An Antimicrobial Cationic Reactive Dye: Synthesis and Applications on Cellulosic Fibers

Tao Zhao,[1] Gang Sun,[2,3] Xinyuan Song[1]

[1]*College of Chemistry and Chemical Engineering, Donghua University, Shanghai, China*
[2]*Division of Textiles and Clothing, University of California, Davis, California 95616*
[3]*Modern Textile Research Institute, Donghua University, Shanghai, China*

Received 21 October 2007; accepted 5 December 2007
DOI 10.1002/app.27859
Published online 29 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An antimicrobial cationic reactive dye was synthesized by reacting aminoanthraquinone with cyanuric chloride, 3-dimethylamino-1-proponol, and lauryl chloride in sequence. The chemical structure of the dye was fully characterized by using ^{1}H-NMR, ^{13}C-NMR, and FTIR analysis. This dye demonstrated adequate antimicrobial properties in aqueous solution. The minimum inhibitory concentration of the dye against bacterial concentrations of 10^6–10^7 colony forming units (CFU)/mL of both *E. coli* and *S. aureas* were only 10 ppm. The dye can react with cotton without addition of any salt as electrolyte. The dyed fabrics showed proper color washing durability. But the antimicrobial functions were severely affected by laundry. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1917–1923, 2008

Key words: cationic reactive dye; synthesis; characterization; antimicrobial; anthraquinone; quaternary ammonium salts

INTRODUCTION

Antimicrobial textile materials have attracted significant attentions in recent years because of the increasing concern on cross-contamination of diseases in public places and hospitals.[1–7] Using antimicrobial materials in hospitals could help to reduce rates of disease transmission and infection there. Antimicrobial functions are usually incorporated onto fabrics in chemical finishing processes. Some of the wet finishes may affect dyeing and other finishes on the materials. Moreover, the antimicrobial finish may require separate wet treatment processes, and repeated dyeing and chemical finishing on the products could bring more concerns to the properties of the materials and the environment. Thus, approaches have been made to unify dyeing and functional finishing in one bath by preparing dyes that have color and additional functional properties together. For example, antimicrobial cationic dyes were prepared by incorporating long alkyl chain quaternary ammonium salts (QAS) to anthraquinone chromophores through covalent bonds.[8–10] These dyes showed excellent color and antimicrobial functions in solutions and could be effectively introduced to acrylic fibers to achieve simultaneous coloration and antimicrobial efficacy. However, these dyes do not have affinity to cellulose which is the composition of cotton, the most popular natural fiber.

On the other side, fiber reactive dyes can form chemical bonds (covalent bonds) with cellulosic fiber, and are generally considered to possess excellent washing fastness.[11] The conventional reactive dyes are made water-soluble by incorporation of anionic groups such as sulfonate groups (—SO_3Na) and carboxylate groups (—COONa) into the dye molecules. However, the surfaces of wet cellulosic substrates are negatively charged, and thus tend to repel anionic dyes. Therefore, the application of the reactive dyes conventionally requires use of extremely high amounts of salt such as sodium chloride (NaCl) or sodium sulfate (Na_2SO_4), as a dyeing auxiliary for accelerating the dyeing process and increasing the dye uptake. The use of the salt increases the cost of dyeing and the toxicity of the dye-bath, and the disposal of the exhausted salt-containing dye-bath has hazardous impact on fishes in rivers and lakes. Therefore, development of new environmentally friendly reactive dyes is desirable.

In this research, antimicrobial QAS structures are incorporated into reactive dyes as both water-soluble and cellulosic fiber interactive groups. Such a structural design could simultaneously impact the dye possessing multiple functions such as antimicrobial, fiber reactive and environmentally friendly. The QAS are water soluble and more importantly contain positive charges in water, which will increase dyes interaction with negatively charged cellulosic surfaces.

Correspondence to: G. Sun (gysun@ucdavis.edu).
Contract grant sponsor: China Ministry of Education; contract grant number: 111 Project B07024.

Thus, the antimicrobial reactive dye molecule can assist dye exhaustion onto cellulosic fibers without using salts and possibly increase reactivity between the cellulose and the dye, and consequently reduce potential hydrolysis of the reactive dyes. The QAS with the long chain length of 12 carbons was used since longer alkyl chains are more effective as antimicrobial agents.[12] Meanwhile, the chromophore of this dye is anthraquinone structure which renders good chemical stability.

