

Esterification of Cochineal Carmine Used For Dyeing Cationic Modified Cotton with High Color Fastness

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ABSTRACT

In order to reduce the electronic cloud density for higher color fastness, ester groups were introduced into cochineal carmine matrix structure. The optimum esterification conditions were selected by varying the level of acid-binding agent, the reaction temperature, the reaction time, and the amount of acetylation reagent. The structure and properties of esterified cochineal carmine was characterized by UV-vis spectroscopy, FT-IR spectrometry and metallographic microscopy. The build-up property, dyeability, light fastness, perspiration and rubbing fastness of cochineal carmine before and after esterification on cationic modified cotton were investigated. The results show that the optimum esterification condition is treating 1.0 g cochineal carmine with 50 mL acetic anhydride and 4.0 g anhydrous sodium acetate at 80°C for 2.0 hours. The acid perspiration fastness and wet rubbing fastness of the resulting dyed samples were increased by one grade. The perspiration fastness to alkalis and the light fastness were improved by one-half grade.

Keywords: Cochineal carmine; Esterification; Characterization; Fastness; Build-up property

INTRODUCTION

Synthetic dyes are widely used in the wide applications in the textile industry. However, during the past few decades, the use of synthetic dyes has gradually decreased due harmful effects on living organisms [1-3]. Thus, natural colorants have regained attention based on their environmentally friendly characteristics and biocompatibility [4].

Natural dyes are derived from plant and animal renewable resources. Several of them, such as carotenoids, anthraquinones, naphthoquinones, flavonoids and chlorophylls, have been traditionally used in foods, medicines and textiles [5].

As a result of their availability and low cost, black rice and capsicum were used as an alternative sensitizer in a dye-sensitized solar cell [6]. Alkanet and rhubarb were used for pigment printing of natural fabrics [7]. The feasibility of corn cob powder as a substrate for production of pigments by *Monascus purpureus* in solid-state fermentation was investigated [8]. An eco-friendly dyeing process using brown pigment from chestnut shells was developed. This can be used in recycling a reproducible biomass resource, economizing petroleum, avoiding water pollution and protecting human health [9].

Generally, it is difficult to dye fabrics with natural dye due to poor stability and fastness. The most common way for improving color fastness and range of naturally dyed fabrics dyed is to add mordant. However, mordant usually contains metal ions that are relatively toxic and generate wastewater which negatively impacts the environment [10]. In order to improve the dyeing properties on cotton and wool fabrics, some fibers were dyed after being treated with the cellulose enzymes, alpha-amylase and trypsin [11]. In addition, UV absorbers and antioxidants, such as vitamin C and gallic acid are used to neutralize the destructive attack of UV light and can then improve the light fastness of selected natural dyes [12]. However, the industrialization of the aforementioned technologies still has certain limitations. Thus, attention has focused on developing new methods of structural modification to enhance the fastness of dyed fabric with natural dyes.

Cochineal carmine is one of the most well-known red dyes, and is approved by the Food and Drug Administration (FDA) and European Economic Community (EEC). This kind of dye is mainly

obtained from the dried bodies of females of the scale insect species, namely *Dactylopius coccus* Costa, which feed on wild cacti and is indigenous to Peru, Mexico, Bolivia, Chile and Spain [13-15]. Cochineal carmine (*Figure 1*) contains a large glucose unit which is attached by an anthraquinone with multiple hydroxyl groups and a carboxyl group. Because of its high density of electron cloud in a conjugated molecular system, it easily absorbs luminous energy, resulting in oxidation, which in turn causes decomposition and discoloration. As a result, the light fastness of the fabrics dyed with cochineal carmine is very poor [16].

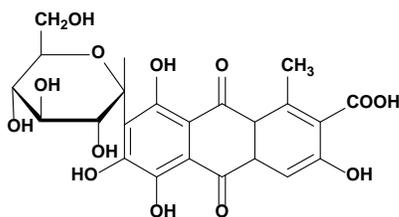


FIGURE 1. Chemical structure of cochineal carmine.

In order to reduce the electronic cloud density and increase color fastness, the ester groups acting as electron withdrawing groups were introduced into cochineal carmine matrix structure. The optimum esterification conditions for the modification of cochineal carmine and best dyeing performance of esterified cochineal carmine determined.

