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〈Research Paper〉

The Dyeability and Antibacterial Activity of Wool Fabric Dyed with Cochineal

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Abstract— The purpose of this study was to investigate the dyeability and antibacterial activity on wool fabric dyed with cochineal at variable dyeing conditions. Al, Cr, Fe, Cu and Sn were used as mordants and adsorption was compared with different mordanting methods. The optimum dyeing conditions of wool fabrics were dyeing concentration 2.0%(o.w.s), dyeing temperature 60℃, pH 3 and dyeing time 30 minutes. The pre-mordanting method was preferred for Al and Cr, and the post-mordanting one was preferred for Cu, Sn and Fe to achieve better dyeing. The optimum mordanting conditions of wool fabrics dyed with cochineal were mordanting concentration of 1%(o.w.s), mordanting temperature 60℃, and dyeing time 30 minutes. Wool fabrics dyed with cochineal showed a little antibacterial activity, but it was increased by Cu and Sn mordanting. The light fastness and perspiration fastness of wool fabric treated with cochineal were improved by mordanting.

Keywords: *Cochineal, dyeability, antibacterial activity, fastness, optimum conditions*

1. Introduction

Cochineal, which changes its color into red, red-purple, or gray-red depending on mordants, is called Coccus Cacti L in a scientific term[1,2]. Its main ingredient is Carminic acid and has a chemical structure composed of -OH and -COOH.

Carminic acid was found in an amorphous state by Pelletier and Caventou in 1818, and in a crystallized state by P.Schutzenberger in 1856. Carminic acid extracted from Cochineal is a substance of red~dark brown purple liquid, mass, powder, or syrup state, which smells a little fishy and is solved not in oil, but in water, ethanol, ether, propyleneglycol or caustic soda. The color of solution shows "halochromism," color changing phenomenon according to pH variations -- yellowish red in acidity(below pH 3), red~red purple in neutrality(pH5~6) and red purple~purple in alkali(above pH7) respectively[3]. This phenomenon is a reversible reaction. The maximum absorption wavelength is 496nm. Although lightfastness is excellent and stable, the lightfastness becomes worse as pH rises[4]. This phenomenon is similar to that of general coloring materials.

Cochineal has been used as dyeing material for cotton, silk, wool, etc. from ancient time, and it is also used as cosmetic and food coloring material. Red ink extracted from Cochineal is well known as a material of no color change and decoloration[5]. The original ingredient of this coloring material is Carminic acid, which is classified as a C-glycoside following "structure classification" of natural coloring material. In general, this kind of coloring material, extracted from plants or animals, is not dissoluble because its stability is high.

Cochineal mainly inhabits in areas of Mexico and mid South America, and is bugs, which

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parasitic on "crab-claw cacti, or Sapoten." From red-colored female bugs, red coloring material is extracted. Female bugs sticking on plants are first collected just before spawning. After being treated in hot water or steam, the bugs are dried, heated and grinded. Cochineal is obtained through this process.

In Cochineal research, Cho[3] investigated thermodynamic characteristics of silk and wool fiber, and Han and Chu[5] compared and reviewed dyeing characteristics of Cochineal coloring material and Carminic acid's dyeing to silk fiber.

This research investigated the optimum coloring conditions of Cochineal for wool fiber. Based on the conditions, fastness and antibacterial activity were measured to improve functional capacity of Cochineal by means of natural dyeing.

2. Experimental

2.1. Specimens

Fabric specimens used in this research were standard experimental fabrics for fastness measurement, which were designated in KS K 0905. Characteristics of materials were shown in Table 1.

Table 1. Characteristics of fabrics

Sample	Weave	Count		Density (thread/5cm)		Weight (g/m²)
		warp	weft	warp	weft	
Wool	plain	1/52	1/68	142	136	102±5

2.2. Dyeing Material

Cochineal used in this experiment was Cochineal powder(a product of Mikwang International Co. Ltd.), which could be easily obtained in the market. The original coloring ingredient of Cochineal was carminic acid-($C_{22}H_{20}O_{13}$) of anthraquinone and its chemical structure was shown in Fig. 1.

