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Natural Dyeing using the Colorants extracted from American Fleabane (I)
-Dyeing properties on wool-

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개망초 추출물을 이용한 천연염색(I)
-모섬유에 대한 염색성-

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Abstract

개망초로부터 색소를 추출, 분말화하여 FT-IR 분석을 행하고, 모섬유에 대한 염색조건과 매염이 염착량(K/S값) 및 색상에 미치는 영향을 조사하였다. 또한 염색한 시료의 견뢰도를 측정하여 실용성을 확인하였다. 개망초 색소는 모섬유에 높은 친화력을 보였으며, Langmuir형의 등온흡착곡선을 보여 염착이 주로 이온결합에 의해 이루어지는 것으로 나타났다. 염착량이 pH 3.0에서 최대가 되었으나 강한 산성조건은 강도 저하를 비롯한 섬유에 손상을 주기 때문에 pH를 조절하지 않고 염색하였다. 피염물의 색상은 모두 Y 계열을 나타내었다. 철매염 처리한 경우를 제외하고 매염처리가 염착량 증진에 미치는 영향은 그다지 크지 않았으며, 매염제 종류를 달리하여 염색한 모섬유의 색상은 크롬과 주석으로 매염한 경우 YR 계열을 나타내고 그 밖의 매염제에 의해서는 Y 계열의 색상을 나타내어 큰 변화는 없었다. 매염처리하지 않은 시료의 견뢰도는 매우 양호하였으며 매염처리가 견뢰도 증진에 미치는 영향은 크지 않았다.

Key words: American fleabane colorants, adsorption isotherm, mordanting, dye uptake, fastness; 개망초 색소, 등온흡착곡선, 매염, 염착량, 견뢰도

I. Introduction

Recently the use of natural dyes is growing because of harmful influence to environment and toxicity associated with synthetic dyes. Natural dyes have more compatibility with the environment and better biodegradability in general (Deo & Desai, 1999). Considerable researches are carried out on the application of natural dyes conventionally being used. However, there are few works reported on exploiting the potential resources of natural dyes.

American fleabane is a readily available weed in our neighborhoods. Although its origin is North America, it has been naturalized around the world. It contains quercetin and apigenin-7-glucoside in its flowers. Components such as gallic acid and tannic acid exist in its stems and leaves. Other components are chlorogenic acid, d-limonen, etc (Roth et al., 1992; Schweppe, 1992; Yook, 1997). American fleabane has been used as an oriental medicine for cold, stomachache, diarrhea, hemostatic, etc. We became to notice its potentiality as a new resource of natural dye.

In this study, the dyeing and fastness properties of colorants extracted from American fleabane were investigated. Effects of dyeing conditions and mordanting were evaluated in terms of dye uptake (K/S value) and CIELAB color. Also, effect of mordanting on fastness was assessed.

II. Experimental

1. Materials

Fabric used is a scoured and bleached 100% wool (plain weave, 30x28/cm^2, 105g/m^2, 0.23mm thickness). American fleabane was cropped in the campus of Chonnam National University in June and July, 2001, dried after removing roots for 2 weeks, and used for dyeing. Mordants including aluminium ammonium sulfate ($Al_2(SO_4)_3$ ($NH_4 \cdot 24H_2O$), ferric sulfate ($FeSO_4 \cdot 7H_2O$), cupric sulfate ($CuSO_4 \cdot 5H_2O$), potasium dichromate ($K_2Cr_2O_7$), and stannic chloride ($SnCl_2 \cdot 2H_2O$) were used.

2. Methods

1) Preparation of colorants

Aqueous extracts of American fleabane were prepared by adding 50g dried plants to 1500 ml distilled water. The mixture was held at 100°C for 60 min, filtered and dried into powder by evaporizing at 60°C in a vacuum oven. Yield of colorants was about 25%.

2) Dyeing and mordanting

Dyeing was done at a liquor ratio of 50:1, colorants concentration 0.5~5% (o.w.b.), 40~120°C, 30~150min. pH of dyeing solution was adjusted to 3~11 by the addition of acetic acid and sodium hydroxide. Three different methods of pre-mordanting, simultaneous-mordanting and post-mordanting were employed. Mordanting was carried out in 1% (o.w.f.) mordant solution at a liquor ratio of 50:1 by holding at 60°C for 30min. In the simultaneous-mordanting, mordants were applied during the dyeing process. Dyeing and mordanting were carried out in an automatic laboratory dyeing machine (Ahiba Nuance, Datacolor International, USA).