EXPERIMENTAL

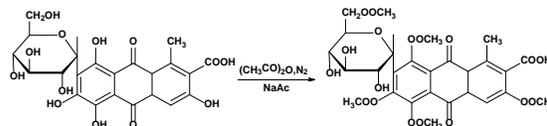
Materials And Chemicals

Cotton fabric (Cationic modified, 201.7g/m²) and cochineal carmine were obtained from Esquel Group (Guangdong, China). Sodium acetate trihydrate and acetic anhydride were all AR grade and supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Esterification Of Cochineal Carmine

The esterification reaction formula is given as *SCHEME 1*. Based on the polarity and the steric hindrance of hydroxyl, cochineal carmine can only be partially esterified. The specific procedure of esterification was as follows: cochineal carmine (1.0 g), acetic anhydride (40 mL, 50 mL, 60 mL, 70 mL, 80 mL) and CH₃COONa (1.0 g, 2.0 g, 3.0 g, 4.0 g, 5.0 g) were added to a three-necked flask equipped with a thermometer and under nitrogen flow. After magnetic stirring for 10 min at room temperature, the reaction system was heated up to different temperature (60°C, 65°C, 70°C, 75°C, 80°C), maintaining each temperature for different

times (1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h) under stirring. After completion of the reaction, the solution in the flask was cooled to room temperature, poured into the ice water and stirred until all solids precipitated, then titrated to neutral washed, and dried at 70°C.



SCHEME 1. Esterification of cochineal carmine.

UV/vis Absorption Spectra Of Cochineal Carmine Before And After Esterification

The UV/vis absorption spectra were recorded using a UV/vis spectrophotometer (UV755B, Shanghai Precision Scientific Instrument Co., Ltd, China) to see the shift of maximum absorption wavelength of cochineal carmine before and after esterification.

FT-IR Spectra

The characteristic functional groups of cochineal carmine before and after esterification were detected by using a Fourier infrared spectrometer (640-IR, Varian, USA) in the range of 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ using KCl powder as the diluent.

Dyeing Procedure

Dyeing was conducted in a high temperature-pressure dyeing machine (RHH-100, Rapid Company, Taiwan) at the liquor-to-goods ratio of 20:1. Cationic modified cotton was dyed with a 2% o.w.f. Dyeing started at 25°C for 10 min. The temperature was increased to 95°C at a rate of 2°C /min and held for 60 min. After dyeing, the samples were washed with water at 85°C for 15 min once and 65°C for 15 min twice. Finally, the samples were rinsed with tap water, and dried at ambient temperature.

Surface Morphology Of Dyed Fabric

The color change and morphology of cationic modified cotton fabric dyed with cochineal carmine and esterified were observed by metallographic microscope (80i, Nikon, Japan).

Build-up Property of Esterified Cochineal Carmine

Build-up property of esterified cochineal carmine was carried out by dyeing cationic modified cotton fabrics with different levels of cochineal carmine

before and after modification. The dye concentrations based on the weight of the fabric (o.w.f.) were 1.0%, 2.0%, 3.0%, 4.0% and 5.0% respectively. The K/S values were tested by a Datacolor SF600PSUS tester (Datacolor, USA) at λ_{max} with illuminant D65 and 10° observer.

Color Measurements and Fastness Testing

Color parameters including K/S values, brightness L^* value, red and green axis a^* value, yellow and blue axis b^* value, chroma c^* , hue angle h value between were measured using Datacolor SF600PSUS tester. Color fastness to light of the dyed samples was performed according to ISO105-B01 (1994) by using an ATLAS-150 sunlight fastness tester (ATLAS, USA). Color fastness to rubbing of the dyed samples was executed based on ISO105-E04 (2013). Color fastness to perspiration of the dyed samples was carried out by following ISO105-X12 (2001).

RESULTS AND DISCUSSION

Optimization of the Esterification Reaction Conditions

Acid-binding Agent

Typical esterification involves the reaction between a carboxylic acid and an alcohol in the presence of a dehydrating agent and a catalyst. The acid-binding agent causes dehydrogenation, which is favorable for the esterification reaction. Figure 2 shows the K/S values and different fastness of cationic modified cotton dyed with cochineal carmine esterified with different amounts of sodium acetate. It is found that the use of sodium acetate has a substantial effect on the esterification reaction. Acetate ions activate the hydroxyl groups in cochineal carmine and form negative oxygen ions, promoting the esterification reaction equilibrium. When the added level of sodium acetate is 4.0 g, wet rubbing fastness of the dyed samples were the highest. Light fastness improved by half a grade. However, the K/S value decreased greatly due to the large number hydroxyl groups inactivated. This is confirmed by the corresponding images of the dyed samples, which are at the top of Figure 2.

