 4, and pH 5, showing no change. The color fastness to light of all fabrics treated with Al mordanting was grade 1, which was lower than for fabrics dyed in the same tone under different conditions.

Table 5. Color fastness grades of dyed fabrics depending on PCCS tones

PCCS tone	Dyeing condition	Rubbing		Perspiration						Dry cleaning Perchloroethylene			Light
				Acidic			Alkaline						
		Dry	Wet	Color change	Stain		Color change	Stain		Color change	Stain		Color change
					Silk	Cotton		Silk	Cotton		Silk	Cotton	
pale	20% & pH 10	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
light	20%	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	2-3
	20% & pH 8	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5	3-4
	20& & Al	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	1
light grayish	20% & Fe	4-5	4-5	3-4	4-5	4-5	3-4	4-5	4-5	4-5	4-5	4-5	1-2
	20% & pH 5	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	2-3
soft	40%	4	4-5	4	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	2
	20% & pH 4	4-5	4-5	2-3	4	4-5	2-3	4	4-5	4	4-5	4-5	3
	40% & Al	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	1
dull	80%	4	4-5	4	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	1-2
	20% & pH 3	4-5	4-5	4	4-5	4-5	3-4	4	4	4-5	4-5	4-5	2-3
	80% & Al	4-5	4-5	4	4	4-5	4	4	4-5	4-5	4-5	4-5	1
deep	80% & pH 3	4	4	3-4	4	4-5	3-4	4	4	4-5	4-5	4-5	1-2
	300%	4	4-5	4	4	4	4	4	4	4-5	4-5	4-5	1-2
	300% & Al	4-5	4-5	3-4	4-5	4-5	3-4	4	4-5	4-5	4-5	4-5	1
grayish	40% & Fe	4-5	4-5	3-4	4-5	4-5	3-4	4-5	4-5	4-5	4-5	4-5	1-2
dark	300 & Fe	4-5	4-5	3-4	4-5	4-5	3-4	4-5	4-5	4-5	4-5	4-5	2

In the case of dye solutions of the same concentration, their tone was bright and the color fastness to light improved when the alkalinity was strong.

In summary, rubbing, dry cleaning, and sweat fastness were mostly grades 4-5 and in general dyeing with *Ecklonia cava*. In the case of color fastness to light, stronger alkalinity such as 20% under pH 10 and 20% under pH 8 resulted in better fastness grades than other identically toned silk without any pH adjustment. Mordanting seemed to have little effects on any fastness although it contributed to producing new darker tones including grayish and dark especially in case of Fe.

7. UV Protection Properties

Among the silk fabrics dyed with hot water extracts from *Ecklonia cava*, those dyed at 20%, 40%, 80%, and 300% concentrations representing each tone were evaluated for their UV protection properties. The results were presented in <Table 6>.

The UPF index, which indicates the UV blocking effect among silk fabrics without dyeing, was 6.7, but this figure increased significantly to 37.1 (very good protection) and 59.7 (excellent protection) when silk fabrics were dyed with 20% and 40% concentrations, respectively. The UPF indices of fabrics dyed at 80% and 300% were 110.7 and 213.3, respectively. The UPF indices of all the samples from soft to deep were 50+, representing excellent protection. The result of the UV protection tests for dyed silk showed a UV cutting rate of 93.3 or higher for UV-A, and 98.4 or higher for UV-B. In particular, the UV-A cutting rate of dyed silk fabric was significantly increased compared to undyed fabric. Undyed silk fabric in this study had lower UPF index (UPF: 6.7) than that of cotton counterpart (UPF: 8.4) in Sarmandakh et al.'s (2017) study. Nevertheless silk fabric has obtained better barrier efficiency than cotton in the previous work in that silk dyed with a 20% concentration of *Ecklonia cava* extract showed 37.1 of UPF similar to the UPF by cotton fabric dyed with a 50% concentration solution (UPF: 30.7). These results means that dyeing of silk with hot water extract from *Ecklonia cava* contributed to the improvement of UV protection rate of the silk even under lower dye concentration like 20%.

