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Effect of reactive anionic agent on dyeing of cellulosic fibers with a Berberine colorant—part 2: anionic agent treatment and antimicrobial activity of a Berberine dyeing

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Abstract

A reactive anionic agent containing dichloro-*s*-triazinyl reactive group was synthesized and applied to the cotton fabric. Berberine as a natural cationic colorant showed considerable substantivity towards anionic agent modified fabric. This Berberine can be also employed in antimicrobial finishes as a natural agent due to its characteristic of cationic quaternary ammonium salt. It was found that the adsorption of Berberine onto cotton fabric pretreated with the anionic agent was greatly increased when compared to that of untreated counterpart. The addition of neutral salts was greatly effective to increase the exhaustion–fixation efficiencies (%EF) of the anionic agent onto the cotton fabric. In terms of antimicrobial activity of Berberine dyeing, the dyed sample with Berberine showed very effective antimicrobial functions showing about 99.5% of bacterial reduction against *Staphylococcus aureus*.

Keywords: Berberine; Cotton; Fastness; Anionic agent; Antimicrobial activity

1. Introduction

In recent years, a number of reviews on the application of natural materials have attracted most attention due to their environmentally friendly characteristics. These applications can be represented as enzyme treatments, dyeings with natural colorants, chitosan finishes, antimicrobial utilizations and so on [1–8]. Although these natural materials might be limited in their practical use, it seems that they are considered to give several good advantages to the several applications such as non-toxic functions, specific medical actions and environmentally friendly finishes. However, it is commonly thought that in terms of application the natural materials display very low substantivity towards fibers due to lack of interaction sites or groups within substrates. Thus, improvement of the exhaustion is generally required using chemical modification methods on the substrates. In this study, a novel reactive anionic agent was designed to provide proper dyeing sites for cationic Berberine (Fig. 1).

In this context, the aim of this work was to modify the cotton fiber using a synthesized reactive anionic agent and to examine further application behaviors. Finally, fastness tests and the antimicrobial activity of Berberine dyeings were also discussed. As mentioned in the previous paper [9], if Berberine can be employed to the substrates properly, it can be utilized in antimicrobial finishes as a naturally occurring agent due to its cationic quaternary ammonium salt.

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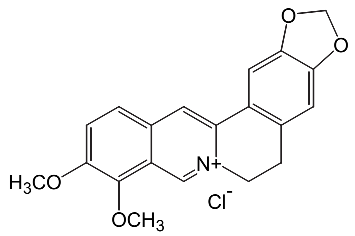

Fig. 1. Chemical structure of Berberine chloride.

2. Experimental

2.1. Fabric

The 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 used.

2.2. Preparation of reactive anionic agent (sodium, 4-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate) and its treatment to the cotton

The reactive anionic agent being applied to cotton fiber was prepared. The methods for synthesis of the reactive anionic agent and resulting analysis data were described in previous part of this paper [9]. The treatment conditions with the anionic agent were followed by the method mentioned in previous paper [9]. In addition, the effect of salt addition and treatment time were also determined at various conditions.

2.3. Berberine dyeing

As described earlier [9], the cotton fibers (1.0 g) pretreated with the anionic agent (10% owf) under optimum conditions were dyed with the Berberine (Natural Yellow 18, as Berberine chloride, Sigma, 2% owf) at 30 °C for 1 h. The liquor ratio was 1:30. After dyeing, the samples were rinsed thoroughly in tap water and dried in the open air.

2.4. Color measurement

All colorimetric measurements were carried out using the equipment and procedure described previously [9].

2.5. Fastness tests

The fastnesses tests of the dyed fabric to washing, dry cleaning, rubbing, and chlorinated water were conducted using the methods of ISO 105-C06 A1S, ISO 105-D01, ISO 105-X12 and ISO 105-E03, respectively.

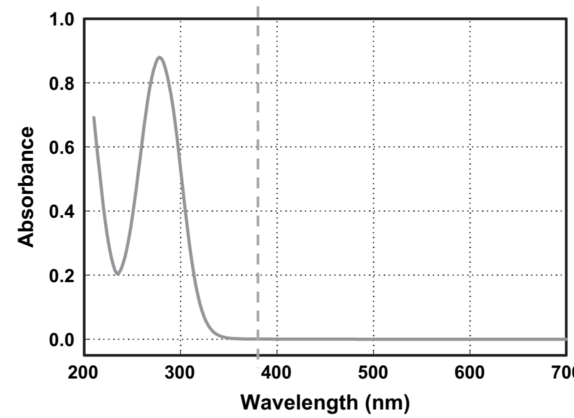

Fig. 2. UV–visible spectrum of the reactive anionic agent in water.