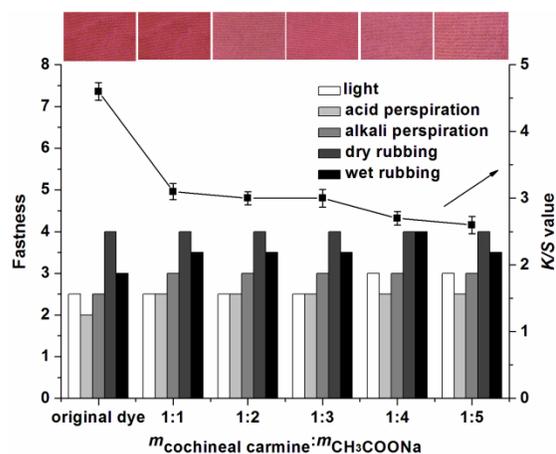


FIGURE 2. K/S values and different fastness of cationic modified cotton dyed with cochineal carmine esterified under different amount of CH_3COONa (constant parameters: 1.0 g cochineal carmine, 50 mL acetic anhydride, at 80°C , for 2.0 h).

Reaction Temperature

The effect of reaction temperature on the esterification reaction and the corresponding dye-ability of the samples are shown in Figure 3. Color strength, measured by the K/S value, decreased with increasing reaction temperature, as noted in the images of dyed samples at the top of Figure 3. This is a result of the large numbers of hydroxyl groups involved in the reaction, which weakens the interactive force between cochineal carmine and fabric. The perspiration fastness is optimized at a reaction temperature of 80°C . The light fastness is increased by half a grade compared to that of the original dye.

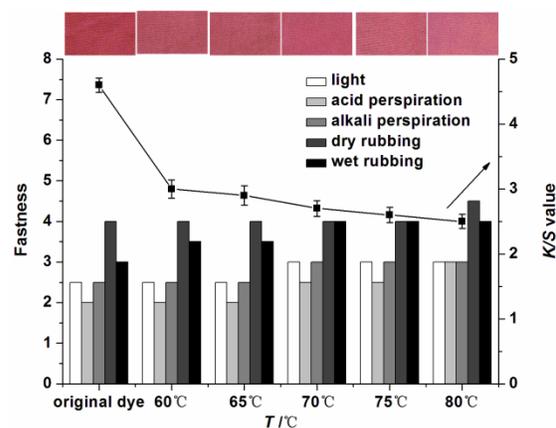


FIGURE 3. K/S values and fastness properties of cationic modified cotton dyed with cochineal carmine esterified under different reaction temperature (constant parameters: 1.0 g cochineal carmine, 50 mL acetic anhydride, 4.0 g anhydrous sodium acetate, for 2.0 h)

Reaction Time

Figure 4 illustrates the influence of reaction time on the esterification reaction and the dye-ability of cationic modified cotton dyed with esterified cochineal carmine. It is found that the K/S values of dyed samples rise with the extension of reaction time. This is verified by the images of dyed samples on the top of Figure 4. Light fastness improves by half a grade at a reaction time of 2.0 h. The light fastness and perspiration fastness begin to decrease when the reaction time is longer than 2.0 h. Hence, the optimum reaction time is 2.0 h.

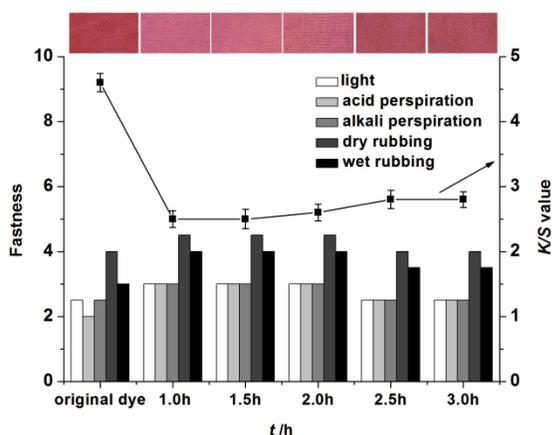


FIGURE 4. K/S values and fastness properties of cationic modified cotton dyed with cochineal carmine esterified under different reaction time (constant parameters: 1.0 g cochineal carmine, 50 mL acetic anhydride, 4.0 g anhydrous sodium acetate, at 80°C)

Amount of Acetylation Reagent

Acetic anhydride plays an important role as a reactant and solvent during the esterification of cochineal carmine. As shown in Figure 5, the K/S values increase when the volume of acetic anhydride rises from 40 mL to 50 mL per gram of cochineal carmine. However, after the volume of acetic anhydride exceeds 50 mL per gram of cochineal carmine, the K/S value begins to decrease. The change in color strength is revealed directly by the images of dyed samples shown at the top of Figure 5. A potential reason for the color change is that more carboxyl groups are able to react with hydroxyl groups when excess acetic anhydride is present. As the volume of acetic anhydride continues to rise, the fastness remains constant. When the volume reaches 50 mL, the K/S value is the highest and the light fastness is increased by half a grade compared to that of the original dye. The optimum amount, therefore, is 50 mL per gram of cochineal carmine.

