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Flavonol-quercetin functionalized silk dyeing under different liquid fermentation conditions

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Onion peels have been fermented prior to dyeing of silk to enhance the dyeing efficiency. The conditions have been changed by mixing the nutrients and microorganisms, and the differences in color and fastness are evaluated. Sucrose and dry yeast (*Saccharomyces cerevisiae*), important factors affecting the fermentation, have been used as nutrients and microorganisms for fermentation. The study has also been done without any additive and by adding only sucrose or yeast for comparison. The fermentation conditions are maintained at 35 °C for 8 h. The L^*, a^*, b^*, and *K/S* values of silk has been measured using a colorimeter. The value of L^* is found highest when microorganisms are added, while a^*, b^* and *K/S* values are found lower after fermentation under all conditions. The value of a^* is found the lowest when both yeast and sucrose are added simultaneously; b^* is the lowest when microorganisms are added. Fastness to light, washing, and perspiration are found higher after fermentation. The dyeing of silk using fermented solutions made of onion peels shows a distinctive color change and good color fastness. This may be helpful in developing natural dyeing products of various colors.

Keywords: Fastness properties, Fermentation, Natural dyeing, Onion peels, Waste resources, Silk

1 Introduction

As social interest in sustainable development has increased in recent years and research studies on utilizing natural resources in an efficient manner have accelerated[1-3]. In particular, natural dyeing is a representative example that includes the use of natural resources. However, natural dyeing also has certain difficulties in terms of its industrial development because the processes for obtaining the main raw materials are not constant, and the production process is somewhat complicated and difficult, with low fastness, color stability, and economical efficiency[4]. To reproduce and generalize the properties of these materials, various studies have been carried out for improving dye fastness and standardization of traditional colors in a systematic and consistent manner[5-9].

Therefore, in this study, efforts have been made to improve the dyeability of natural dye from onion (*Allium cepa*) peels[10-13], which are a typical waste material but can produce a large amount of dye. For natural dyeing, onion peel is known to achieve a yellowish brown colour in polychromatic dyes. The main dye components of onion peel are flavonols, such as kaemferol, isorhamnetin-3-O-glucoside, quercetin, glycoside rutin, quercetin-4'-O-glucoside, quercetin-4',7-O-diglucoside, quercetin-3,7-O-diglucoside, and isoquercetin. Onion peel extracts have been reported to contain more than 53% quercetin ($C_{15}H_{10}O_5$) as a flavonol, the structure of which can be seen in Fig. 1 (refs 14,15). Most plant dye materials, such as onion peels, are multicolored and vary in color, depending on the type and concentration of the mordants and additives used. The purpose of this study is to investigate the effects of onion peel on the color change after fermentation without a mordant, which has not been explored so far to the best of our knowledge.

In addition, fermentation is a type of decomposition of an organic material by microorganisms, and fermentation and corruption proceed through similar processes. As a result of decomposition, when a useful substance is produced, it is said to have undergone fermentation, whereas if it has a stench or is a harmful substance, it is considered corrupt. Fermented foods are often not to be used even when they are called "fermentation". Recent studies have also reported alternative energy sources for using in fermentation[16]. In a natural dyeing industry, fermentation dyeing has been commonly applied using a conventional fermentation apparatus and a fermentation method, which continues for a long time. There have been many studies related to fermentation, but most of them have

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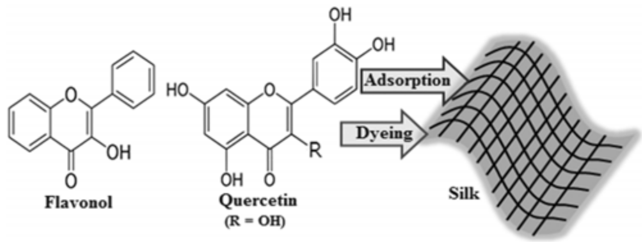

Fig. 1 — Backbone of flavonol and quercetin

considered fermented dyes ; fermentation occurs due to the naturally occurring process taking place during the summer, particularly at an ambient temperature, which along with the humidity is not consistent[17, 18].

Therefore, in this study, we investigated the dyeing characteristics through liquid fermentation as well as explored the possibility of colour development in samples when dyed with fermented solutions under various conditions, by artificially controlling the temperature, time, nutrients, and microorganisms, which are the factors affecting the fermentation.

