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Effects of introduced chemical groups on the dyeability of cotton fabrics with *Phellodendron amurense* Rupr.

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Abstract

The dyeability of cotton fabrics with natural basic dye, *Phellodendron amurense* Rupr. was improved by applying anionic and hydrophobic groups on cotton fibers. The dye uptake was increased by interactional force and the change of fine structure by fiber modification. After introducing cross-linking using formaldehyde, the wash fastness had been improved. The wash fastness relied on the degree of swelling of fabric during washing and the number of the entrapped dyes.

Keywords: Natural dye; Amur cork tree; Cotton; Modification; Wash fastness

1. Introduction

Natural dyes are usually deeper and softer in color shades than synthetic dyes. With the increase of worldwide concern for the environment, use of natural dyes is being widely studied. Natural dyes may overcome many defects of synthetic dyes such as harmfulness to the human body and water pollution [1,2]. However, natural dyes show very low dye exhaustion on cotton fiber compared to silk or wool, and no satisfying result has been obtained in spite of many experimental attempts of repeating dyeing and mordant treatment.

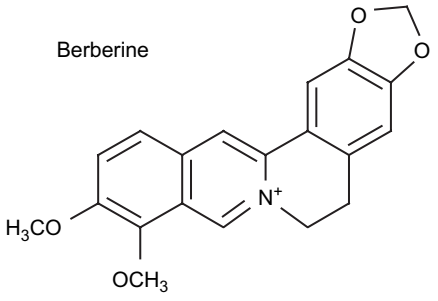
Several studies have been conducted on applying anionic [3] and hydrophobic groups on cotton fibers, and shown that these groups can improve dyeability and color fastness of cotton fabrics with basic dye. These treatments on cotton fibers, however, have not been studied for natural dye.

This study reports an investigation of the wash fastness of *Phellodendron amurense* Rupr. on modified cotton fabrics. The effects of cotton modification on changes of shade and the improvement of wash fastness were also studied. The wash properties were evaluated in terms of Kubelka–Munk (*K*/*S*) values, obtained before and after washing.

2. Experimental

2.1. Materials

The natural dye used was *P. ammurence* Rupr. (from the amur cork tree). Scheme 1 shows the chemical structure of the chief colorant, Berberine. Extraction of chief colorant, Berberine (Scheme 1), was carried out in the following



Scheme 1. Chemical structure of the chief colorant.

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procedure. Amur cork tree bark (10 g) and methanol (300 ml) were put in a 1-l round-bottom flask fitted with a reflux condenser, refluxed for 1 h at 67 °C, and this procedure was repeated 2–3 times. The resultant extract was mixed, filtered, and concentrated to 20 ml. In the preparation of cotton derivatives, scoured cotton fabrics (66.3 g/m^2) having the following specifications were used: warp density, 35 threads/cm; weft density, 31 threads/cm; weight, 105 g/m^2; warp count 16.5 tex weft counts 14 tex and plain weave. All chemicals were of the highest purity grade.

2.2. Preparation of cotton derivatives

In the following treatments, the pick up ratio of PDC (padding–drying–curing) method was 100% and the bath ratio of deposition method was 1:30. The introduction of various chemical groups into cotton fabrics was identified by an FT-IR spectrophotometer (Impact 400D, Nicolet) and was reported in the previous paper [4].

Acid groups on cotton fibers were applied by carboxyethylation, sulfonation, and carboxymethylation. In the case of carboxyethylation of cellulose (CEC), cotton fabrics were dipped in an aqueous solution with 15% acrylic acid and 0.45% ammonium chloride. Fabrics were padded, mounted on a frame, dried for 5 min at 70 °C, and cured for 30 min at 140 °C. For the sulfonation of cellulose (SFC), fabrics were dipped in an aqueous solution of 0.01 M sodium metaperiodate for 30 min at 30 °C. Dialdehyde cotton fabrics were treated in an aqueous solution with 5% sodium hydrogen sulfite for 60 min at 85 °C. In the case of carboxymethylation of cellulose (CMC), cotton fabrics were treated in an aqueous solution with 2% sodium chloroacetic acid and 2% sodium hydroxide for 30 min at 10 °C, and then were treated continuously for 45 min at 60 °C. All treated fabrics were washed and air-dried at room temperature.