3) FT-IR analysis

Colorants powder was prepared as a KBr pellet and then analyzed with a FT-IR spectrometer (Nicolet 510, USA).

4) Color measurement

Color values were evaluated in terms of K/S values and CIE $L^*a^*b^*$ data(Illuminant D_{65}/10°Observer) with a Macbeth Coloreye 3100 spectrophotometer at 420nm, maximum absorption wavelength. H V/C values were obtained from $L^*a^*b^*$ data using CIE Munsell conversion program.

5) Fastness testing

Fastness of the dyed samples was evaluated by standard procedures; wash fastness by KS K 0430-A; rubbing fastness by AATCC method 116-1989; perspiration fastness by KS K 0715. Fastness was assessed by using gray scale for color change and chromatic transference scale. Light fastness was assessed in terms of color difference (ΔE) according to AATCC method 16-1998 with Fade-Ometer (Atlas Electric Devices Co, USA). Color differences were measured with a Macbeth Coloreye after irradiating for 5, 10, 20, and 40 hours.

III. Results and Discussion

1. FT-IR analysis of colorants

The spectrum of extracted colorants is shown in Fig. 1. It shows the broad absorption peak at 3388cm^{-1} which represents the stretching of phenolic –OH. Also, aliphatic C-H stretching at 2927cm^{-1}, carboxy C=O stretching at 1637cm^{-1}, aliphatic C=C stretching at 1411cm^{-1}, and C-O

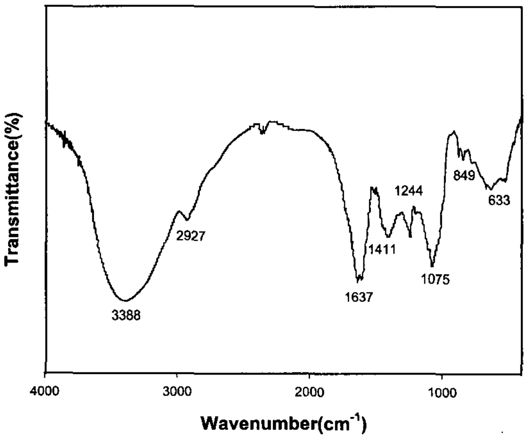


Fig. 1. FT-IR spectrum of the extracted colorants.

stretching at 1075cm^{-1} are shown (Lee, 1991). From the results in Fig. 1, it is speculated that functional groups such as carboxylic acid and hydroxyl groups exist in the extracted colorants.

2. Effect of dyeing conditions on dye uptake and color

Figs. 2~5 show effects of colorants concentration, dyeing temperature and time, and pH on dye uptake (K/S). Dye uptake increases remarkably as concentration increases up to 2%, thereafter its increment is not significant. The adsorption isotherm in Fig. 2 is considered as Langmuir type, indicating that adsorption of the colorants occurs mainly by ionic bonding. (Kim and Lee, 1998; Trotman, 1975) As an example, ionic bonding between wool and gallic acid is shown in Scheme 1.

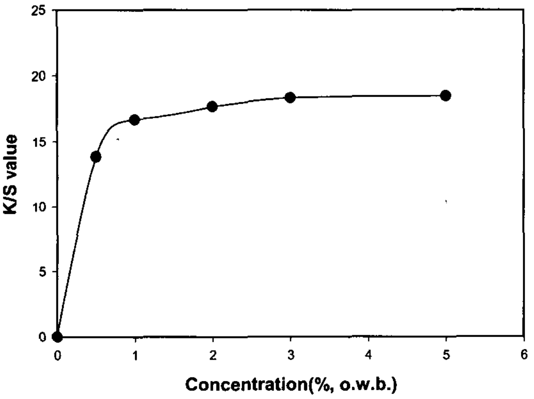


Fig. 2. Effect of dye concentration on dye uptake (100°C, 60min).