2 Materials and Methods

2.1 Pre-treatment of Silk through Scouring

The samples used in the experiment were purchased from the Korea Silk Research Institute. Raw silk fabric [Satin weave, 205 × 135 fabric count (5 cm × 5 cm), 34.34 g/m^2 area density and 0.09 mm thickness] was used. The silk fabric was treated with a liquid detergent used for dishwashing (baking soda, Aekyung, Co. Ltd, Korea) containing detergent 15% and soda 85%, and sodium carbonate (Na_2CO_3, Duksan Chemical, Co. Ltd, Korea). The silk was then washed with distilled water and dried. The fabric was treated with 20% (owf) neutral detergent and 5% (owf) Na_2CO_3 at 90 °C for 20 min with a liquid ratio of 1:30.

2.2 Dye Extraction from Onion Peels

Onion peel (30 g) was added to 1500 mL of distilled water to prepare a dyeing solution. The mixture was extracted by stirring at 100 °C for 45 min until it became 75% of the stock solution. To make the dyeing solution free from impurities, it was cooled down and accurately filtered several times through a Buchner funnel to achieve a clear liquid.

2.3 Fermentation and Dyeing

2.3.1 Liquid Fermentation

The fermentation of the onion peel extract was done based on four methods depending on the temperature, nutrient source and addition of microorganisms. The nutrient used for fermentation was sucrose (KS H 2003, CJ Co Ltd., Korea) and the microorganisms were dry yeast containing 98.5% active dry yeast *Saccharomyces cerevisiae* (Societe Industrielle Lesaffre, France). The first liquid fermentation was carried out at 35 °C for 8 h without the addition of nutrients or microorganisms using a food fermenter (NYM-531KC, NUC, Korea) under controlled temperature and humidity. The second fermentation condition applied sucrose, and the third fermentation process was carried out at 35 °C for 8 h with only instant dry yeast added. The final liquid fermentation method was applied at 35 °C for 8 h using the same temperature and humidity with both sucrose and yeast added. The temperature and humidity were set at the same conditions during this experiment to obtain the optimum results, in which the undiluted solution is not denatured for microbial activities or fermentation.

2.3.2 Dyeing

Onion peel extracts were fermented under various conditions, and filtered several times to remove any residual microorganisms and nutrients. The turbidity was measured to check the solution after the fermentation, and the fermentation broth from which impurities were completely removed was used for dyeing while stirring at 80 °C for 30 min using 1:50 liquid ratio. After dyeing, the silk was washed several times and dried naturally. The scouring, liquid fermentation, and dyeing method of the sample are shown in Fig. 2.

2.4 Dye Absorbance, Sugar and *p*H

The absorbance was measured using an UV/VIS/NIR spectrophotometer (Cary 5000, Aglient, USA) for analysis before and after fermentation.

A *p*H and sugar content test before and after fermentation was carried out using a pocket *p*H tester (Hanna, Romania) and portable sugar meter (Refractometer, PAL-1, Atago, Japan) respectively.

2.5 Surface Color and Color Difference

Before and after fermentation, three stimulus values (X, Y, and Z); three parameters [L^* (lightness), a^* (redness-greenness value), and b^* (yellowness-blueness value)] were measured five times each using a colorimeter (CE 3100, Gretag Macbeth, Germany) according to the CIELab system, and the average values were applied. In addition, the C^* (chroma) and h (hue angle) values were determined from the L^*, a^*, and b^* colorimetric system as shown below:

Metric chroma, $C^* = \sqrt{(a^*)^2 + (b^*)}^2$ … (1)

Metric hue-angle (h), deg = $\tan^{-1}(\frac{a^*}{b^*})$ … (2)

The color difference (ΔE^*) between the fermented and unfermented dyed fabrics was obtained from the CIE L^*, a^*, and b^* color system. When the coordinates of standard color is lightness L_1^* and the chroma coordinates a_1^* and b_1^*, and the coordinates of the color to be compared are the lightness L_2^* and the chroma coordinates a_2^* and b_2^*, various colour difference are shown below:

Light difference (ΔL^*) $= L_2^* - L_1^*$

Redness-greenness (Δa^*) $= a_2^* - a_1^*$

Yellowness-blueness (Δb^*) $= b_2^* - b_1^*$

Color difference (ΔE^*) $= (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{½}$

The color strength of samples before and after fermentation was evaluated using a computer color matching system (CCM, X-Rite 8200, USA). The system was set to D 65 illuminant/10° standard observer system in 400 ~ 700 nm. Five measurements were taken from each sample at different 4 portions and the average value was recorded. The relative color depth by *K/S* value at the maximum absorption wavelength was calculated by the Kubelka–Munk equation.