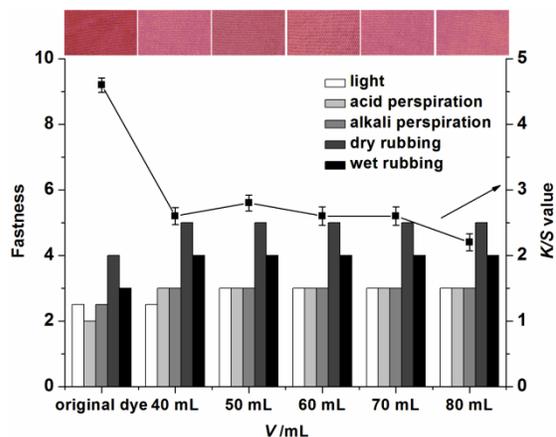


FIGURE 5. K/S values and fastness properties of cationic modified cotton dyed with cochineal carmine esterified under different acetylation reagent amount (constant parameters: 1.0 g cochineal carmine, 4.0 g anhydrous sodium acetate, at 80°C, for 2.0 h)

Build-up Property

The build-up property of cochineal carmine before and after esterification is shown in Figure 6. The optimized esterification parameters used to obtain the build-up property are to treat 1.0 g cochineal carmine with 50 mL acetic anhydride and 4.0 g anhydrous sodium acetate at 80°C for 2.0 h. When the dye concentration original the cochineal carmine reaches 3.0% o.w.f., the K/S value of the dyed sample shows only a small change. However, the K/S values of the dyed samples increase significantly between 1.0% o.w.f. and 5.0% o.w.f. when using the esterified cochineal carmine, indicating that esterification facilitates dyeing. Since cationic modified cotton contains many ester functional groups in their main chain, introducing the ester group into the dye matrix structure can increase the interaction sites and dispersive force between the dye molecules and cotton molecules.

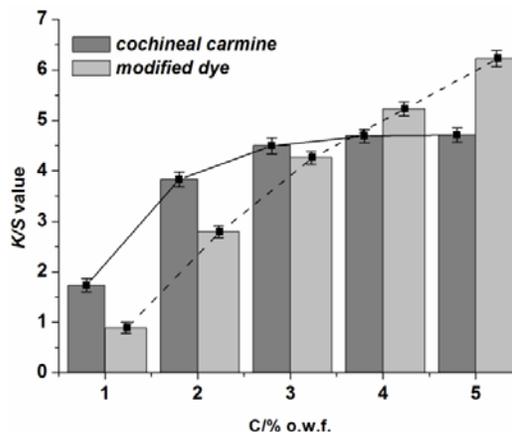


FIGURE 6. Building-up property of cochineal carmine before and after esterification.

Structural Identification and Related Properties of Esterified Cochineal Carmine

Shift Of λ_{max}

UV/vis absorption spectra of cochineal carmine before and after esterification are shown in *Figure 7*. It is found that the value of λ_{max} undergoes a blue shift after esterification. The reason is that the hydroxyl groups were replaced by carbonyl groups, which decrease electron cloud density and bring about light shade effects.

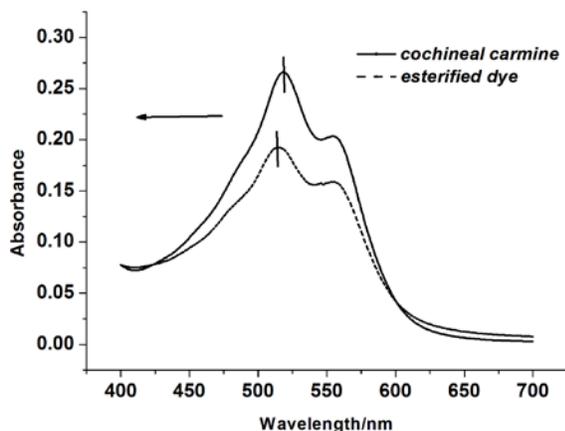


FIGURE 7. λ_{max} Shift of cochineal carmine before and after esterification.

