Structure and Dyeing Properties of Cotton Fabric Modified by Protein from Waste Feathers

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Abstract. The waste feather protein was extracted as modifier to modify cotton fabric. The modified process was selected: the mass fraction of the protein modifier was 4% (weight to the fabric), the mass fraction of the cross-linking reagent was 2%, the processing temperature was 70 °C, and the processing time was 60 min. The structure of the cotton fabric modified was analyzed by infrared spectrometer, scanning electron microscope, XRD and thermogravimetric analysis. The dyeing mechanism and properties of natural naphthoquinone dyes on the cotton fabric modified were analyzed. The results showed that the feather protein grafted onto the cotton fabric by the cross-linking agent. The cross-linking reactions occurred mainly in the amorphous area of the fabric. Furthermore, the dyeing properties of natural naphthoquinone dyes were significantly improved by protein cross-linking agent. The K/S value increased from 1.27 to 7.05 and the color fastness to dry and wet rubbing improved by about one grade.

1. Introduction
Natural naphthoquinone dyes were found in henna, the chromophoric group was 2-hydroxy-1, 4-naphthoquinone, naphthoquinone compounds had good anti-ultraviolet, bactericidal, anti-cancer and other functions [1-3]. At present, most naphthoquinones were mainly used for dyeing proteins fabrics, but the dyeing effect on cotton fibers was poor [4-5]. In order to improve the dyeing performance of cotton fiber fabric, cationic modification was usually carried out on cotton fabric [6-8]. The cationic reagent molecules often contained amine or proton nitrogen atoms. After modification, the negative charge on the surface of cotton fiber decreased and at the same time gave cotton fiber a certain positivity, which reduced the repulsion between cotton fiber and anionic natural dye, and the coulomb force between dye and fiber improved the dyeing rate and apparent color yield of cotton fabric [9-11].

In this paper, the cotton fabrics were modified by waste feather protein. Because the feather protein contained more amino and carboxyl groups, the cross-linking agent used in the paper also contained protonated nitrogen atoms, so that the cotton fabrics modified can provide more dyeing bases combined with natural naphthoquinone dyes, and the binding force of dyes and modified cotton fabrics not only had coulomb gravity, but also hydrogen bond and van der Waals force, which greatly improved the dyeing rate of cotton fabrics. At the same time, the waste feathers can be recycled.

2. Materials and Methods

2.1. Experimental Materials
The cotton bleached woven fabrics of 28 tex × 28 tex, 296 pcs/10 cm × 286 roots/10 cm were supplied by Sunvim Group Co. Ltd. Gaomi, China. 1,4-naphthoquinone dyes and the feather protein made in...
the laboratory. The reagents and chemicals used were analytical grades in this work, such as the detergent was purchased from Guangdong Zhongfang Fine Chemical Co., Ltd. The anhydrous sodium carbonate was provided by Shanghai Kunling Chemical Reagent Co., Ltd. The cross-linking agent EH was purchased from Shanghai Tiantan Chemical Auxiliary Co., Ltd and the sodium hydroxide was supplied by Shanghai Kunling Chemical Reagent Co., Ltd.

2.2. Experimental Methods

2.2.1. Pretreatment of Cotton Fabrics. First, the detergent and anhydrous sodium carbonate were added to deionized water to obtain a certain amount of solution, put the cotton fabric into the solution and dealt with it in boiling state for 30 min. Then the fabric was washed at 60 °C for 10 minutes. Finally, net washed with water and air-dried at indoor temperature.

2.2.2. Modification of Cotton Fabrics. First, the cross-linking agent, feather protein extract and sodium hydroxide were dissolved in deionized water to obtain a modified liquid, the optimum mass fraction of feather protein was 4%, and the optimum mass fraction of the cross-linking agent was 2%. Then the cotton fabric pretreated was placed in the modified liquid for 60 min at 70 °C. Finally, the cotton fabric was washed and dried.

2.2.3. Dyeing. Both unmodified cotton fabrics and modified cotton fabrics were dyed with 1,4-naphthoquinone dyes. The dye concentration (o.w.f) was 5%, the pH was 4.5, and the bath ratio was 1:30. After dyeing for 60 min, the fabric was removed, washed and dried.