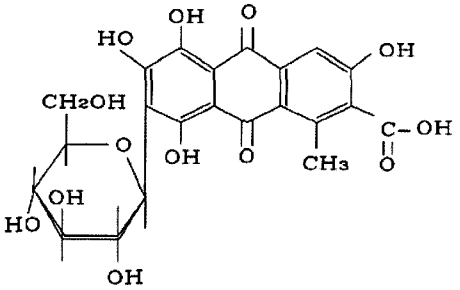

Fig. 1. Structure of Carminic acid.

2.3. Chemical Reagent

The original first class reagent of Aluminium potassium sulfate[$AlK(SO_4)_2$], Chromium(III) potassium sulfate[$CrK(SO_4)_2 \cdot 12H_2O$], Copper(II) sulfate($CuSO_4 \cdot 5H_2O$), Tin(II) Chloride dihydrate-($SnCl_2 \cdot 2H_2O$), Iron(II) sulfate($FeSO_4 \cdot 7H_2O$) is used as mordant. CH_3COOH and NaOH are used as a guarantee reagent to adjust pH degree.

2.4. Dyeing and Mordanting

2.4.1 Dyeing

Cochineal purchased in the market is used for dyeing under the conditions of the following: dyeing concentration(0.5, 1, 1.5, 2, 2.5, 3%) (o.w.s.), dyeing time(30, 40, 50, 60, 80, 90 minutes), dyeing temperature(30, 40, 50, 60, 80, 90℃) and bath ratio(1:100) under the fixed pH.

2.4.2 Mordanting

Both pre-mordanting and post-mordanting methods are adopted for mordanting. Mordanting conditions are mordanting time(30 minutes), mordanting temperature(60℃) and mordanting concentration(0.5, 1, 2, 3, 4, 5%) respectively.

2.5. Measurement and Analysis

2.5.1 UV-Vis Spectrophotometery

By using UV-Vis spectrophotometer(8452A Diode Array Spectrophotometer from Hewlett Packard Asia Ltd., USA), absorption was measured contingent on pH variations of dyeing solution.

2.5.2 K/S value measurement

By using Computer Color Matching System-(Color Quest XE, Hunterlab, U.S.A), dye uptake-(henceforth, K/S) was calculated by standard

reflectance obtained from a 496nm wavelength.

2.5.3 Color Difference Measurement

By using Computer color matching system (Color Quest XE. Hunterlab. USA), color difference (henceforth, ΔE) was measured in the colorimetric data L*, a*, b*.

2.6. Dyeing Fastness Measurement

Based on light, friction, perspiration, dry-cleaning and washing, dyeing fastness was measured by using Cochineal with and without mordants.

Light fastness was measured by weathering method depicted in the KS K 0707-80 , friction fastness was measured by crockmeter method depicted in the KS K 650-80, perspiration fastness was measured by persipirometer depicted in the KS K 0715-80.

Dry-cleaning fastness was measured by petroleum solvent method depicted in the KS K 0644-80 and washing fastness was measured by launder-o-meter method depicted in the KS K 0430.

2.7. Antibacterial Activity Measurement

By using staphylococcus aureus, antibacterial activities of Cochineal and mordants in themselves were measured by MIC(Minimum Inhibitory Concentration) test. Antibacterial activities of specimens dyed with Cochineal or mordanted with various mordants were done by the bacteria number measurement depicted in the KS K 0693.

3. Results and Discussion

3.1. Absorption on pH variations of Cochineal

The following Fig. 2 shows the curve of absorption changing on dyeing solution pH variations of Cochineal coloring material.