8. Deodorization

The deodorization results regarding the silk fabric dyed with *Ecklonia cava* extract were shown in <Table 7>. Dye concentrations of 20%, 40%, 80%, 300% were chosen for each PCCS tone, that is, light, soft, dull, and deep. The deodorization of fabric dyed with low concentrations (20%, 40%, and 80%) was 98%, even after 30 minutes. Deodorization at a high concentration of 300% was 99% or higher. All of the deodorization measurements after 60 minutes were 99% or higher. These results implies that dyeing of silk with *Ecklonia cava* extract seemed to impart superior deodorization efficiency to silk considering the deodorization percentage of undyed silk of 70% around. Therefore silk dyed with *Ecklonia cava* extract is expected to exhibit deodorization during its uses by reducing unpleasant odors that might arise from many different sources such as food, human sweat, smoke, and so on.

Table 6. UV protection rate of dyed silk fabric depending on PCCS tones

PCCS tone	Dye concentrations (%, owf)	UV protection factor		UV cut ratio (%)	
		UPF	Grade	UV-A	UV-B
-	Undyed	6.7	5	71.7	90.4
light	20	37.1	35	93.3	98.2
soft	40	59.7	50+	95.0	98.8
dull	80	110.7	50+	97.2	99.3
deep	300	213.3	50+	98.4	99.6

Table 7. Deodorization efficiency of silk fabrics dyed with Ecklonia cava dye extract depending on PCCS tones

PCCS tone	Dye concentrations (%, owf)	Time (min)			
		30	60	90	120
-	Undyed	70	74	78	78
light	20	98	>99	>99	>99
soft	40	98	>99	>99	>99
dull	80	98	>99	>99	>99
deep	300	>99	>99	>99	>99

IV. Conclusions

The present study investigated colorimetric characteristics and fastness by dyeing silk fabric with hot water extracts from *Ecklonia cava* at 60°C and 80°C for periods of 30 and 50 minutes, with 20-600% and furthermore evaluated UV protection properties and deodorization efficiency of each differently toned silk by *Ecklonia cava* extract. The results were as follows.

1. In terms of dye uptake K/S value for silk fabrics, the dye uptake was the largest at 80°C for 50 minutes. This finding was set as the optimal dyeing condition. The fabric dyed with hot water extracts from *Ecklonia cava* including from low to high concentrations appeared in all YR series even after post mordanting and pH adjustment which contributed to more saturated and darker tones.

2. The dyeing fastness mostly showed grades 4-5 for rubbing fastness, dry cleaning fastness, and perspiration fastness, which means dyeing silk with hot water extracts of *Ecklonia cava* could exhibited very good fastness for rubbing, dry cleaning, and perspiration. However, the color fastness to light under the other dyeing conditions was poor, which calls for improvements in a future.

3. In terms of UV protection and deodorization, silk dyed with more than 20% concentration showed good blocking ability of UV as well as deodorization rate. These results implies that the dyed silk fabric with less saturated tones such as light could be expected as a high value-added products, as the naturally dyed fabrics were found as protecting the skin from UV rays while also as blocking unpleasant smell.

These results lead us to the conclusion that dyeing with hot water extracts from *Ecklonia cava* on silk will be useful in providing UV protection property and deodorization efficacy to textiles as fashion materials with high-added values. More meaningful expectation is that various color tones from light to dark could be together with skin-health functions. If *Ecklonia cava* might be employed in dyeing industry of textiles utilizing the result of this study, it could contribute to both a progress in eco-friendly textile dyeing in textiles and useful consumption of *Ecklonia cava* overabundant in the seashore.

In a future study, the influence of repetition of dyeing and another additives such as tannin to improve dye fastness to light is a further area of interest and the effect of laundry on UV protection and deodorization needs to be tested. Also in a future study, more varied fibers such as nylon and lyocell should be attempted to be dyed for wider application to textile goods.