2.3. Tests

2.3.1. Infrared Spectrum. The samples were pulverized at a temperature of 20 °C and a relative humidity of 65%, the spectrum One-B infrared spectroscopy was obtained from PE company USA. Both unmodified cotton fabrics and modified cotton fabrics were analyzed by KBr method. Scan times:32 min, resolution ratio:4 cm⁻¹.

2.3.2. Scanning Electron Microscope. Put the cotton fabric on the sample folder and selected 3 cotton fabrics in different positions. The JSM-6700F scanning electron microscope was provided by Japan Electronics Co. Ltd. The fabric was subjected to gold spray treatment, and the surface morphologies of the modified cotton fabric and unmodified cotton fabric were observed at a temperature of 20 °C and a relative humidity of 65%.

2.3.3. Dyeing Depth (K/S value). The K/S value was measured by the electronic colorimeter from Hunter. USA. using a D65 light source, the 10° field of view. Each sample was measured 3 times at different positions, and the results were averaged.

2.3.4. Dyeing Rate. The dyeing rate was determined by the residual liquid method, and the absorbance A at the maximum absorption wavelength (530 nm) of the natural dye was measured by an ultraviolet-visible spectrophotometer, and the dyeing rate E was calculated by the following formula.

\[ E\% = (1 - \frac{N_1 A_1}{N_0 A_0}) \times 100\% \]

Among them, \( A_0 \) was the absorbance of the dye solution at a multiple of diluted \( N_0 \); \( A_1 \) was the absorbance of the dye residue at a multiple of diluted \( N_1 \).

2.3.5. Thermogravimetric Analysis. The HCT-2 comprehensive thermal analyzer was purchased from Beijing Hengjiu Scientific Instrument Factory. Thermal analysis was carried out on the modified
cotton fabric and unmodified cotton fabric in the temperature range of 25-600 °C and the heating rate of 20 °C/min.

2.3.6. Color Fastness. The SW-12A washing color fastness Tester was supplied by Wenzhou International Testing Instrument Co., Ltd and the Y571B rubbing fastness meter was obtained from Wuxi Textile Instrument Factory. The applicable standards were GB/T 3920-1997 for rubbing fastness and GB/T 3921-2008 for color fastness to washing.

2.3.7. Breaking Strength. The applicable standard for breaking strength was GB/T 3923.1-2013. Five sections were selected from different positions to test the breaking strength, then the modified cotton fabrics and unmodified cotton fabrics were analyzed.

3. Results and Discussion

3.1. Modification Mechanism
The protein extracted from waste feathers contained many active groups, such as amino groups, carboxyl groups, hydroxyl groups and amide groups in the chemical structure. The cross-linking agent EH had an epoxy group at each end of the molecule. Under alkaline conditions, the epoxy group at both ends of the cross-linking agent opened to accept various groups on the protein extract and the hydroxyl group on the cotton fiber molecules. In this way, the protein extract was connected to the cotton fibers by cross-linking. The modification mechanism was shown in figure 1.

![Figure 1. Modification mechanism of cotton fibers.](image1)

3.2. Infrared Spectroscopic Analysis
The infrared spectra of the cotton fabric modified by feather protein were shown in figure 2. According to the infrared spectrum of the modified cotton fabric, the characteristic peak at 1236 cm\(^{-1}\) disappeared after modification. Instead, there was a new vibrational absorption peak at 808 cm\(^{-1}\), because the epoxy group in the cross-linking agent dehydrogenated with a hydroxyl group in the cellulose molecule to form the -C-O-C- bond. There was a characteristic amide absorption peak at 1552 cm\(^{-1}\), which was caused by the stretching vibration of the cross-linking agent reacting with the amino group in the protein to form a C-N bond. Moreover, there was a characteristic absorption peak of the -CO-group at 1650 cm\(^{-1}\). Based on the change of characteristic peaks before and after modification, it was speculated that the feather protein molecules were grafted onto the cotton fibers by the cross-linking agent.

3.3. Scanning Electron Microscopy Analysis
The surface morphology of cotton fiber after protein modification was shown in figure 3. It can be seen that the surface of modified cotton fiber changed obviously compared with unmodified cotton fiber. The surface of the unmodified cotton fiber was relatively smooth, and there were fine lines on the surface. The surface of the modified fiber was rough and the texture was messy, as if it had been coated in a film. In addition, there was adhesion. These changes to the surface morphology were due to the grafting of the protein onto the cotton fibers by the cross-linking agent.
Figure 2. FT-IR spectra of cotton fibers before and after modification.