Curve A, B, and C show the changing process of absorption activity in pH4, pH7 and pH11 respectively. Carminic acid, which is the main ingredient of Cochineal, shows sensitive color change according to pH variations. In general, the color in acidity-pH4 was equi-red and λmax was 495nm. In pH7 and pH11, red-purple and red color appeared respectively and the values of λmax were 533nm and 577nm. From this experiment, it is observed that Chochineal is very sensitive to pH variations; that is, as pH rises higher, absorption spectrum moves toward long wave. The bathochromic effect featuring red shift is distinctive. Cho[3] suggested that carboxy and hydroxyl group generated negative ions by alkali, so that unsaturated binding increased in the structure.

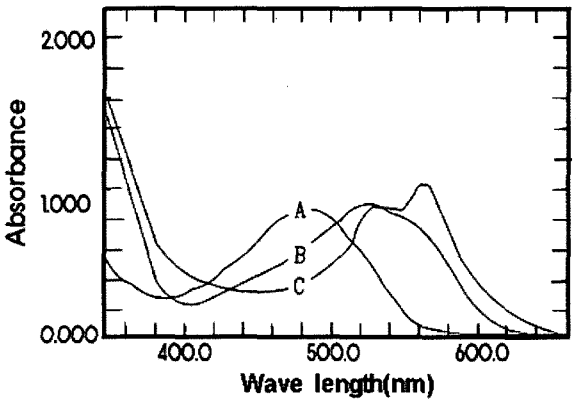

Fig. 2. UV-VIS spectra based on pH variations of Cochineal(A : pH 4, B : pH 7, C : pH 11).

3.2. Effect of Dyeing Conditions on K/S values and Colors

3.2.1 Effect of Dyeing Concentration on K/S values

To measure the relationship between dyeing concentration and K/S values of wool fabric dyed with Cochineal, six different dyeing concentration(0.5%, 1%, 1.5%, 2%, 2.5% and 3%) were examined in this experiment with the other fixed conditions of 60 minutes(dyeing time), 60℃(dyeing temperature) and pH3. The result is shown in Fig. 3.

In this graph, K/S values of wool fabric increased steadily in 2%(dyeing concentration), but above 2% K/S value did not show any increase. We determined that the saturated dyeing concentration of wool fabric was 2%.

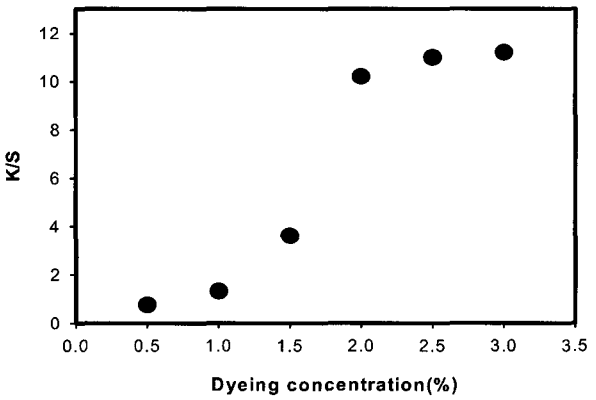

Fig. 3. Relationship between dyeing concentration and K/S values of wool fabric dyed with Cochineal.

3.2.2 Effect of Dyeing time on K/S values

To measure the relationship between dyeing time and K/S values of wool fabric dyed with Cochineal, six different dyeing times(30, 40, 50, 60, 80 and 90 minutes) were given in this experiment with the other fixed conditions of 60℃(dyeing temperature), 2.0%(dyeing concentration) and pH3. The result is shown in Fig. 4.

In this graph, after 60 minutes, there was little difference between K/S values of wool fabric. We estimated that dye molecules of dyeing liquid had gone into fabric within the initial 60 minutes. From this experiment, we concluded that the optimum dyeing time of Cochineal to Wool fabric was 60 minutes.