References

Ahn, M.-J., Yoon, K.-D., Min, S.-Y., Lee, J. S., Kim, J. H., Kim, T. G., … Kim, J. (2004). Inhibition of HIV-1 reverse transcriptase and protease by phlorotannins from the brown alga *Ecklonia cava*. *Biological and Pharmaceutical Bulletin*, *27* (4), 544–547. doi:10.1248/bpb.27.544

Badmaanyambuu, S., Lee, A. R., Kim, Y., & Yi, E. (2018). Dyeing properties and bio-functions of cotton fabrics dyed with naturally fermented Ecklonia cava extract, *Journal of the Korean Society of Clothing and Textiles*, *42*(3), 516–529. doi:10.5850/JKSCT.2018.42.3.516

Bai, S.-k. (2008). Dyeing properties of *Morus alba L.* fruit powder on the silk fabric. *Journal of the Korean Society for Clothing Industry*, *10*(5), 779–783.

Bak, H.-S. (2010). A study on function of natural dyeing of seaweed. *Journal of Fisheries and Marine Science Education*, *22*(4), 490–500.

Cho, E. K., & Choi, Y. J. (2010). Physiological activities of hot water extracts from *Ecklonia cava Kjellman*. *Journal of Life Science*, *20*(11), 1675–1682. doi:10.5352/JLS.2010.20.11.1675

Choi, B. W., Lee, H. S., Shin, H.-C., & Lee, B. H. (2015). Multifunctional activity of polyphenolic compounds associated with a potential for Alzheimer's disease therapy from *Ecklonia cava*. *Phytotherapy Research*, *29*(4), 549–553. doi:10.1002/ptr.5282

Deo, H. T., & Desai, B. K. (1999). Dyeing of cotton and jute with tea as a natural dye. *Coloration Technology*, 115(7-8), 224–227. doi:10.1111/j.1478-4408.1999.tb00360.x

Jo, Y. J., Oh, Y. S., Kim, M. Y., Park, H.-S., & Yum, S. (2016). Transcriptional responses in *Ecklonia cava* to short-term exposure to hyperthermal stress. *Toxicology and Environmental Health Sciences*, *8*(2), 181–188. doi:10.1007/s13530-016-0275-z

Kang, H. S., Chung, H. Y., Kim, J. Y., Son, B. W., Jung, H. A., & Choi, J. S. (2004). Inhibitory phlorotannins from the edible brown alga *Ecklonia stolonifera* on total reactive oxygen species (ROS) generation. *Archives of Pharmaceutical Research*, *27*(2), 194–198. doi:10.1007/BF02980106

Kang, K., Park, Y., Hwang, H. J., Kim, S. H., Lee, J. G., & Shin, H.-C. (2003). Antioxidative properties of brown algae polyphenolics and their perspectives as chemopreventive agents against vascular risk factors. *Archives of Pharmacal Research*, *26*(4), 286–293.

Kim, M. K. (2010). *A study on the dyeing conditions and properties of cotton fabric dyed with natural polygoum tinctoria* (Unpublished master's thesis). Ewha Womans University, Seoul.

Kim, S., & Jeon, S. (2014a). Natural dyeing of silk fabrics with Undaria pinnatifida extracts. *Journal of Fashion Business*, *18*(5), 69–81. doi:10.12940/jfb.2014.18.5.69

Kim, S., & Jeon, S. (2014b). Fabric dyeing with *Laminaria japonica* as a marine resource. *The Research Journal of the Costume Culture*, *22*(6), 890–898. doi:10.7741/rjcc.2014.22.6.890

Korean Agency for Technology and Standards. (2017, December 13). KS K 0650-1:2017 Test method for color fastness to rubbing: Crock meter method. *Korean Standards & Certifications*. Retrieved from https://e-ks.kr/streamdocs/view/sd;streamdocsId=72059197970371628

Korean Agency for Technology and Standards. (2019a, December 17). KS K ISO 105-E04:2013 Textiles — Tests for colour fastness — Part E04: Colour fastness to perspiration. *Korean Standards & Certifications*. Retrieved from https://e-ks.kr/streamdocs/view/sd;streamdocsId=72059197887273701