2.6. Antimicrobial activity

The antimicrobial activity of the cotton fabrics dyed with Berberine was evaluated. The test samples were prepared by treatment with 10% owf of a reactive anionic agent at optimum conditions and followed by dyeing with 2% owf of Berberine at 30 °C for 1 h. As a control sample, the fabric treated with anionic agent was prepared. To assess antimicrobial functions, two test methods were employed. The one is a qualitative Parallel Streak method, namely AATCC Test Method 147-1998. The other is a quantitative AATCC Test Method 100-1999. The bacterium used was *S. aureus*.

3. Results and discussion

3.1. Absorbance of synthesized anionic agent

As mentioned in the previous paper [9], the synthesis and the analysis of a reactive anionic agent were carried out and determined. It is desired that in order to apply cotton fabric, the important requirement of this agent is considered its absorption ranges, which could impart unintended color staining to the treated samples. In this context, Fig. 2 shows the UV–visible spectrum of the synthesized anionic agent. It was found that the λ_{max} in water is observed at 278.2 nm and this agent does not absorb any light in the visible ranges at all. This result explains that the prepared anionic agent is a colorless material and that it does not cause any unintended

Table 1
Colorimetric data of untreated and treated cotton fabrics with a reactive anionic agent

Sample	*L**	*a**	*b**	*C*	*h*°	Color difference
Untreated	97.34	−0.57	1.07	1.21	118.14	–
Treated	97.13	−0.51	1.12	1.23	114.96	0.2

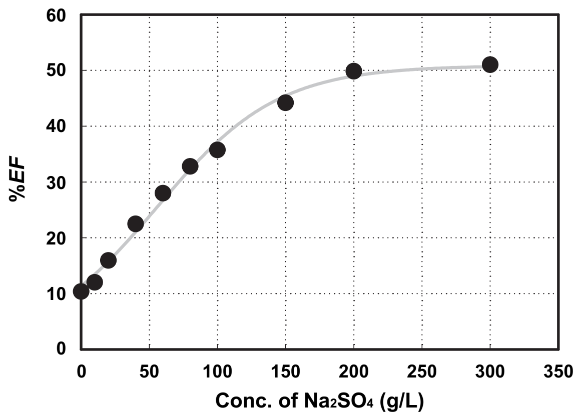

Fig. 3. Effect of neutral salt (Na_2SO_4) on the exhaustion–fixation efficiency (%EF) of anionic agent on to the cotton fabrics.

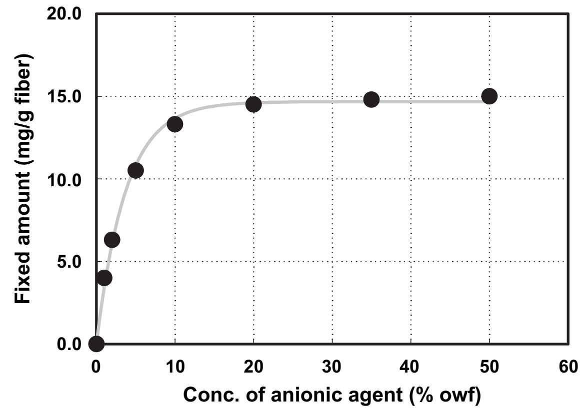

Fig. 5. Effect of concentrations of the anionic agent on to the cotton fabrics.

shade changes of the treated samples. The colorimetric data of the cotton fabric treated with the anionic agent and the untreated fabric are shown in Table 1. Table 1 clearly displays colorimetric data and color differences between both untreated and treated samples. It is evident from the results presented in Table 1 that the reactive anionic agent imparted very little change of shade to the substrate and that the values are virtually similar to the untreated original sample.

3.2. Effect of salt addition and treatment time to the application of the anionic agent

In the first part of this paper [9], to investigate the exhaustion properties of the anionic agent, the effects of application temperatures and pHs were observed. Thus, in this work, the effects of salt addition and treatment time were studied. Neutral salt (Na_2SO_4) could affect the exhaustion properties of the anionic agent on to the cotton fibers with a similar manner to common reactive dyeings [10–12]. The effect of the addition of sodium sulfate on the exhaustion–fixation efficiency (%EF) is shown in Fig. 3. Fig. 3 represents that the %EF generally increased with increasing the concentration of sodium sulfate and that a maximum %EF value was obtained in the amount of salts of 200–300 g/l. However, from the industrial point of view, because those amounts of the salt were too much excessive to employ practically, 100 g/l of sodium salt was considered to be appropriate and used in subsequent experiments. In the case of treatment time, a proper exhaustion–fixation percentage was sufficiently achieved in 1 h (Fig. 4). Fig. 5 represents the build-up properties of the anionic agent with different application concentrations. At about 10–20% owf of the anionic agent, the fixed amount of the anionic agent was reached to the maximum range of values.