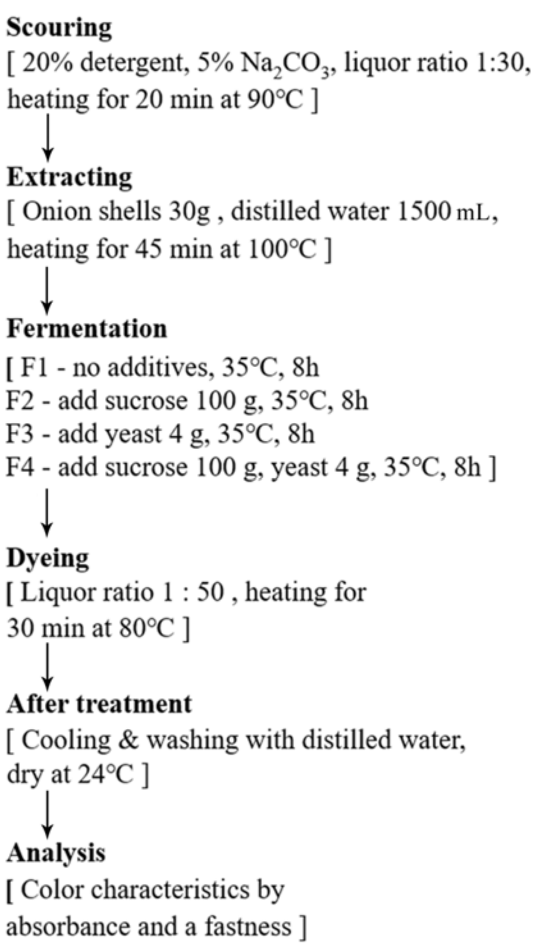

Fig. 2 — Fermentation and dyeing procedures for silk using various types of fermented onion peels

2.6 Fastness

The light fastness, and fastness to washing and perspiration were evaluated. The light fastness was measured using XENON_ARC_LAMP and BLUE SCALE according to KS K ISO 105-B02: 2014, and the washing fastness was carried out using the KS K ISO 105-C106: 2014 (A1S) method with ten beads each, and 0.4% ECE standard detergent at 40 °C for 30 min. The fastness to perspiration was measured using acid and an alkali staining solution for 4 h at 37 ± 2°C in accordance with KS K ISO 105-E04: 2013.

3 Results and Discussion

3.1 Color Change of Dye Solution

Figures 3 and 4 (a) show the absorbance graphs of the qualitative and quantitative differences of the fermented dye solution taken from the laboratory using a fluorescent lamp within the visible region (380 - 780 nm). As shown in Fig. 3, the color of the dye solution before and after fermentation is visually distinguished. It is found that the dye solution extracted during the third method exhibits the most distinctive color difference. It is thought that the flavonol and quercetin, the main pigments of onion peels, are structurally changed through fermentation owing to various changes in the phenolic -OH groups of 3-hydroxyflavone (3-hydroxy-2-phenylchromen-4-one). In addition, as shown in Fig. 4 (a), the absorbance of each fermented dye solution varies from 491 nm to 500 nm (bluish-green), 481 nm to 490 nm (greenish-blue), and 436 nm to 480 nm. In particular, it can be seen that the fermentation solution

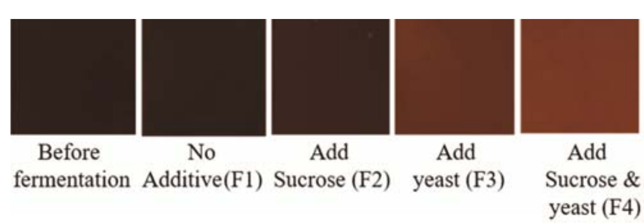

Fig. 3 — Color appearance of liquid fermented onion peel extract

with added yeast shows the clearest change. Therefore, it is found that the presence of microorganisms has a greater effect on the color change through the liquid fermentation of the onion peel extract than the nutrients applied for fermentation. The results of UV-A (90.4%) and UV-B (92.5%) of the silk dyed with onion peels, as shown in a previous study[1], can be confirmed by the results in Fig. 4 (b). In other words, it can be seen that the UV absorption rate of the onion peel dyes within the UV-B region of 280 nm to 315 nm is larger, and in particular, when fermentation was carried out using sugar and yeast, a strong absorption peak at 254 nm could be expected to have a sterilizing effect through the ultraviolet rays.