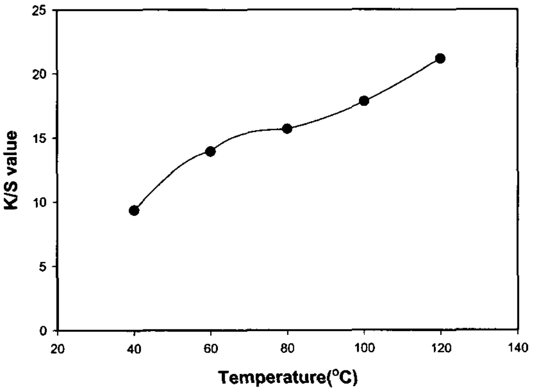
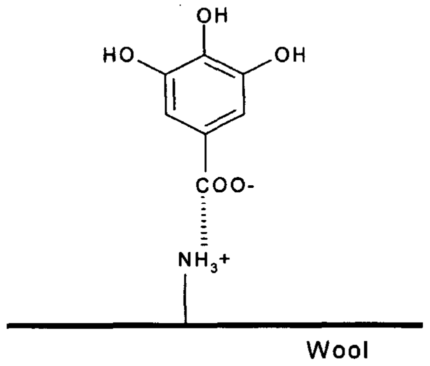


Fig. 3. Effect of dye temperature on dye uptake (2% o.w.b., 60min).



Scheme 1. Ionic bonding between wool and gallic acid.

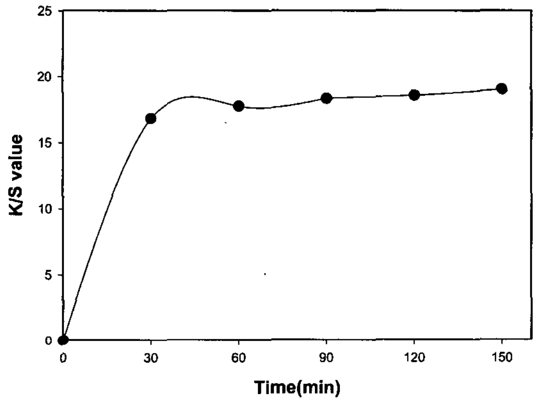


Fig. 4. Effect of dye time on dye uptake (2% o.w.b., 100°C).

Dye uptake increases abruptly for initial 30min and thereafter increases progressively until 60min. It is considered that dyeing equilibrium reaches at 60min. As in Fig. 4, dye uptake increases continuously as temperature increases. The microstructure of wool gives more easily accessible sites to dye molecules at higher temperature, resulting in higher dye uptake (Nam et al., 1995). Maximum dye uptake is observed at stronger acidic conditions, pH 3.0. The dye uptake decreases with increase in pH from neutral to alkaline. This confirms that the colorants function as anionic dyes and form ionic bonding with wool under acidic conditions. pH 5.5 of colorants solution was not adjusted because dyeing at 100°C under strong acidic conditions may cause the strength loss of wool (Choi & Cho, 2001; Lee et al., 1998; Lee et al., 2000).

From the results in Figs. 2~5, dyeing conditions are

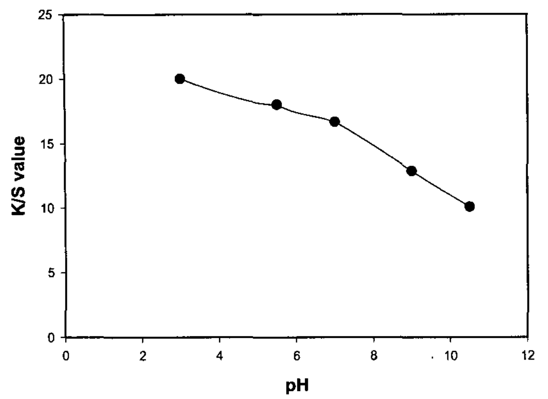


Fig. 5. Effect of pH on dye uptake (2% o.w.b., 100°C, 60min).

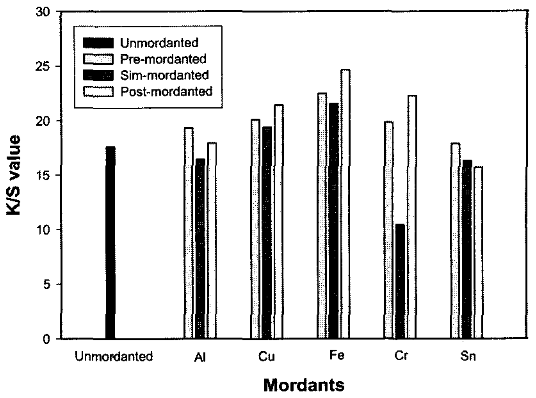


Fig. 6. Effect of mordanting on dye uptake.

fixed 2% (o.w.b.) concentration, pH 5.5, 100°C, and 60 min in the latter experiments.