3.3. Berberine dyeing with an anionic agent treated sample

Although Berberine shows a great substantivity towards protein fibers such as wool and silk due to electrostatic attractive forces, it does not provide dyeing behavior on to cellulosic fibers. However, it was found that the modified cotton fibers with the reactive anionic

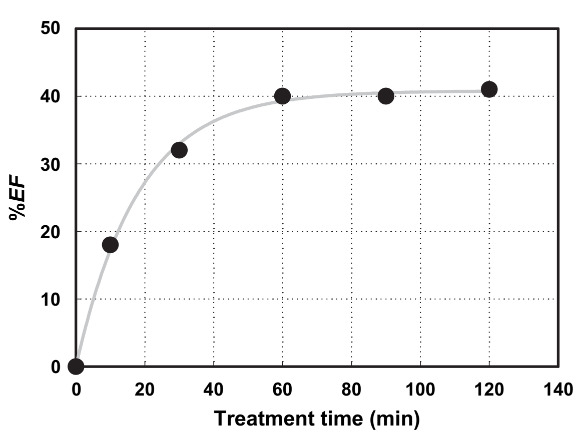

Fig. 4. Effect of treatment time on the exhaustion–fixation efficiency (%EF) of anionic agent on to the cotton fabrics.

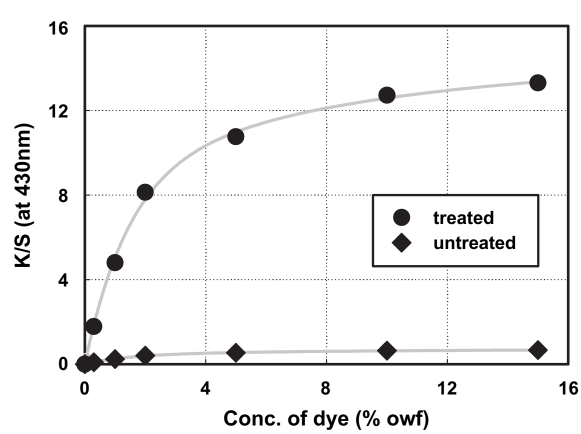

Fig. 6. Effect of Berberine dye concentrations on the color strength (K/S value) to the both untreated and treated samples with the anionic agent.

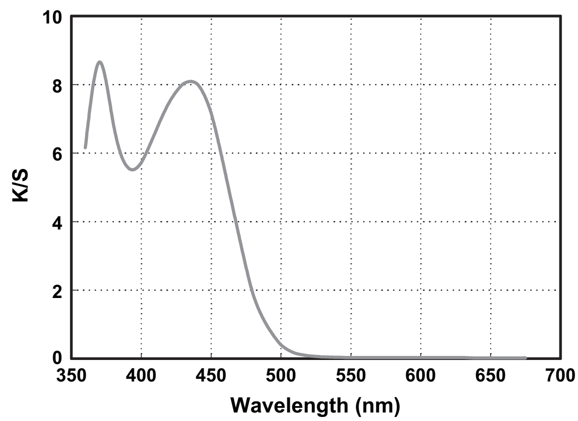

Fig. 7. Color strength (K/S) spectra of the Berberine dyeing pretreated with the anionic agent.

agent imparted strong attraction forces to the cationic Berberine compound [9]. The further work herein comprises an investigation of the effect of dye concentrations. Fig. 6 shows the color strength (K/S value at 430 nm) of Berberine dyeings using different dye concentrations to the untreated and treated samples. Fig. 6 displays that the Berberine did not exhaust towards untreated cotton fibers. However, in the case of the sample treated with the reactive anionic agent, the color strength greatly increased with increasing concentrations of Berberine. This finding can be explained that because the modified cotton fibers using the synthesized anionic agent provided a great number of anionic sites ($-SO_3^-$) within the substrates, the cationic Berberine was effectively adsorbed onto the treated substrates by the ionic interaction. In addition, as mentioned earlier, because the anionic agent is a colorless compound, it does not impart unintended color change of the dyed cotton fabrics with Berberine. The color strength (K/S value) of Berberine dyeing exhibited the maximum value at 430 nm and its absorbance was mainly observed at the range of 400–500 nm (Fig. 7). This result represents that pretreatment with the anionic agent did not alter any shade changes from pure yellow dyeing of Berberine.

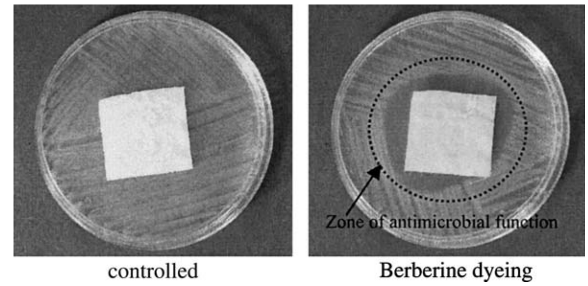

Fig. 8. Effect of Berberine dyeing on inhibition of bacterial growth.