Korean Agency for Technology and Standards. (2019b, December 30). KS K 0850:2019 Test method for ultraviolet protection rate and ultraviolet protection factor of textiles. *Korean Standards & Certifications*. Retrieved from https://e-ks.kr/streamdocs/view/sd;streamdocsId=72059197723529206

Korean Agency for Technology and Standards. (2021a, July 1). KS K ISO 105-B02:2014 Textiles — Tests for colour fastness — Part B02: Colour fastness to artificial light: Xenon arc fading lamp test. *Korean Standards & Certifications*. Retrieved from https://e-ks.kr/streamdocs/view/sd;streamdocsId=72059219161355820

Korean Agency for Technology and Standards. (2021b, July 1). KS K ISO 105-D01:2010 Textiles — Tests for colour fastness — Part D01: Colour fastness to dry cleaning using perchloroethylene solvent. *Korean Standards & Certifications*. Retrieved from https://e-ks.kr/streamdocs/view/sd;streamdocsId=72059219239491253

Lee, H.-S., & Ko, S.-M. (2010). Dyeability of silk fabrics using extracts of Ligustrum japonicum Thunb fruit. *Textile Coloration and Finishing*, *22*(1), 71–76. doi:10.5764/TCF.2010.22.1.071

Li, Y., Lee, S.-H., Le, Q.-T., Kim, M.-M., & Kim, S.-K. (2008). Anti-allergic effects of phlorotannins on histamine release via binding inhibition between IgE and FcεRI. *Journal of Agricultural and Food Chemistry*, *56*(24), 12073–12080. doi:10.1021/jf802732n

Li, Y., Qian, Z.-J., Ryu, B., Lee, S.-H., Kim, M.-M., & Kim, S.-K. (2009). Chemical components and its antioxidant properties in vitro: An edible marine brown alga, *Ecklonia cava*. *Bioorganic & Medicinal Chemistry*, *17*(5), 1963–1973. doi: 10.1016/j.bmc.2009.01.031

Park, M.-O., & Yoon, S.-L. (2010). Properties of natural dyeing of bast fiber(Part 2): Pre mordanting dyeing of sappan wood, gardenia and gallnut. *Journal of Korea TAPPI*, *42*(4), 1–14.

Sa, A.-N., Choi, H. J., & Lee, J. S. (2013). Dyeing properties and functionalities of *Alnus japonica* bark and heartwood extracts. *Textile Science and Engineering*, *50*(5), 283–291. doi:10.12772/TSE.2013.50.283

Sarmandakh, B., Kim, C., & Yi, E. (2018). Preparing bi-component dye of unripe Diospyros kaki THUNB. fruit and *Ecklonia cava* and investigating its dyeing properties on fabric. *Journal of the Korea Academia-Industrial cooperation Society*, *19*(4), 525–531. doi:10.5762/KAIS.2018.19.4.525

Sarmandakh, B., Lee, A. R., & Yi, E. (2017). Dyeing properties and bio-function of cotton fabrics with Ecklonia cava extract. *Textile Science and Engineering*, *54*(5), 386–396. doi:10.12772/TSE.2017.54.386

Serisawa, Y., Yokohama, Y., Aruga, Y., & Tanaka, J. (2002). Growth of *Ecklonia cava* (Laminariales, Phaeophyta) sporophytes transplanted to a locality with different temperature conditions. *Phycological Research*, *50*(3), 201–207. doi: 10. 1046/j.1440-1835.2002.00274.x

Venkatesan, J., Kim, S.-K., & Shim, M. S. (2016). Antimicrobial, antioxidant, and anticancer activities of biosynthesized silver nanoparticles using marine algae *Ecklonia cava*. *Nanomaterials*, *6*(12):235. doi:10.3390/nano6120235

Yi, E., & Choi, J. (2009). Color sensibility factors for yellowish and reddish natural dyed fabrics by 40s middle-aged consumers. *Science of Emotion and Sensibility*, *12*(1), 109–120.

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