The synthesis and characterization of the cationic reactive dye as well as its applications in dyeing cotton fabrics are discussed. The antimicrobial ability of the dye in aqueous solution was also evaluated against Gram-positive and Gram-negative bacteria with concentrations of 10^6–10^7 colony forming units (CFU)/mL by a minimum inhibitory concentration (MIC) procedure. The dyeing properties and theory of the dye on cotton will be discussed as well.

EXPERIMENTAL

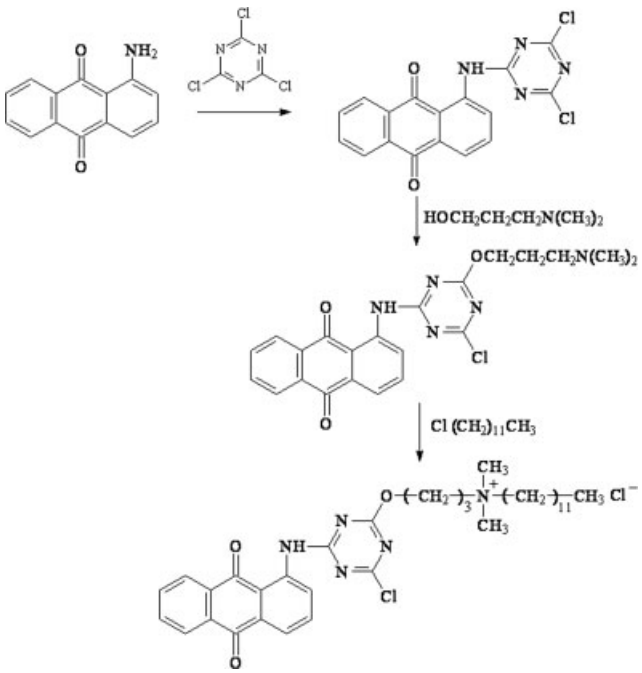
Materials and instrumentation

1-aminoanthraquinone (97%, Sigma-Aldrich, USA), cyanuric chloride (99%, Acros, USA), 3-dimethylamino-1-proponol (99%, Acros, USA), lauryl chloride (99%, Acros, USA) were purchased and used as received. Fourier transform infrared (FTIR) spectra were taken on a Nicolet 6700 FTIR spectrometer (Thermo, USA) using KBr pellets. The samples were made thin enough to ensure that the Beer-Lambert law was obeyed. Nuclear magnetic resonance ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a DRX 500 Spectrometer. Electronic absorption spectra were recorded on a Hitachi U-2000 spectrophotometer.

Cotton fabrics used in the study were purchased from Testfabrics Inc. (West Pittston, PA). The fabrics were thoroughly scoured with AATCC standard detergent WOB (AATCC Test Method 124-1996), then rinsed thoroughly in tap water and dried in the open air before use. Sodium sulfate (EM Science, USA), sodium carbonate (EM Science, USA) were used as received.

Synthesis

Scheme 1 shows the reactions for synthesizing this antimicrobial reactive dye. The first step was an acetylation of 1-aminoanthraquinone group using cyanuric chloride. 0.075 mL of 1-aminoanthraquinone, 150 mL nitrobenzene, and 0.11 mol of cyanuric chloride were mixed together and heated to 90°C with vigorous stirring. The reaction mixture was further stirred for 1 h, and then the temperature was increased to 120°C and the mixture was stirred at this temperature for another hour. The suspension



Scheme 1 Synthetic procedures of the antimicrobial cationic reactive dye.

was cooled to room temperature, and yellow crystals were obtained from the mixture, washed with methanol and dried at 60°C in a circulating air cabinet.

The second step was a nucleophilic substitution of *s*-triazine group in 1-(4,6-dichloro-2-triazinylamino)-anthraquinone with 3-dimethylamino-1-proponol. 0.03 mol of 1-(4,6-dichloro-2-triazinylamino)-anthraquinone were added with stirring to 150 mL toluene and 0.02 mol of triethylamine at 20°C. The mixture was then heated to 40°C when a solution of 3-dimethylamino-1-proponol was added drop-wise over 1 h. The mixture was then heated to 55–60°C for another hour before cooling. The precipitate was obtained and washed twice with a little toluene and then with petroleum ether. The product was dried at 60°C in a circulating air cabinet.