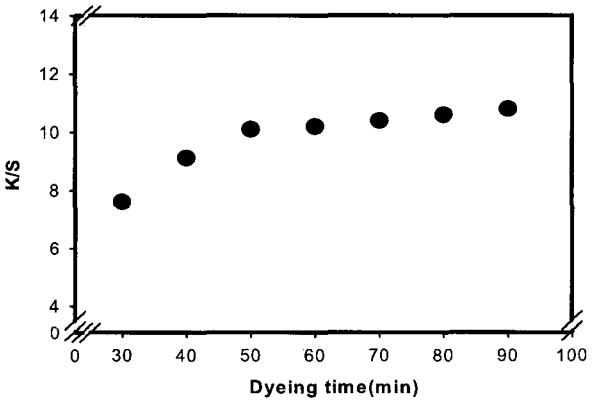

Fig. 4. Relationship between dyeing time and K/S values of wool fabric dyed with Cochineal.

3.2.3 Effect of Dyeing Temperature on K/S values

To measure the optimum dyeing temperature of Cochineal to each fabric, 6 different dyeing temperatures (30℃, 40℃, 50℃, 60℃, 80℃ and 90℃) were given in this experiment under the other fixed conditions of 60 minutes(dyeing time), 2.0%(dyeing concentration) and pH3. The result is shown in Fig. 5.

In this figure, K/S values increased steadily between 30℃ and 60℃, but above 80℃ there was little difference and a Milling phenomenon was observed. Wool fabric became shrunk and rough above 80℃[8]. From the result, we concluded that the optimum dyeing temperature of Wool fabric dyed with Cochineal was 60℃.

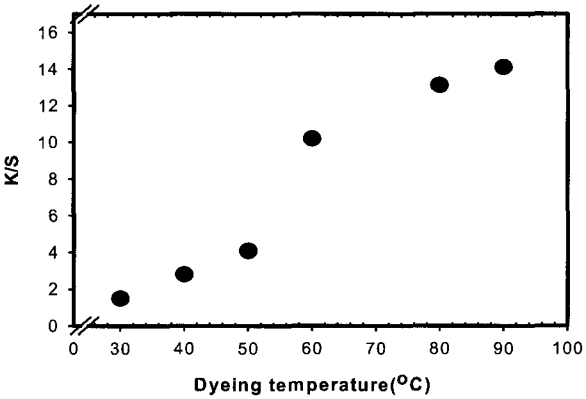

Fig. 5. Relationship between dyeing temperature and K/S value of wool fabric dyed with Cochineal.

3.2.4 Effect of Cochineal's pH values on K/S values

To measure the relationship between K/S values of wool fabric and pH values of Cochineal, five different pH values(3, 4.5, 7, 9.5 and 11) were given in this experiment under the other fixed conditions of 60 minutes(dyeing time), 60℃ (dyeing temperature) and 2.0%(dyeing concentration). The result is shown in Fig. 6.

In this figure, K/S value of wool fabric was the highest in pH 3. While pH values increased, K/S values decreased. We estimated that this result had come from property changing caused by the increase of unsaturated bindings by negative ions which were generated by alkali sensitive to pH variations. We observed that the optimum dyeing pH value of Cochineal was 3.

Cochineal alters color depending on dyeing solution pH values. Cochineal shows halo-

chromism, color changing depending on dyeing solution pH values and is a functional dyeing material with various colors[6]. For wool fabric, the optimum pH value is around pH3, in which K/S value is the highest. This result is in agreement with Cho's[3]. Above pH3, K/S values decrease and it is almost impossible to dye wool fabric above pH 7.

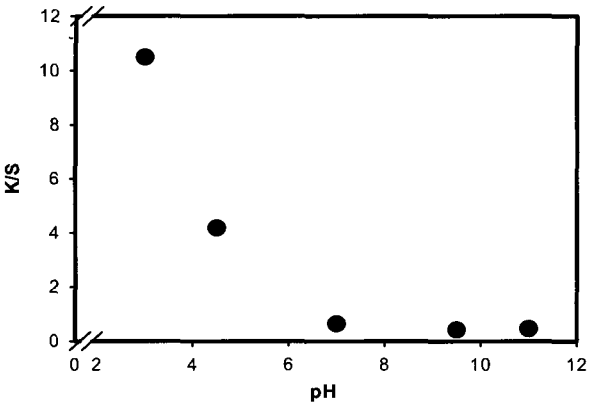

Fig. 6. Relationship between K/S values of wool fabric and pH values of Cochineal.

