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Effect of reactive anionic agent on dyeing of cellulosic fibers with a Berberine colorant

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Abstract

Berberine, a natural cationic colorant, is the major component of Amur Cork tree extract. Due to ionic interactions, while it shows high exhaustion towards protein fibers such as wool and silk, it exhibits little substantivity onto cellulosic fibers. In this context, in order to apply the colorant to cellulosic fibers, the new approach of employing the anionic agent containing a dichloro-*s*-triazinyl reactive group was conducted. Berberine could display considerable substantivity towards anionic agent finished fibers. It was found that the anionic agent was covalently bonded to the cellulosic substrates by virtue of the covalent nature of its attachment to the fibers and also gave anionic sites to the substrate for electrostatic interaction with cationic Berberine. The effectiveness of the anionic agent in improving the exhaustion of Berberine on the cellulosic fibers was achieved.

Keywords: Anionic agent; Cotton; Berberine; Amur Cork tree; Tannic acid; Natural dyes

1. Introduction

Cotton is the most abundant of all naturally occurring organic substrates and is widely used. It is used either alone or in conjunction with other synthetic fibers in various ranges of apparel. This material characteristically exhibits excellent physical and chemical properties in terms of water absorbency, dyeability and stability [1,2].

Over the years a number of studies on the finishing of cotton fibers have been carried out to improve dye-uptakes and exhaustion properties. The focus of most research was to provide cationic sites on the cotton fibers for interacting with anionic dyes. These studies which were commonly involved chemical modification employing cationization of cotton fibers with suitable cationic agents, providing attractive sites for anionic dyes [3–7].

While several classes of dye can be successfully applied to the cotton fibers, including direct, azoic, vat and reactive dyes, the application of cationic dyes has not gained widespread success. In this study, for applying cationic Berberine to the cotton fibers the anionic agent containing a dichloro-*s*-triazinyl reactive group was synthesized and its effect was determined. This modification was expected to enhance the affinities of cationic compounds, such as cationic dyes, chitosan,

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quaternary ammonium antibacterial agents and metal ions, by operating the electrostatic attractive force.

Berberine, a natural cationic colorant, is the major component of Amur Cork tree extract [8]. Thus, the aim of this work was to modify the cotton fiber using a prepared reactive anionic agent and to examine the feasibility of using this agent for improving exhaustion properties of Berberine. Furthermore, if Berberine can be employed to the substrate properly, it can be also utilized in antibacterial finishes as a natural agent due to its cationic quaternary ammonium salt [9–11]. The structure of Berberine is shown in Fig. 1.

In this article, the exhaustion of Berberine on cotton fiber treated with the anionic agents is investigated and its properties discussed.

2. Experimental

2.1. Synthesis of reactive anionic agent (sodium, 4-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate)

4-Amino-benzenesulfonic acid (**1**, 5.20 g, 0.03 mol) and sodium carbonate (1.70 g, 0.016 mol) were dissolved in distilled water (48 ml) in order to change the sulfonic acid of **1** to the sodium salt (**2**) and then the solution (solution 1) was cooled to 0–5 °C.

2,4,6-Trichloro-1,3,5-triazine (**3**, 5.53 g, 0.03 mol) was dissolved in acetone (40 ml), and this solution was poured in distilled water (90 ml) with crushed ice (90 g). 2N hydrochloric acid aqueous solution (0.6 ml) was added to the system (pH 1–2). The reaction system (solution 2) was stirred maintaining the temperature at 0–5 °C in the ice bath.

Solution 1 was slowly added to solution 2 and then a 20% aqueous solution of sodium carbonate was added dropwise to the reaction mixture to give a pH of 6. The reaction mixture was stirred at 0–5 °C for 1 h. After the reaction was completed, the white precipitated solid (**4**) was filtered, washed with acetone under reduced pressure and allowed to dried in a vacuum at room temperature (yield 79%, 8.11 g) (Fig. 2).

HPLC/MS (negative mode, m/z, relative intensity): 318.9 ([M–Na]$^-$, 100.0), 320.9 ([M–Na + 2]$^-$; isotopic peak, 70.7), 322.9 ([M–Na + 4]$^-$; isotopic peak, 14.6).

Elemental analysis: Calculated for $C_9H_5Cl_2N_4NaO_3S$: C, 31.50; H, 1.47; N, 16.33; S, 9.35%. Found: C, 31.21; H, 1.50; N, 16.17; S, 9.51%.

UV–vis: λ_{max} (H_2O) 278.2 nm, $\varepsilon(H_2O)$: 2.32×10^4.