3.2 *p*H and Sugar Content of Dye Solution

Table 1 shows the *p*H and sugar content of the dye solution used. The *p*H of the extracted onion peels prior to fermentation was measured as 4.1. The *p*H of the dye solution after fermentation is found the highest when sucrose and yeast are added together, and a significant change is confirmed when only yeast was added. It is found that the sugar content remains constant, except when artificial nutrition sources are added.

The microorganisms have a significant effect on the fermentation of dye solution, and nutritional sucrose is found to affect the *p*H of the solution through the aggressive activity of the microorganisms. Therefore, it can be seen that the *p*H of the sucrose used as the nutrient is slightly lowered, and the *p*H of the yeast is increased. When added together, the *p*H is significantly reduced from 4.1 to 3.2, and the sugar content drastically increases from 1.9 Brix to 7.7 Brix, which is due to the decomposition of various pigment components of the onion peels through liquid fermentation. It can be assumed that the component itself goes through denaturing process. In Fig. 3, the apparent color changes from dark before fermentation to light as a result of the fermentation, which may also affect the dyeability.

Table 1 — *p*H and Brix of onion peel extract before and after liquid fermentation

Code	Fermentation	*p*H	Brix, °Bx
F0	Before fermentation	4.1	1.9
F1	No additives	4.0	1.9
F2	Add sucrose	4.0	11.1
F3	Add yeast	4.4	1.9
F4	Add sucrose & yeast	3.2	7.7

3.3 Color Yield of Dyed Fabrics

Table 2 shows the dyeability on L^*, a^* and b^* values of each sample when using the onion peel extract before and after liquid fermentation on silk. The L^* value of the lightness is found 55.8, which indicates a deep dark colour when the dyeing is performed after

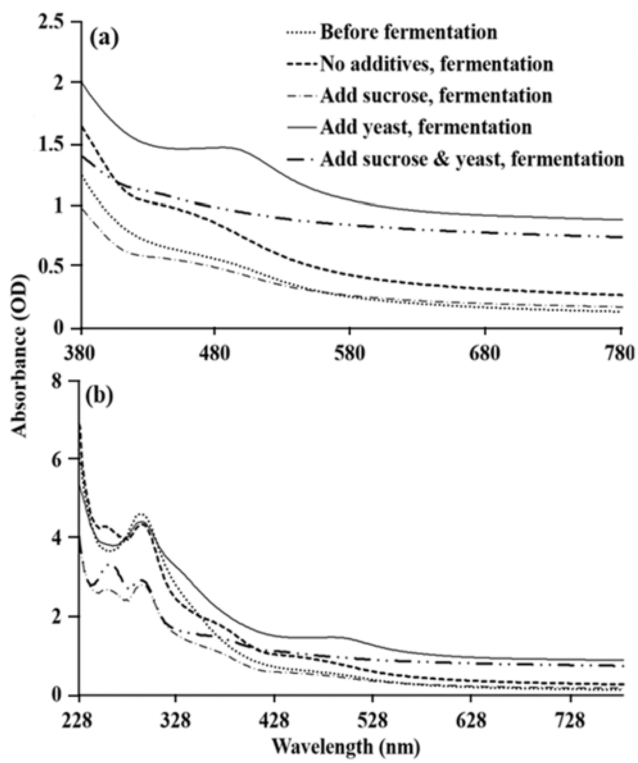

Fig. 4 — Absorbance of onion peel extract before and after liquid fermentation at different wavelengths (a) absorbance of 380 nm to 780 nm and (b) 228 nm to 728 nm

Table 2 — Color values of fabrics dyed with onion peel extract before and after liquid fermentation