3.3. Effect of Mordants on K/S values and Colors

3.3.1 Effect of Mordant concentration on K/S values and colors

To obtain the optimum concentration of mordants for fabric dyed with Cochineal, five concentration rates of mordants(0.5%, 1%, 2%, 3%, 4% and 5%) were given under the other fixed conditions of 30 minutes(mordanting time), 60℃(mordanting temperature) and pre-mordanting(mordanting method). The result is shown in Fig. 7.

Fig. 7 shows the K/S value variations based on concentration values of various mordants applied to wool fabric. In the figure, between 0.5% and 1% concentration all the mordants except Al showed little change, while K/S values became higher. However, the Al mordant increased K/S values slightly as the mordant concentration was raised.

From this result, we estimated that the amount of dyeable mordant inside fabric had already been saturated and reached dyeing equilibrium. This means that, although mordant concentrations increased, there was no increase in dyeing uptake amount. From this, we concluded that the optimum concentration rate of mordant for wool fabric was 1.0%.

Because carboxyl and hydroxyl groups exist inside the structure of Cochineal, dyestuff and metal ions form chelate. By adding metallic salt, bathochromic shift occurred. This absorption wavelength movement is called the bathochromic effect.

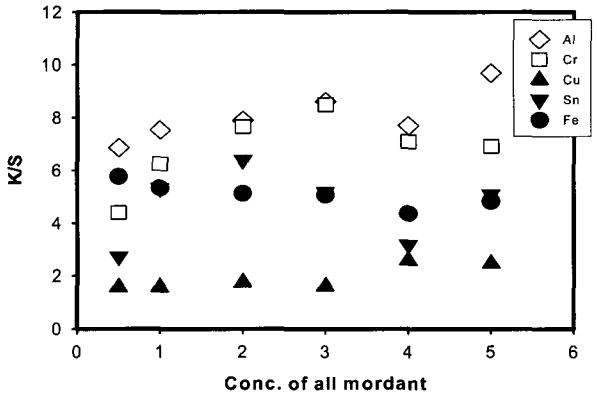

Fig. 7. Relationship between concentration of mordant and K/S values of Wool fabric dyeing with Cochineal under the optimum condition.

3.3.2 Effect of Mordanting methods on K/S values and colors

To measure the effect of mordanting methods on K/S values of Wool fabric dyed with Cochineal, pre-mordanting and post-mordanting methods were executed under the same conditions(30 minutes-mordanting time and 60℃ mordanting temperature) to obtain the optimum mordanting concentration. The optimum concentration of mordanting obtained in the previous experiment is fixed in 1.0%. The result is shown in Fig. 8.

In the figure the pre-mordanting method with Al and Cr mordants obtained higher K/S values than the post-mordanting one did. With Cu, Sn and Fe mordants, the post-mordanting method was preferred to get higher K/S values. From this experiment, we found that for better color manifestation Al and Cr mordants had to be treated by the pre-mordanting method.

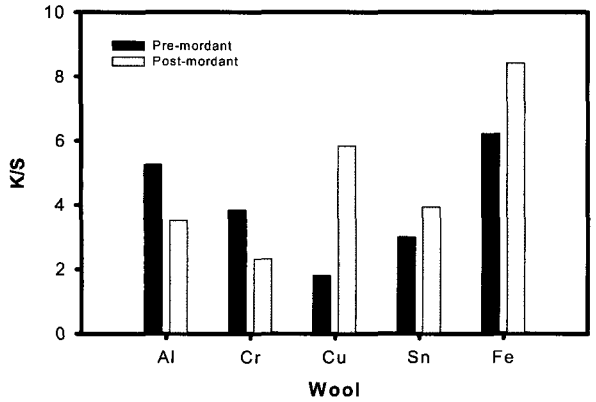

Fig. 8. Effect of mordanting methods on K/S values of wool fabric dyed with Cochineal.