Color change of the dyed samples depending on pH is shown in Table 1. As pH increases, L^* values increase, meaning that shade is getting lighter. a^* decreases with increase of pH, which relates with the reduction of reddish shade. And b^* increases up to pH 5.5 and then decrease. Although all of the dyed samples show Y color irrespective of pH, hue increases up to pH 9.0 indicating the reduction of yellowish shade. Value increases with increase in pH while chroma reaches to maximum at pH 5.5.

3. Effect of mordanting on dye uptake and color

Mordants play an important role in natural dyeing because they usually have substantivity for both the fiber and the colorants. They form coordination bonds with fiber and at the same time, form insoluble chelate with the dye.

Fig. 6 shows dye uptake depending on mordant type and method. Fe and Cu improve dye uptake substantially irrespective of mordanting method. Both these metals are well known for their ability to form coordination complexes, and readily chelated with the dye. Since the coordination numbers of Fe and Cu are 6 and 4, respectively, some coordination sites are unoccupied when they interact with the fiber. These unoccupied sites are accessible to functional groups such as amino and carboxylic acid groups on the fiber. Thus these metals can form a ternary complex on one site with the fiber and on the other site with the dye. Such a strong coordination tendency enhances the interaction between the fiber and the dye, resulting in high dye uptake (Bhattacharya and Shah, 2000). Dye uptake values of the samples simultaneous-mordanted with Al and Cr, and simultaneous- and post-mordanted with Sn are smaller than that of the unmordanted sample. Al is one of metals forming weak coordination complex with the

Table 1. Effect of pH on L*, a*, b*, & H V/C values of the dyed samples

pH	L^*	a^*	b^*	H	V/C
3.0	43.980	7.857	28.449	0.04Y	4.24/4.58
5.5	55.597	5.853	31.747	1.09Y	5.38/4.97
7.0	59.422	5.117	30.746	1.22Y	5.76/4.80
9.0	63.539	3.609	27.831	1.63Y	6.17/4.29
10.5	64.084	3.624	26.375	0.43Y	6.23/4.08

Table 2. L*, a*, b* & H V/C values of the dyed samples

		L*	a*	b*	H	V/C
Um†		57.110	5.451	32.283	1.28Y	5.53/5.02
		ΔL*	Δa*	Δb*		
Al	Pre-mordant	−28.353	7.221	29.356	1.59Y	5.11/5.72
	Sim-mordant	−20.450	6.402	28.183	1.60Y	5.90/5.60
	Post-mordant	−24.898	6.550	26.066	1.55Y	5.45/5.26
Cu	Pre-mordant	−37.357	7.490	23.768	1.33Y	4.23/4.96
	Sim-mordant	−38.134	5.594	19.842	2.01Y	4.16/4.23
	Post-mordant	−38.238	4.958	23.701	2.68Y	4.15/4.76
Fe	Pre-mordant	−54.509	4.968	3.998	0.25Y	2.57/2.11
	Sim-mordant	−49.212	3.663	5.396	1.75Y	3.09/2.20
	Post-mordant	−56.485	1.643	1.070	4.04Y	2.38/1.52
Cr	Pre-mordant	−34.666	11.238	36.047	0.45Y	4.59/7.05
	Sim-mordant	−24.590	1.595	14.722	3.70Y	5.48/3.35
	Post-mordant	−44.987	11.103	19.941	9.07YR	3.50/4.86
Sn	Pre-mordant	−22.573	19.769	56.640	8.44YR	5.69/10.90
	Sim-mordant	−19.480	21.539	63.498	8.24YR	5.99/12.07
	Post-mordant	−25.620	11.993	41.592	0.30Y	5.38/7.90

Um†; unmordanted

dye. This metal has tendency to form stronger bonds with the dye than with the fiber. Thus it blocks the dye and reduce its interaction with the fiber (Bhattacharya and Shah, 2000). Some of the dye are lost in the simultaneous-mordanting because it forms insoluble complexes in the dyebath.