Fermentation	X	Y	Z	L^*	a^*	b^*	ΔE	C^*	h
Before fermentation	19.89	18.16	9.42	49.69	13.92	24.39	-	28.08	60.28
F1 (No additives)	21.28	19.97	10.89	51.81	11.59	23.63	0.94	26.31	63.88
F2 (Sucrose)	22.43	21.62	12.24	53.63	9.15	23.05	2.96	24.80	68.35
F3 (Yeast)	32.39	32.75	22.28	63.69	4.91	19.42	0.00	20.03	75.82
F4 (Sucrose & Yeast)	28.58	28.59	18.06	60.41	5.89	21.32	0.14	22.12	74.54

fermentation with no additives. However, when only sucrose is added, there are no significant changes. The lightness is 71.64 when the dye is added with yeast only, whereas the addition of yeast and sucrose shows a lightness of 66.72, which is higher than prior to fermentation. When the yeast and sucrose are added together, the a^* value is found much lower than before fermentation, and the b^* value shows no significant difference in terms of the fermentation. Figure 3 shows that the nutrients and microorganisms slightly increased the red color through liquid fermentation, whereas a^* value is decreased in the actual color measurement of the dyed silk fabrics. These results suggest that yeast affects the lightness of the dyed silk and the reddish coloration of the onion peel, which is a polychromatic dyestuff. Their relative values are also determined by taking an unfermented sample as the standard. It can be seen that the color differences through fermented dyeing achieve the best results when sucrose is added. In case of no additive, addition of sucrose-yeast, and addition of only the yeast, the color difference is found to be zero, although L^*, a^* and b^* values can be measured. Figure 5 shows the surface color of silk dyed before and after fermentation of the onion peels. The same liquid ratio (owf) is applied, but the fermentation shows a remarkable color change. It can be seen that the color of the fermentation solution is significantly different from those shown in Fig. 3, and its color is significantly lightened. However, it can be inferred that the dyeing is improved owing to the new dyeing adhesion between the silk amino group ($-NH_2$) and the chemical structures which is changed through liquid fermentation. As shown in Fig. 6, the *K/S* value of silk dyed with anion peel adding only sucrose is the highest 8.62, and the *K/S* values before fermentation and when both sugar and yeast are added, are found to be one more higher than in case of no-additives. However, after fermentation, the difference in *K/S* value from 2.02 to 5.24 is not large. It is also found that the value after fermentation is slightly decreased.

3.4 Color Fastness

To evaluate the dyeing fastness before and after fermentation of the onion peel extract, the fastness, (light fastness) having the greatest disadvantage in natural dyeing, and the perspiration and wash fastness having other significant problems with silk dyeing, are measured. As shown in Table 3, the fastness of light is superior to that of grade 3 or higher after fermentation. This grade is much higher than the grades 1 and 2, generally obtained in natural dyeing products. Hence, the proposed process is expected to be useful for future commercialization. In particular, the sample dyed after yeast fermentation and the addition of sucrose + yeast result in a very good color

Fig. 5 — Appearance in color of fabrics dyed with onion peel extract before and after liquid fermentation

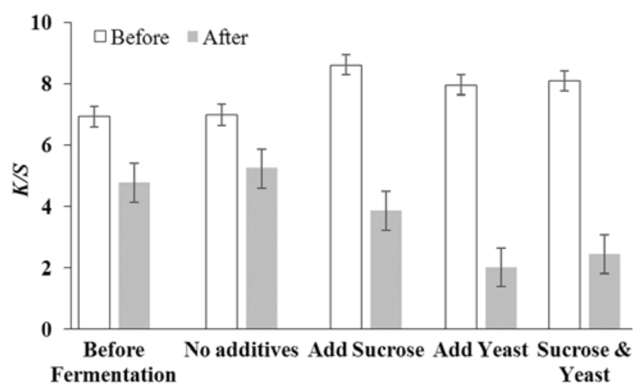

Fig. 6 — *K/S* values of fabrics dyed with onion peel extract before and after liquid fermentation

Table 3 — Fastness to light, perspiration, and washing of fabrics dyed with onion peel extract before and after liquid fermentation

Fermentation	Light (20h)	Washing			Perspiration (acidic)		
		Change in color	Stain		Change in color	Stain	
			Cotton	Silk		Cotton	Silk
Before fermentation	3	4	3-4	4	4-5	3	3
No additives (F1)	3	4	3-4	4	4-5	3	3
Add sucrose (F2)	3	4	3-4	4	4-5	3-4	3-4
Add yeast (F3)	3-4	3-4	3-4	4	4-5	3-4	3-4
Sucrose & Yeast (F4)	3-4	3-4	3-4	3-4	4	3	3-4

fastness of grades 3 and 4. This indicates that dyeing through liquid fermentation using microorganisms and nutrients can maintain a sufficiently high level of light fastness even when a mordant is not used, as compared to the findings of previous studies[13, 19], in which the light fastness of non-fermented onion peels is measured as grade 2. In addition, the wash fastness test shows that most of samples dyed with the fermented dye solution achieve grades 3 and 4. These results are expected to provide relatively stable durability after washing as compared to the results obtained for non-fermented onion peels grades (2 and 3)(ref.18). This is expected to be applied as the basis for predicting the possibility of mass liquid fermentation dyeing. Table 3 also shows the results of perspiration fastness, and the color difference of silk after liquid fermentation with onion peels. As a result, most of the silk achieve a grade higher than 3 or 4, indicating that the fastness under acidic and alkaline perspiration is superior to that of the sample dyed prior to fermentation.