Cu, Sn and Fe mordants had to be treated by the post-mordanting one when wool fiber was processed. This higher K/S value may be due to chelate generated by binding carboxyl and hydroxyl group of Cochineal. And, it may also be due to metallic ions of mordants on fiber after bindings between mordants and fiber, and also between Cochineal and fiber. We concluded that, to improve coloring effect in wool fabric dyeing, the choice of mordanting methods was depended on the kinds of mordants.

3.4. Dyeing Fastness

Table 2 shows the result of fastness measured from specimens dyed under the optimum conditions for wool fabric. Wool fabric processed with no mordants produced high values for all the fastness except light fastness(1st grade). But, light fastness of wool fabric treated with Al, Cr, Cu, Sn or Fe mordants raised 1~2 degrees, but friction fastness lowered on the contrary. Although Fe mordant lowered friction fastness a little, almost all the fastness of wool fabric treated with Fe mordant improved, compared to that of no mordant treatment. From this output, we may think that using Fe mordant for Cochineal dyeing will be very helpful for fastness improvement.

3.5. Apparent Color Changes on Dyeing Methods

Table 3 shows the apparent color changes according to dyeing methods for wool fabric. In this table, K/S values of the pre-mordanting method treated with Al or Cr mordants are higher than those of the post-mordanting one. For Cu mordant, post-mordanting had a better result in coloring. For Sn and Fe mordants, both pre-mordanting and post-mordanting had a positive dyeing effect. This result is in agreement with Chu's report[9].

The pre-mordanting wool specimen treated with Al mordant resulted in 3R 3/7(H V/C value), and this value demonstrated that the color of this specimen was closer to red purple than red. The color of the actual dyed specimen appeared purple.

The pre-mordanted dyed specimen treated with Cr mordant had 1.3 RP 3/6(H V/C value) which appeared slightly red violet. The post-mordanted dyed specimen had 4P 3/2 which appeared dark violet. The dyed specimen treated with Sn mordant had 0.2R 4/10 in both pre-mordanting and post-mordanting methods.

Table 2. Fastness of dyed fabrics with Cochineal, using various mordant

Fabric	fastness \ mordant		non	Al	Cr	Cu	Sn	Fe
Wool	Light		1	2	3	3	1	3
	Perspiration	Acidity	4	4	3	4	4	4-5
		Alkalinity	4	4	3	4	4	4-5
	Rubbing	Dryness	4	1	2-3	4	1	3-4
		Wet	3	1	1	1	1	2-3
	Drycleaning		4	4	4	4	4	4-5
	Washing		4-5	4-5	4-5	4-5	4-5	4-5

Table 3. The colorimetric value of wool fabrics dyed with Cochineal

Fabric	method	Mordant	L*	a*	b*	⊿E	C	H	H V/C	K/S
Wool	non		88.264	-0.617	7.742		7.767	94.591	3.35 Y 9/1	
	pre	Al	33.301	30.918	9.957	63.406	32.482	17.844	3 R 3/7	5.7260
		Cr	35.510	24.263	-10.517	61.118	26.444	336.575	1.3RP3/6	3.8465
		Cu	55.614	6.203	-1.979	34.742	6.511	342.312	2RP 5/2	1.8140
		Sn	40.972	41.352	7.101	63.266	41.957	9.740	0.2 R 4/10	3.0000
		Fe	29.593	3.333	-4.040	59.973	5.237	309.543	3.4 P 3/1	6.2285
	post	Al	39.649	35.883	12.850	61.006	38.114	19.695	3.2 R 4/8	3.5170
		Cr	43.537	28.566	6.148	53.429	29.220	12.141	0.6 R 4/6	2.3185
		Cu	30.044	7.382	-8.029	60.846	10.402	310.329	4 P 3/2	5.8400
		Sn	37.630	44.369	7.058	67.735	44.927	9.035	0.2 R 4/10	3.9305
		Fe	26.555	1.819	-4.838	63.025	5.169	290.633	8 PB 3/1	8.4150

The color of this treatment was very bright, clear pink-red.