Color values are compared in Table 2. ΔL* shows (-) value in all of the mordanted samples, meaning that shades of the samples get darker and duller by mordanting. Both Δa* and Δb* show (+) value, indicating the increase in reddish and yellowish shades, respectively. Irrespective of mordant type and method, the samples show Y color except for those post-mordanted with Cr and pre- and simultaneous-mordanted with Sn, which show YR color. The samples mordanted with Al and Sn show brighter shade, while the samples mordanted with Fe are darker and duller. Ferrous sulfate changes into ferric form because of oxygen in the air. Both forms of Fe coexist on the fiber and their spectra are overlapped, resulting in the shift of λ_{max} and consequent change into darker shade (Shin and Choi, 1999).

VI. Fastness

Fastness of the mordanted and unmordanted samples is compared in Table 3. The unmordanted samples show comparatively good fastness properties. The pre-mordanted samples were used for evaluating fastness. Pre-mordanting gives marginal effect on the fastness properties. Wash fastness and rubbing fastness are relatively good regardless of mordanting. Fastness to perspiration is also relatively good even though alkaline perspiration gives a little bit lower rating than acidic perspiration.

Fig. 7 shows color difference of the dyed samples depending on irradiation time. As expected, photofading of the dyed samples increases as irradiation time increases, especially the Sn-mordanted sample shows a striking fading. Nonetheless, mordants except for Sn improve light fastness slightly after 40 hours irradiation. Improvement of light fastness by metal mordant is attributed to the stabilizing effect of chelate formed with the peptide chain of wool fiber (Yoon and Kim, 1993). All of the samples except for Sn-mordanted one showed relatively

Table 3. Fastness of the dyed samples

Mordant	Wash			Perspiration (acidic)			Perspiration (alkaline)			Rubbing	
	Color change	Stain		Color change	Stain		Color change	Stain		Dry	Wet
		Cotton	Wool		Cotton	Wool		Cotton	Wool		
Um	4	4/5	5	4/5	4/5	5	5	4	4	5	4/5
Al	4	4/5	5	5	4/5	5	5	3/4	4	4/5	4/5
Cu	4/5	4/5	5	5	4	4/5	5	3/4	4/5	4/5	4/5
Fe	5	4/5	5	5	4/5	5	5	4	4/5	4/5	4
Cr	4	4/5	5	5	4/5	5	5	3/4	4/5	4/5	4/5
Sn	4	4/5	5	4/5	4/5	5	5	4/5	4/5	4	4

Um[†]; unmordanted

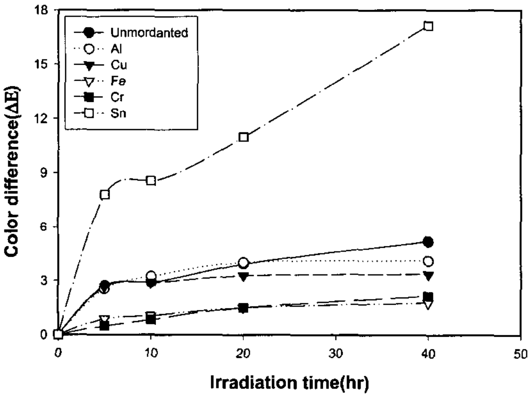


Fig. 7. Effect of irradiation time on color difference.

good light fastness above 4/5 rating. Fastness properties are quite satisfactory without mordanting.

V. Conclusion

The dyeing and fastness properties of the colorants extracted from American fleabane on wool were investigated. Effects of dyeing conditions and mordanting were evaluated in terms of dye uptake (K/S value) and CIELAB color. Also, effect of mordanting on fastness was assessed.

American fleabane colorants shows high affinity to wool. Dye uptake increases remarkably as concentration increases up to 2%. It is thought that adsorption of colorants on wool occurred mainly by ionic bonding because it has Langmuir type isotherm. Dye uptake increases continuously with increase in temperature. Dyeing equilibrium reaches at 60min. Maximum dye uptake is observed at stronger acidic conditions, but pH of solution (5.5) was not adjusted because of possible strength loss of wool. The dye uptake decreases with increase in pH from neutral to alkaline. The dyed samples show Y color except for those post-mordanted with Cr and pre- and simultaneous-mordanted with Sn, which have YR color. The unmordanted samples show relatively good fastness properties. Mordanting has insignificant effect on fastness.

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