FT-IR

Figure 8 is the FT-IR spectrum of cochineal carmine before and after esterification. The absorption peak of carbonyl group in anthraquinone ring appears at 1650 cm^{-1} and that of carbonyl group in the ester functionality emerges at 1749 cm^{-1} . The peak at of 1230 cm^{-1} is assigned to the stretching vibration of carbon-oxygen bonds in the ester group. The wavenumber of 2925 cm^{-1} is ascribed to the stretching vibrations of saturated hydrocarbons. The peaks at 1435 and 1375 cm^{-1} are assigned to the bending vibrations of methyl groups. However, the O-H stretching vibration of hydroxyl groups at 3400 cm^{-1} in the original dye is significantly reduced in magnitude compared to that of the esterified dye. This confirms that significant quantities of hydroxyl groups in the cochineal carmine have been modified to ester groups.

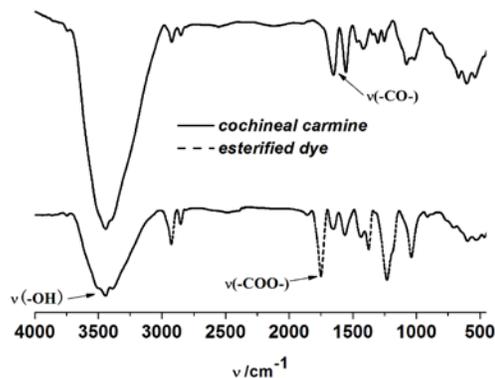


FIGURE 8. FT-IR spectra of cochineal carmine before and after esterification.

Color Change and Surface Morphology of Dyed Fabric

Figure 9 shows the color change and surface morphology of the cationic modified cotton fabric dyed by cochineal carmine and the esterified one. From *Figure 9* it can be seen that the dyed samples with cochineal carmine before and after esterification all show good color levels. However, the color depth becomes lighter and the brightness decreases after esterification. This is because chemical modification reduces the number of hydroxyl groups in the structure and further decreases the binding groups between dye and fibers. Therefore, the dye-uptake decreases.



FIGURE 9. Color change and surface morphology of cationic modified cotton fabric dyed by cochineal carmine and esterified one: (a) 2% o.w.f. original dye; (b) 0.5% o.w.f. esterified dye; (c) 2% o.w.f. esterified dye; (d) 5% o.w.f. esterified dye.

Color Parameters of Cationic Modified Cotton Dyed with Cochineal Carmine Before and after Esterification

Figure 10 compares the color parameters of dyed samples with cochineal carmine before and after esterification. Compared with original cochineal carmine, dyed samples with esterified cochineal carmine under optimum reaction conditions exhibit brighter color, less red tone, similar blue tone, almost the same chroma and hue angle, but lower K/S values. As a result, esterification with cochineal carmine mainly causes changes in brightness and red tone.

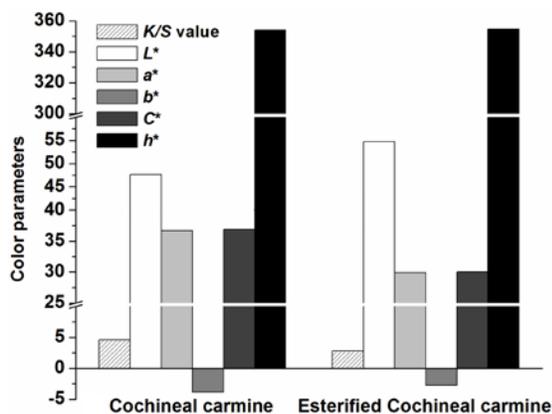


FIGURE 10. Color parameters of dyed samples with different dyes.

CONCLUSION

The color fastness of cationic modified cotton can be greatly improved by esterification of cochineal carmine. The optimum esterification condition was achieved by using 1.0 g cochineal carmine modified with 50 mL acetic anhydride and 4.0 g anhydrous sodium acetate at 80°C for 2.0 h. Further improvement was observed as the build-up increased. In addition, blue shifting of the maximum absorption wavelength occurred after esterification. Fastness, especially light and perspiration fastness of cochineal carmine are increased compared to those of unmodified materials. Chemical modification of cochineal carmine is a promising technique for improving the dye fastness properties of cationic modified cotton.

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