The tertiary amino group was reacted with alkyl halide to form a quaternary salt. 0.014 mol of the second step product was suspended in 150 mL dimethylformamide (DMF), together with 0.03 mol lauryl chloride. The mixture was heated at 110°C for 5 h. After removal of DMF under reduced pressure, the product was purified with ethyl ether. Total yield was 63% (melting point: 236.7°C). The final product was characterized by FTIR, UV, and NMR. ^{1}H-NMR spectra data (DMSO-*d*6, δ): 12.229 (singlet, 1H, —N*H*—CN—); 9.039–9.023, 8.808–8.821, 8.584–8.597, 8.389–8.403, 8.242–8.299, 8.166–8.184, 7.638–7.668 (doublet, doublet, triplet, doublet, doublet, doublet, multiplet, 7H, protons attached to C_2, C_3, C_4, C_5, C_6, C_7, C_8 in anthraquinone); 4.432 (broad peak, 2H, —O—C*H*$_2$—CH$_2$—CH$_2$—); 3.459–3.512

(triplet, 2H, —$OCH_2CH_2CH_2$—$N^+(CH_3)_2$—CH_2—); 3.072–3.100 (triplet, 2H, —$N^+(CH_3)_2CH_2$—CH_2—$C_{10}H_{21}$); 3.003 (singlet, 6H, —$N^+(CH_3)_2$); 2.216 (broad peak, 2H, —O—CH_2—CH_2—CH_2—); 1.662 (broad peak, 2H, —$N^+(CH_3)_2CH_2$—CH_2—$C_{10}H_{21}$); 1.153–1.247 (broad peak, 18H, —$N^+(CH_3)_2CH_2$—CH_2—$(CH_2)_9$—CH_3); 0.800–0.833 (triplet, 3H, —$N^+(CH_3)_2CH_2$—CH_2—$(CH_2)_9$—CH_3). ^{13}C-NMR spectra data (DMSO-*d*6, ppm): 187.049, 182.658, 171.993, 166.662, 142.136, 136.461, 135.567, 134.481, 134.264, 133.278, 132.825, 128.015, 127.801, 127.151, 126.265, 122.091, and 117.963 are 17 carbons in anthraquinone ring and *s*-triazine ring; 65.603 (—$OCH_2CH_2CH_2$—$N^+(CH_3)_2$—CH_2—); 63.744 (—$N^+(CH_3)_2CH_2$—CH_2—$C_{10}H_{21}$); 60.770 (—$N^+(CH_3)_2$); 50.913 (—O—CH_2—CH_2—CH_2—); 32.021, 31.447, 29.772, 29.731, 29.615, 29.455, 29.549, 29.310, 26.493, 26.066, 22.913, 22.799, and 14.254 are other carbons in alkyl group. FTIR: 3419, 3304, 1666, and 1520 cm^{-1}. UV λ_{max} is 435 nm.

Antimicrobial assessment of the dye

Antimicrobial properties of the reactive dye, benzalkonium chloride (benzyldimethyl-hexadecylammonium chloride), *N*-cetylpyridinium chloride (CPC), and cetyltrimethyl ammonium bromide (CTAB) in aqueous solution were evaluated using a MIC, a concentration at which no growth of bacteria was observed following such a procedure.[13] One milliliter of an aqueous suspension containing 10^6 to 10^7 colony-forming units (CFU)/mL of *Escherichia coli* (K-12 Gram-negative) and *Staphylococcus aureus* (ATCC 12600, Gram-positive) were placed into 9 mL aqueous solutions with different cationic reactive dye concentrations. After 1, 5, 30, 300, and 720 min (defined as the contact time), the resultant solution was diluted with sterilized water to 10^1, 10^2, 10^3, and 10^4 in series. One hundred microliter of the dilution was placed onto a nutrient agar plate and incubated at 37°C for 24 h. The same procedure was applied to a distilled water solution without cationic reactive dye as a control.

Dyeing of fabrics

Cotton fabrics were dyed with the reactive dye in a solution containing 1.0% (on weight of fabrics, owf) in a shaking bath. The bath liquor ratio was 50:1. The cotton fabrics were immersed into the dyeing solution under temperatures 60, 70, 80, 90°C, respectively, over 60 min. During this period the required amount of sodium sulfate (0, 15, 30, 45, 60 g/L) was added in two portions at an interval of 30 min. Dyeing was continued at these conditions for 60 min. After 60 min exhaustion dyeing, the reactive dye was then fixed (sodium carbonate 30 g/L) on fiber at 80°C for 60 min. Hitachi U-2000 UV–vis spectrophotometer (Hitachi, Japan) was used to measure the UV–vis absorbance of the dye solutions before and after exhaustion. The concentration of dyes was calculated based on a calibrated absorbance-concentration relationship at the λ_{max} 434 nm of the dyes. After dyeing, unfixed dye from the samples was extracted by boiling water and also measured by the UV–vis spectrophotometer. The exhaustion percent *E* of the dye on the fibers after 60 min neutral dyeing was calculated by eq. (1).

$$E = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\% \quad (1)$$

where A_0 is the initial the absorbance of the dye solutions before exhaustion, A_t is the absorbance of the dye solutions after exhaustion.