2.2. Optimum treatment conditions of the anionic agent on cotton fibers

To determine the optimum conditions, scoured and rinsed cotton fabrics (warp 20 tex/yarn 28 yarns/cm, weft 16 tex/yarn 27 yarns/cm, 100 ± 5 g/m^2) were treated with the anionic agent (1% owf) at various temperatures (30–80 °C) and pH values (7–11) for 1 h. The liquor ratio was 1:20 and sodium sulfate (100 g/l) was used as a neutral salt. The pH was adjusted using sodium carbonate. At the end of the treatment, the fabrics were

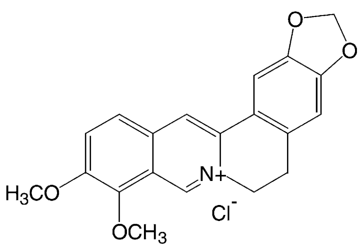

Fig. 1. Chemical structure of Berberine chloride.

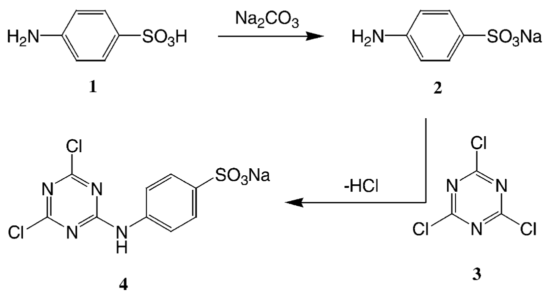

Fig. 2. Synthesis scheme of the anionic agent (sodium, 4-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate).

removed, rinsed thoroughly in tap water and allowed to dry in the open air.

Absorbance measurements of the original bath and the exhausted bath were carried out using a UV/VIS spectrophotometer. Using a previously established absorbance/concentration relationship at the λ_{max} of the anionic agent, the quantity of the anionic agent in solution was calculated and the extent of exhaustion (%E) achieved was determined using Eq. (1), where D_0 and D_t are the quantities of anionic agent initially in the bath and in the final bath, respectively.

$$\%E = \frac{(D_0 - D_t)}{D_0} \times 100. \tag{1}$$

Unfixed anionic agent from the fabrics was extracted using 25% aqueous pyridine solution and then measured spectrophotometrically. The extent of fixation (%F) and fixation efficiency (%EF) were calculated using Eqs. (2) and (3), respectively, where D_e is the amount of extracted anionic agent.

$$\%F = \frac{(D_0 - D_t - D_e)}{(D_0 - D_t)} \times 100 \tag{2}$$

$$\%FE = \frac{(E \times F)}{100}. \tag{3}$$

2.3. Dyeing with Berberine

The cotton fabrics (1.0 g) pretreated with the anionic agent (10% owf) under optimum conditions were dyed with Berberine (Natural Yellow 18, as Berberine chloride, Sigma, 2% owf) at various temperatures (30–90 °C) and pH values (3–11) for 1 h. The liquor ratio was 1:30. The pH was adjusted using acetic acid and sodium carbonate. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and dried in the open air. The exhaustion of Berberine was determined by the same way [Eq. (1)] as that for applying anionic agent.

2.4. Tannic acid treatment

To compare with effects of the synthesized anionic agent, the cotton fabrics (1.0 g) were pretreated with tannic acid (Aldrich, M.W.: 1701.23) prior to dyeing with the Berberine. The amounts of tannic acid were 10, 30 and 50% owf and the liquor ratio was 1:20. The treatment was carried out at 40 °C for 1 h. At the end of treatment, the treated samples were rinsed in tap water and allowed to dry.

2.5. Color measurement

Colorimetric data of dyeings were determined using a Datacolor SF 600 plus spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer.

2.6. Color fastness

The wash fastness of the dyeing was tested using the method ISO 105 C06 A1S.

3. Results and discussion

3.1. Synthesis of the anionic agent

To provide anionic sites on the substrate, a reactive anionic agent capable of covalent interaction was synthesized by the method shown in Fig. 2. The equal molar amounts of compounds **1** and **3** were reacted in an ice-bath and the white solid of the anionic agent was obtained. The synthesized anionic agent has a dichloro-*s*-triazinyl reactive group in its chemical structure that is one of the reactive groups usually used in the preparation of reactive dyes. This reactive group can be covalently bonded to cotton fibers by a nucleophilic substitution reaction at room temperature [12]. Its reaction mechanism is similar to that of commercial reactive dyes. Therefore, the anionic agent could give anionic sites (–SO_3^-) to the cotton fibers, providing electrostatic interactions with cationic compounds. In addition, it is proposed that the marked durable fastness property of the anionic agent could be obtained by virtue of the covalent nature of the agent–fiber bond.