3.4. Color fastness tests

The results of fastness tests on Berberine dyeings are shown in Table 2. Table 2 shows that in the case of wash fastness, the change in color of the dyed fabric was 3–4 grade and the extent of the staining onto the adjacent fabric was at least 3 grade. The fastness to dry cleaning was all 4–5 grade for both the color change and the staining. The rubbing fastness was 4 grade in a dry condition and 3 grade in a wet condition. The fastness to chlorinated water was 4 or 4–5 grade. All these results of Berberine dyeings are fairly acceptable levels considering this is a natural colorant.

3.5. Antimicrobial activity

It is very well known that the organic compounds containing a structure of the quaternary ammonium salt strongly show antimicrobial functions. As shown in Fig. 1, it contains a positively charged nitrogen atom in its chemical structure. Therefore it is acceptable that Berberine dyeings could be utilized in functional finishing process for antimicrobial purposes. This work herein discusses a useful approach of employing Berberine colorant, a natural cationic quaternary ammonium salt, to achieve desired durable antimicrobial functions. In order to determine antimicrobial properties, the bacteria, namely *S. aureus* was used. The two kinds of test method were employed; the one was qualitative Parallel Streak method (AATCC Test Method

Table 2
The color fastness results of the cotton fabrics dyed with Berberine

Fastnesses	Change in color	Staining					
		Acetate	Cotton	Nylon	PET	Acrylic	Wool
Washing	3–4	3	4	3	4–5	4–5	3
Dry cleaning	4–5	4–5	4–5	4–5	4–5	4–5	4–5
Rubbing	Dry			Wet			
	4			3			
Chlorinated water	Concentration of active chlorine						
	20 mg			50 mg			100 mg
	4–5			4–5			4

Table 3
Bacterial reduction (%) of the Berberine dyeing against *Staphylococcus aureus*

Test method	Description	Bacterial reduction (%)	
		Controlled	Berberine dyeing
AATCC Test Method 100	Percent reduction of bacteria	~0%	99.5%
AATCC Test Method 147	Zone of inhibition	0 mm	4 mm

147-1998) by which the zone of growth inhibition of bacteria was observed. The other was quantitative AATCC Test Method 100-1999 by which the reduction in numbers of the bacteria was evaluated.

In the qualitative AATCC Test Method 147, the prepared fabric samples were placed on the flat-bottomed petri dish containing a nutrient broth and bacterial inoculum. After both testing and control swatches had been contacted with *S. aureus* under the controlled conditions, the inhibition of bacterial growth was observed. Photographs of the both testing and control samples are shown in Fig. 8. The circled zone represents a restraint effect of bacterial growth. It occurs as a result of diffusion of the antimicrobial active materials from the Berberine dyeing. For undyed control sample, which was treated with anionic agent only, the zone of bacterial inhibition was not found. However, for the Berberine dyeing, the zone of bacterial inhibition was clearly observed. This corresponding result can be explained that the positive charges in the Berberine molecules could destroy the negatively charged cell membrane of bacteria due to disturbing charge balances of the cell membrane [13,14].

In the quantitative AATCC Test Method 100, *S. aureus* was inoculated on the prepared fabric swatches. The fabric swatches were placed in the controlled condition for certain period time. After contacting with bacterial inoculum, bacteria were extracted from the fabric swatches. The extracted bacteria solution aliquots were plated on a nutrient agar and incubated in accordance with test procedures. The colonies of the bacterium on the agar plate were counted and the reduction in numbers of the bacterium was calculated. The results are presented in Table 3. Indeed, the dyed sample with Berberine displays very effective antimicrobial activity showing 99.5% of reduction in the number of bacteria. As a consequence of these tests, it is proposed that the cationic Berberines are adsorbed onto the modified cotton fibers with a reactive anionic agent and that corresponding its positive charges from the quaternary ammonium salts function the antimicrobial activity to be like commercial antimicrobial agents.

4. Conclusions

The reactive dichloro-*s*-triazinyl anionic agent was synthesized and applied to the cotton fibers. The cotton fibers were dyed with Berberine, a cationic natural colorant. The adsorption of Berberine onto cotton fibers pretreated with the anionic agent was greatly increased when compared to that of untreated counterparts. The Berberine dyeing provides very strong antimicrobial functions showing 99.5% of reduction in the number of bacteria. In the future works, other cationic functional compounds, such as cationic dyes, chitosan, quaternary ammonium antimicrobial agents and metal ions, will be studied.

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