Hydrophobic groups were applied on cotton fibers by esterification and urethane formation. In the case of esterification, cotton fabrics were treated in DMF (*N*,*N*-dimethylformamide) solution containing 0.2 M acetyl chloride, 0.2 M propionyl chloride, and 0.2 M butyryl chloride. Esterification included treatments of acetyl chloride for 150 min at 50 °C, of propionyl chloride for 75 min at 90 °C, and butyryl chloride for 75 min at 90 °C. All modified fabrics were washed in DMF solution and air-dried at room temperature. In order to introduce hydrophobic groups by urethane formation of cellulose (UFC), phenyl isocyanate and toluene diisocyanate were used as aromatic compounds and butyl isocyanate and hexamethylene diisocyanate were used as aliphatic compounds. Cotton fabrics were treated in DMF solution including 0.15 M butyl isocyanate, 0.1 M hexamethylene diisocyanate (HMDI) and 0.12 M phenyl isocyanate for 60 min at 130 °C. A 5 ml of 2,4-toluene diisocyante (TDI) in 30 ml dimethyl sulfoxide (DMSO) solution was also applied to the cotton fabrics for 240 min at 30 °C. Finally, they were washed and air-dried at room temperature.

For the cross-linking of cotton fabrics, untreated or carboxymethylated cotton fabrics were soaked in 3, 6, 9, and 12% (v/v) aqueous solution of formalin with 2% magnesium chloride for 20 min at 27 °C, dried for 7 min at 70 °C, and were cured for 5 min at 150 °C.

2.3. Dyeing procedure

Dyeing was processed in a bath containing 1 ml/50 ml extracts of amur cork tree bark and 2% acetic acid for 60 min and then 5% sodium carbonate was added to the dye bath for 45 min. Dyed fabrics were washed and air-dried at room temperature.

2.4. Color strength

Macbeth Coloreye 700 spectrophotometer (illuminant D65, 10° observer) was used to evaluate samples based on the Kubelka–Munk analysis (*K*/*S*). The *K*/*S* values obtained before and after washing indicate the concentration of adsorbed and fixed dye of the samples. AATCC 61 No. 1A method was used for washing fastness test.

3. Results and discussion

3.1. Effects of anionic groups

Table 1 shows the *K*/*S* values of anionized cotton fabrics such as CEC, CMC, and SFC, which were dyed using amur cork tree extract. The anionized cotton fabrics showed an increase in *K*/*S* values compared with those of the untreated cotton fabrics. The *K*/*S* values of untreated cotton fabrics are low and this is caused by the weak interaction force between the dyes from the amur cork tree extract and the cotton fibers. When the anionizing agent is applied on cotton fibers, anion sites of treated cotton fibers enhance the formation of ionic bonds with cationic dyes. Anionization of cotton fibers improves the dye adsorption as shown in Table 1. *K*/*S* values of the CMC fabric show great influence on dyeability when comparing the values of CEC and SFC fabrics. This result indicates that the increase of adsorbed dye does not seem to have any relationship to the strength of the acid groups introduced by anionization.

In the case of washed samples, all *K*/*S* values were low. This is due to the weak bonding forces between dyes and

Table 1
K/*S* values and wash fastness (WF) of cotton fabrics with introduced acid groups

Cotton modification	Color strength (*K*/*S*)		WF
	Adsorbed[a]	Fixed[b]	
Unmodified	1.47	0.29	1
Carboxyethylation	6.01	0.54	<1
Carboxymethylation	10.93	1.39	<1
Sulfonation	5.84	0.37	<1

[a] *K*/*S* values of samples before washing at λ_{max}.
[b] *K*/*S* values of samples after washing at λ_{max}.