3.2. Treatment conditions of the anionic agent

To determine the optimum treatment condition of the anionic agent on cotton fiber, the exhaustion (%*E*) and fixation (%*F*) were obtained at various temperatures and pH values. In the range of 30–80 °C (Table 1), it is evident that the %*E*, %*F* and %*EF* of the treatment increased with decreasing temperature. The findings could be explained in that the two electronegative chlorines of the anionic agent increased the reactivity of the *s*-triazinyl group with the cellulosic substrate even at room temperature [13–15]. The effects confirm the view of its mechanism to be like commercial reactive dyes that involve the nucleophilic reaction of dichlorotriazine dyes, namely cold type dyes.

To support the reactivity of the dichloro-*s*-triazinyl group of the anionic agent towards cotton fibers, the addition of alkali was generally used [13–15]. Table 2 shows the effect of application pH on %*E* and %*F* of the anionic agent. As the pH increased, the %*E* slightly increased, but the %*F* highly increased up to 90.4% at pH 11. In the alkaline condition, the hydroxyl groups within the cotton fibers were ionized to cellulosate anions and the nucleophilies attack the carbon atom of the dichloro-*s*-triazinyl group. However, as predicted, both acidic and neutral treatment conditions did not result in a significant production of nucleophiles, and provided a smaller chemical reaction.

Table 1
Effect of application temperature on %*E*, %*F*, and %*EF* of the anionic agent

Temperature (°C)	%*E*	%*F*	%*EF*
30	44.4	90.5	40.2
40	42.1	80.5	33.9
50	35.3	62.0	21.9
60	29.6	56.8	16.8
70	26.2	50.8	13.3
80	25.2	49.2	12.4

Table 2
Effect of application pH on %*E*, %*F*, and %*EF* of the anionic agent

pH	%*E*	%*F*	%*EF*
7	41.5	55.8	23.2
8	41.9	76.9	32.2
9	44.1	86.2	38.0
10	44.6	89.1	39.7
11	44.6	90.4	40.3

3.3. Dyeing with Berberine

The resulting modified cotton fibers with the anionic agent could enhance an interaction with cationic compounds such as cationic dyes, chitosan, quaternary ammonium antibacterial agents, metal ions and so on. As mentioned earlier, Berberine shows a great substantivity towards protein fibers such as wool and silk, but it provides little tendency to be dyed on to cellulosic fibers.

The anionic agent-treated samples were dyed with Berberine. To investigate the effect of temperature and pH on the exhaustion, the samples pretreated with the anionic agent were dyed in the range of temperatures 30–90 °C and then the dye exhaustions were measured. As shown in Fig. 3, higher exhaustions were achieved at a lower range of temperatures. It is thought that because the size of the Berberine molecule is smaller than that of the commercial synthetic dyes, the diffusion of Berberine into the fibers could occur very easily and rapidly even at a lower temperature. In addition, the ionic interaction between the anionic site and the cationic Berberine, meant that the adsorption was more favorable at lower tempera-

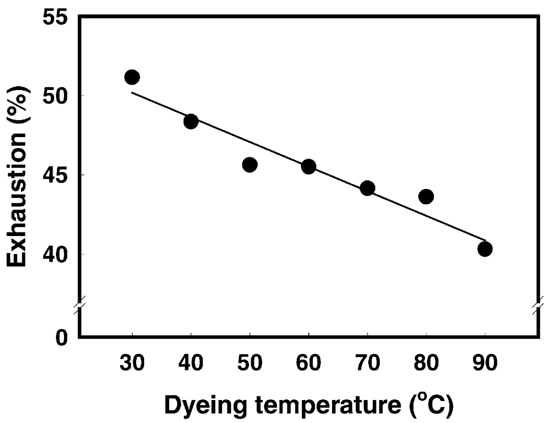

Fig. 3. Effect of dyeing temperature on the exhaustion of Berberine to the cotton fibers treated with anionic agent.

ture than at higher temperatures. In other words, the affinity of the dyes to the fiber substrate increases with decreasing temperature [16]. Having ascertained that dyeing was optimally achieved at 30 °C, this temperature was used in subsequent experiments.