The dyed specimen with Fe mordant appeared violet-white in the pre-mordanting method, and appeared grayish close to black color in the post-mordanting method.

3.6. Antibacterial Activity

3.6.1 Antibacterial Activities of Cochineal and all Mordants

Table 4. Antibacterial activities of Cochineal and all mordant

Material	Minimum Inhibitory Concentration (ppm)
Cochineal	100
Al mordant	1000
Cr mordant	100
Cu mordant	10
Sn mordant	100
Fe mordant	1000

Table 4 is the result of antibacterial activities of Cochineal and all mordants obtained from the MIC test. The outputs were as follows: 100ppm(Cochineal), 100ppm(Cr mordant), 10ppm-(Cu mordant) and 100ppm(Sn mordant). From the result, we identified that Cu mordant antibacterial activity was the strongest, and Cochineal, Cr and Sn mordants have a certain degree of antibacterial activity.

3.6.2 Antibacterial Activity of Dyed specimens

Table 5 shows the result of the antibacterial activities of specimen fabrics dyed with Cochineal under the optimum conditions for each fabric.

These numerical values were measured by the number of bacteria incubated by the standard white specimen and all the specimens which were treated with each mordant.

Even though Cochineal itself had a certain degree of antibacterial activity, Cochineal dyeing of wool fabric with bo mordants showed 0% bacteria diminution rate. Therefore, we could not expect satisfactory antibacterial activity of wool fabric dyed only with Cochineal. But specimens treated with Al, Cu, or Sn showed 50% decrease in bacteria. Wool fabric treated with Sn mordant revealed 100% decrease in bacteria. However, compared to the antibacterial activity of Cu itself, the antibacterial activity of wool fabric dyed with Cu post-mordanting decreased.

Even though Cu had the highest antibacterial activity among Cochineal and mordants, wool fabric dyed with Cochineal recorded 83% in the actual dyeing and Cu showed less activity value than Sn. Judging from this result, we realized that wool fabric should be treated by

Table 5. Antibacterial activities of the fabrics dyed with Cochineal

Dyed Fabrics \ Antibacterial activities		Reduction ratio of colonies(%)
		Staphylococcus aureus
Wool	Non	0
	Al	52.8
	Cr	28.3
	Cu	83.0
	Sn	100
	Fe	33.9

Cu or Sn for improving antibacterial activity.

Furthermore, Sn mordant will be very effective to increase antibacterial activities of dyed specimens because it showed 100% antibacterial activity in the experiment.

4. Conclusions

In this study, Cochineal, which has a dyeing material with various colors that can be extracted from animal-natured bugs, was used to investigate dyeability, antibacterial activities and so on.

The following are the results from the research;

1. The optimum dyeing conditions of Cochineal for wool fabric are dyeing concentration -2.0%(o.w.s.), 60℃(dyeing temperature), 60 minutes(dyeing time) and pH 3.
2. The optimum mordanting conditions were 1.0%(mordanting concentration), 60℃(mordanting temperature) and 30 minutes(mordanting time). As for mordanting methods, pre-mordanting was preferred for Al or Cr mordants, and post-mordanting is preferred for Cu, Sn or Fe mordants to achieve better dyeing.
3. The light fastness after mordanting treatment except with Sn mordant for wool fabric increased to some extent, but friction fastness of all the mordants decreased on the contrary.
4. MIC test results in antibacterial activities revealed that the antibacterial activity of Cu was the highest among mordants, but Sn mordant was the most effective in antibacterial activities after mordanting treatment of wool fabric.

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