The fixation rate *F* on the fabric was calculated by eq. (2).

$$F = \left(\frac{A_0 - A_t - A_w}{A_0}\right) \times 100\% \quad (2)$$

where A_w is the absorbance of the dye in the extracted solution.

Antimicrobial assessment of the fabrics

Antimicrobial activities of the treated cotton fabrics were evaluated against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) according to AATCC test method 100–1999. Following this method, circular fabric swatches (about 1.0 g) was challenged with 1.0 ± 0.1 mL of bacterial inoculums. The inoculum was a nutrient broth culture containing $1.0 \times 10^6 \sim 10^7$/mL colony-forming units (CFU) of bacteria (*E. coli* or *S. aurea*). The inoculated fabric samples were then placed into a 250 mL container for a measured duration of 5 h (defined as the contact time). After the dyed and control swatches were in contact with bacteria for over 5 h, 100 mL of sterilized water were poured into the container, and the mixture was vigorously shaken, and then the supernatant was diluted to 10^1, 10^2, 10^3, and 10^4 in series. One hundred microliters of each dilution was placed onto a nutrient agar and incubated for over 24 h at 37°C. Finally, viable bacteria colonies on the agar plate were counted, and the percentage reduction in numbers of bacteria was calculated using eq. (3)

$$R = \left(\frac{A - B}{A}\right) \times 100\% \quad (3)$$

where *R* is the percentage reduction of the bacterium; *A* represents the numbers of bacterial colonies

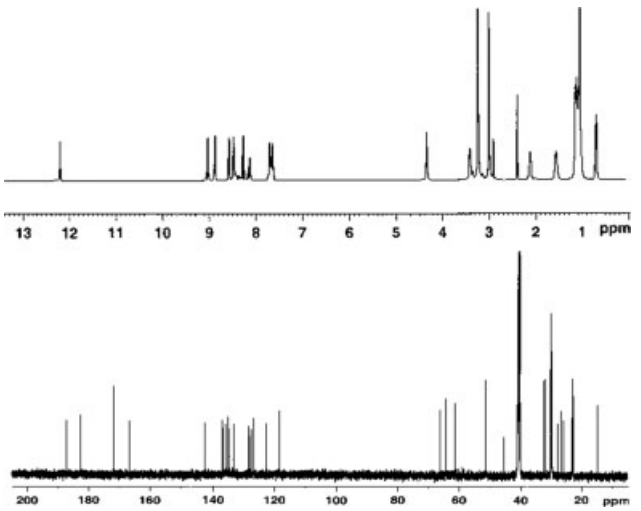


Figure 1 ^{1}H-NMR and ^{13}C-NMR spectra of the cationic reactive dye.

from control fabric (an untreated fabric), and *B* represents the number of bacterial colonies from treated fabrics.

The treated fabric was also washed in a Launder-Ometer (Atlas, USA) according to AATCC Test Method 61-2001 to evaluate the washing durability of the treated fabrics. One cycle of a Launder-Ometer washing is equivalent to five machine washes in a home laundry. The CIE L^*, a^*, b^*, c^*, and h^0 color coordinates as well as K/S values of the finished cotton fabrics after different times of machine washes were measured with ColorEye 7000A (Gretagmacbeth, USA) reflectance spectrometer under illuminant D65 and a 10° standard observer.

RESULTS AND DISCUSSION

Characterization

The final dye structure was confirmed by using FTIR, ^{1}H, ^{13}C-NMR spectroscopy. Infrared absorbance bands at 3419, 3304, and 1666 cm^{-1} can be attributed to *N*—H and C=O stretching band of 1-aminoanthraquinone, respectively. 1520 cm^{-1} is most likely caused by —C=N— ring stretching (skeletal bands).[14] Figure 1 shows both ^{1}H and ^{13}C spectra of the cationic reactive dye. The multiple peaks in the region of 7.638–9.039 ppm are aromatic protons and triazine ring.[13] The peak centered at 12.229 ppm should be the amide proton, and the signal at 3.003 can be attributed to 6H ($—N^{+}(CH_3)_2$). The ^{13}C peaks at 187.049 and 182.058 ppm are the two carbonyl carbons in the anthraquinone structure. The other fifteen peaks in the range of 117.963–171.993 ppm are the 15 carbons in the aromatic ring and triazine ring, and the sixteen peaks within 10–70 ppm are corresponding to the 17 alkyl carbons, which are in 16 different chemical environments.