A further set of experiments was carried out to examine the effect of pH. The samples treated with the anionic agent were dyed at various pH conditions (3–11) and the dye exhaustions were determined (Fig. 4). The higher pH conditions led to high exhaustion since the cationic Berberine was more attractive to the negatively charged sulfonate anions under basic conditions. It is proposed that these results might be related to the dissociation of the sodium salts ($-SO_3^-Na^+$) of the anionic agent in the dyeing solution. In other words, the sodium salts of the sulfonates were generally dissociated to the sodium ions (Na^+) and the sulfonate anions ($-SO_3^-$) in water. However, in acidic conditions the extent of the sulfonic acid form ($-SO_3H$) might be greatly increased due to protonation to the sulfonate anions. The dissociations of the sulfonic acids are much weaker than those of the sodium salts of sulfonates. Thus, the resulting number of available anionic sites on fibers in alkaline conditions is relatively larger than those sites in acidic conditions and the exhaustion of the cationic Berberine was increased in alkaline dyeing solutions.

Fig. 5 shows the exhaustions of Berberine to the cotton fibers pretreated with different amount of anionic agents. It is found that the equilibrium exhaustion of 2% owf Berberine was achieved when the sample was treated with a concentration of 10% owf for anionic agent. In the case of 2% owf Berberine applied, considering the efficiency of the amount of anionic agent used, the optimum concentration of the anionic agent was thought to be 10% owf, where the maximum exhaustion of Berberine has been reached.

Commonly, to be dyed with cationic dyes cellulosic fibers have been pre-mordanted with tannic acid that gives carboxylic acid groups (–COOH) to the fibers [17]. In this context, a comparison of tannic acid and the anionic agent was carried out to determine whether the use of the anionic agent would be more effective than the traditional tannic acid system.

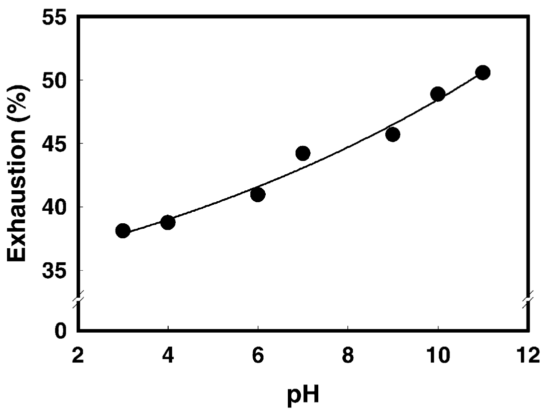

Fig. 4. Effect of pH on the exhaustion of Berberine to the cotton fibers treated with anionic agent.

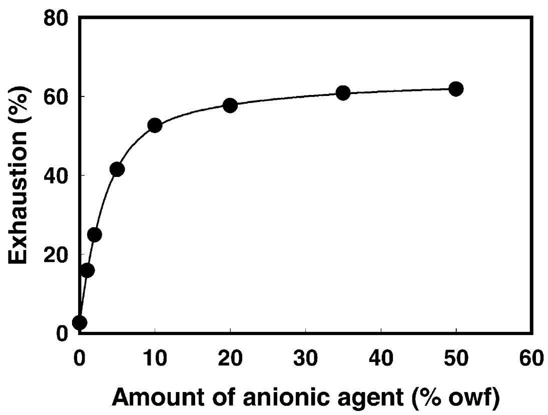

Fig. 5. The exhaustion of Berberine to the cotton fibers treated with different amounts of anionic agent.

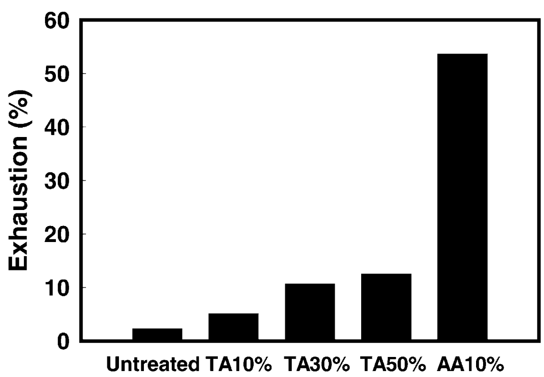

Fig. 6. A comparison of the effect of tannic acid and anionic agent treatment on the exhaustion of Berberine.

Fig. 6 displays that Berberine exhaustion was low towards untreated samples (%E 2.3%) due to the absence of anionic sites. To the samples treated with tannic acids at 10 (TA10%), 30 (TA30%) and 50% (TA50%) owf, Berberine showed increased substantivity with a little amount. The exhaustions obtained were 5.1, 10.6 and 12.5%, respectively. In the case of the sample treated with the anionic agent at 10% owf (AA10%), however, the exhaustion of Berberine was increased to 53.7%. This value is 23-times higher than that of the untreated sample and 10 times higher than that of the sample treated with an equal amount (10% owf) of tannic acid. The results can be explained in that the dissociation of sodium salts of sulfonates are much stronger than that of the carboxylic acids of tannic acid. Therefore, in the case of the anionic agent, the number of anionic sites available is larger than in the tannic acid.