4 Conclusion

The inference drawn by the study is given below :

4.1 The absorbance of most of the fermented solution is increased within the ranges of 491 – 500, 481 – 490, and 436 – 480 nm, and the fermented solution with yeast added shows the greatest change in absorbance.

4.2 The *p*H and sugar content of the solution achieved through liquid fermentation are higher than those found in the fermentation solution with added nutrients, and this shows a change in color. As a result, the fermented solution is affected more by the microorganisms than by the nutrient source.

4.3 The L^*, a^* and b^* values of the dyed silk fabrics show that L^* increases and a^* decreases with the addition of yeast. It is also found that the *K/S* value after fermentation is slightly decreased.

4.4 To evaluate the durability of dyeing, the fastness to light, washing, and perspiration is measured, and most of the fastness shows a grade better than 3 or 4.

4.5 Using fermentation of the solution without a mordant used in the dyeing of silk with a polychromatic dye, it is possible to show various colors with the change in fermentation conditions at the same concentration. Better dyeing fastness is exhibited after fermentation.

4.6 This method can be used as a more practical and environment-friendly dyeing process. In particular, it is considered that the effects of microorganisms, which are applied as a fermentation condition, are greater than the influence of the nutrient source. Therefore, to improve the various colors and dyeability that are achievable, further research in this area need to be conducted.

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References

1 Sim H J & Park Y M. Park, *Text Color Finish*, 29 (2017) 62.
2 Adeel S, Gulzar T, Azeem M, Rehman F, Saeed M, Hanif I & Iqbal N, *Radiation Phys Chem*, 130 (2017) 35.
3 Park Y M, Koo K & Kim S S, *Text Color Finish*, 21 (2009) 29.
4 Lee J B, Sustainable modern product development utilizing the value of eco-friendly traditional dyeing, *Proceedings, Sustainability Science Society Spring Conference* (The Society of Sustainability Science, Seoul), 2016, 133.
5 Shin J D & Choi J M, *Res Costume Culture*, 24 (2016) 777.
6 Yeo Y M & Shin Y S, *Text Color Finish*, 29(3), (2017) 171.
7 Hwang E K & Kho T, *J Asian Ethno-Forms*, 13 (2014) 73.
8 Han J H & Moon E B, *J Korea Soc Color Studies*, 31(1), (2017) 15.
9 Shin Y J, *J Korea Fashion Costume Design Assoc*, 17(2), (2015) 45.
10 Rehman F, Adeel S, Shahid M, Bhatti I A, Nasir F, Akhtar N & Ahmad Z, *Radiation Phys Chem*, 92 (2013) 71.
11 Lee J E, Kim H J & Lee M C, *Text Color Finish*, 13(3), (2001) 11.
12 Bae S E and Shin I S, *Text Color Finish*, 10(6), (1998) 27.
13 Kwak E J, *A Study on the Dyeability and Color for Dyeing from Quercetin : Focused on the Onion Shell*, M S thesis, Konkuk University, Seoul, Korea, 2000.
14 Wu C H, Shieh T M, Wang K L, Huang T C & Hsia, S M, *J Funct Foods*, 19(A) (2015) 495.
15 Rs K S, Suh H J, Chung S H & Son J Y, *Korean Soc Food Sci Technol*, 29(3) (1997) 595.
16 Dębowski M, Zieliński M & Dudek M, *Energy Procedia*, 105 (2017) 681.
17 Heo B G, Park Y S, Lee S P, Choi J R, Jang H G & Kim Y H, Effect of temperature treatment on the coloring of the cotton fabrics dyed with the fermented persimmon liquor, *Proceedings of Korean Society for Horticultural Science* (Seoul) 25(10) 2007 112.
18 Song K H, J Korean Soc, *Food Sci Nutrition*, 46(8) (2017) 86.
19 Im IS, *J Korean Soc Food Sci Nutrition*, 46(8) (2017) 86.