![Figure 2](image)

Figure 3. SEM pictures of cotton fibers before and after modification.

(a) Cotton fibers before modification  (b) Cotton fibers after modification

Figure 3. SEM pictures of cotton fibers before and after modification.

3.4. Thermogravimetric Analysis

The thermal spectra of modified and unmodified cotton fabric were shown in figure 4. As can be seen from figure 4, the main cracking stage of the unmodified cotton fiber was at 323.35 °C-379.68 °C with a weight loss rate of 65.63%. The residue cracking stage was at 379.68 °C-551.35 °C with a weight loss rate of 24.69%. For the modified cotton fiber, the main cracking stage was at 301.04 °C-361.67 °C with a weight loss rate of 58.18%. The residue cracking stage was at 361.67 °C-618.38 °C with a weight loss rate of 33.53%. Compared with the unmodified cotton fiber, the initial temperature of the main and residual pyrolysis of the crosslinked cotton fiber decreased to a certain extent. Moreover, the weight loss rate of the main cracking stage decreased, whereas the weight loss rate of the residue cracking stage increased. This was because the cross-linking reaction mainly occurred in the amorphous region of the fiber so that cracking occurred in the direction in which the residue formed. The grafted protein acted to suppress burning of the fabric when heated [12].

Figure 4. TG thermal spectra of cotton fabric and after the modification.

![Figure 4](image)
3.5. Dyeing Mechanism
After the cotton fiber was modified, the amino group on the feather protein molecular chain attached to the cotton fiber had a positive charge when the pH of the dye solution was less than the isoelectric point, and the 1, 4-naphthoquinone dye was negatively charged. In addition, a charge attraction was generated and formed ionic bonds, so that the binding force between the naphthoquinone dye and the protein modified cellulose fiber formed a strong ionic bond in addition to the hydrogen bonding and van der Waals force. The forming process was shown in the figure 5.

![Figure 5. Dyeing mechanism of cotton fibers.](image)

3.6. Dyeing Properties and Other Properties
The dyeing properties and other properties of the cotton fabric modified by the optimum modification process were tested. The results were shown in table 1. It can be seen that 1, 4-naphthoquinone dye had a poor dyeing ability with cotton fibers and mainly used for dyeing of protein fibers. However, the K/S value and dyeing rate of the cotton fabric modified by protein had been greatly improved. This was because on the surface of the cotton fiber modified by the protein, more activation points which can be combined with the anionic naphthoquinone dye appeared, so that more 1, 4-naphthoquinone dyes were dyed on the cotton fabric. The strong coulomb force between the dye and the fabric increased the color fastness of the cotton fabric by about 1 grade. However, the breaking strength of the fabric decreased to a certain extent, which may be due to the hydrolysis of cellulose by acid dyeing bath. In addition, the crease recovery angle of the fabric was increased to a certain extent due to the network structure formed by the crosslinking agent linking the waste protein and cellulose molecules together.

|                      | Unmodified cotton fabric | Modified cotton fabric |
|----------------------|--------------------------|------------------------|
| Wrinkle recovery angle (°) | 132.5                   | 186.7                  |
| Dyeing rate (%)       | 31.1                     | 94.2                   |
| Breaking strength (N)  | 448                      | 339                    |
| K/S value             | 1.27                     | 7.05                   |
| Rubbing fastness (grade) | 2                       | 3                      |
| Washing color fastness | Dry: 1–2 Wet: 2–3        | Cotton color fastness: 4 Cotton staining fastness: 4–5 Color fastness of wool: 4–5 |

4. Conclusions
(1) Analysis by infrared spectroscopy and scanning electron microscopy showed that the protein was grafted onto the cotton fabric by the cross-linking agent. Thermogravimetric analysis showed that the cross-linked graft occurred in the amorphous region of the fiber, and the protein grafted onto the cotton fabric inhibited the burning of the fabric when heated, resulting in a decrease in the weight loss rate of the modified fabric.

(2) By comparing the dyeing depth and color fastness of the cotton fabrics before and after modification, the dyeing depth and dyeing rate with 1, 4-naphthoquinone dye modified by protein and
crosslinking agent EH were greatly improved, and the rubbing fastness and washing fastness were improved by about 1 grade.

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