3.4. Color measurement

Another aspect which was considered was that the tannic acid shows a pale brown color in itself, which could cause unintended color change to the cotton fibers dyed with Berberine. However, because this particular anionic agent was colorless, a white compound, it imparted little shade change to the dyeing.

The colorimetric data of cotton fabrics pretreated with anionic agent (AA) and tannic acid (TA) are shown in Table 3. In the case of the anionic agent, the extent of this shade change was very similar to that bestowed by the untreated white sample. However, it is evident that the color difference of the samples increased with increasing concentrations of tannic acid. In addition, pretreatment with tannic acid altered the shade of the samples from white to brown.

Fig. 7 shows the colorimetric values of dyed cotton fabrics with Berberine after pretreatment with the anionic agent and tannic acid. The anionic agent system gave a very light shade of pure yellow like Berberine itself. However, the dyeings with tannic acid method imparted a shade change from pure yellow to reddish orange. Also, the lightness value decreased and the shade of depth became dull and dark.

3.5. Wash fastness

A wash fastness test of Berberine dyeing with the anionic agent system was carried out. The

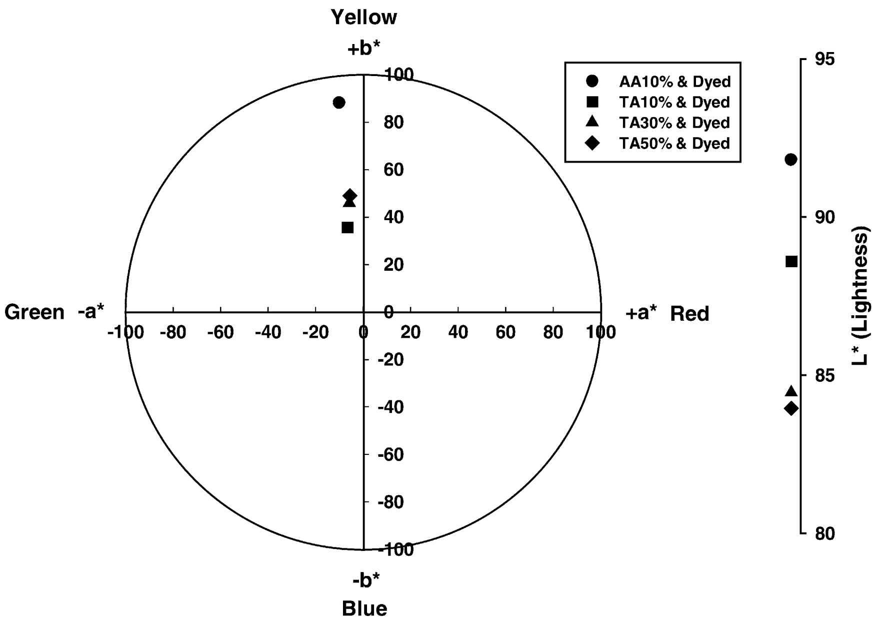

Fig. 7. The effects of tannic acid and anionic agent pretreatment on the colorimetric values of the dyeings.

Table 3
The colorimetric data of cotton fabrics treated with anionic agent (AA) and tannic acid (TA)

Treatments	L^*	a^*	b^*	C	h°	Color difference
Untreated	97.34	−0.57	1.07	1.21	118.14	–
AA10%	97.13	−0.51	1.12	1.23	114.96	0.2
TA10%	95.44	−0.10	3.85	3.85	91.55	3.4
TA30%	94.57	0.32	6.18	6.19	87.06	5.9
TA50%	93.97	0.59	7.11	7.13	85.28	7.0

Table 4
The wash fastness of the Berberine dyeing with anionic agent system

Change in color	Staining					
	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
3–4	3	4	3	4–5	4–5	3

result is shown in Table 4. In terms of gray scale assessment, the change in color of the dyeing was 3–4 grade and the staining onto the adjacent fabrics was at least 3 grade. These results are fairly good considering this is a natural dye.

4. Conclusions

The reactive dichloro-*s*-triazinyl anionic agent was synthesized and applied to the cotton fibers. The dyeing properties of Berberine were determined. The exhaustion of Berberine to the cotton fibers with the anionic agent system was 23-times higher than that of the untreated sample and 10-times higher than that of the sample pretreated with an equal amount of tannic acid. In the case of the anionic agent system, the extent of the shade change of Berberine dyeing was very similar to that bestowed by the untreated white sample. In the future works, other cationic functional compounds will be discussed.

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