Antimicrobial efficacy

The dye was challenged with both Gram-positive and Gram negative bacteria solutions containing 10^6–10^7colony forming units (CFU)/mL bacteria cells according to a MIC procedure. The MICs of the antimicrobial dye against both *S. aureus* and *E. coli* with MIC were only at 10 ppm, indicating that the dye can effectively destroy both bacteria up to 6 log reduction in a concentration of 10 ppm in solutions in a contact time of 24 h.

The antimicrobial efficacy of cationic reactive dye was further assessed by comparing the dye with three QASs biocides at the same concentration of 10 ppm, and the results are listed in Table I. This reactive dye was equal or more effective than benzalkonium chloride (benzyldimethyl-hexadecylammonium chloride), CPC (*N*-cetylpyridinium chloride), and CTAB (cetyltrimethyl ammonium bromide) in providing antimicrobial efficacy in solutions. These findings agree well with other report,[15] which demonstrated that the more hydrophobic characteristic features such as the additional anthraquinone groups also increase antimicrobial power of QASs.

Generally speaking, the lipid bilayer structures of cell membranes are the principal targets for QASs during interaction with microbial cells.[16] The hydrophobic hydrocarbon tail of the QASs and the dye can penetrate into the hydrophobic membrane core, causing cells both to lose osmoregulatory capability and to leak potassium ions and protons. The ability of a potentially active molecule of QAS to interact with the hydrophobic microbial cell membrane may be regarded as the result of its intrinsic hydrophobicity, which increases with the hydrocarbon chain length.[17] Another actual hydrophobic site of the compound, such as anthraquinone group, also could increase its affinity with the membrane phospholipidic bilayer. The anthraquinone group in the dye may further assist the interactions between the entire hydrocarbon chain lengths with the cell membrane and accelerate contact and consequently kill of microorganisms.[17] Thus, among the tested QASs and dye molecules, this cationic reactive dye was the most active molecules against the bacterial species tested.

TABLE I
Antimicrobial Efficacy of Cationic Reactive Dye and Other QASs in Aqueous Solution

Contact time (min)	Antimicrobial efficacy (Log reduction)			
	Dye	Benzalkonium chloride	CPC	CTAB
1	4	1	<1	<1
5	6	2	1	<1
60	6	–	–	–

Concentrations was 10 ppm; contact time is 24 h.

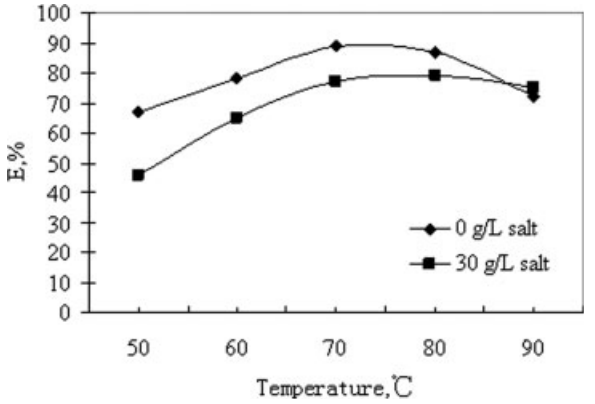


Figure 2 Effect of temperature on exhaustion of the dye (dye conc. = 1% owf; time = 60 min; liquor ratio = 50 : 1).

Effect of dyeing temperature

To investigate dyeing behavior of the dye, the effect of dyeing temperature was investigated under the same neutral dyeing conditions of 0 and 30 g/L Na_2SO_4 and the results are shown in Figure 2. It can be seen from the results that with the temperature increasing from 50 to 90°C, the dye shows an initial increase in equilibrium exhaustion, up to a temperature of maximum exhaustion, and then decreases. The maximum exhaustion temperature of the dye was between 70 and 80°C. Compared with regular anionic reactive dyes, the cationic reactive dye has lower solubility at lower temperature because of more hydrophobic structures. Increasing temperature can promote the dye de-aggregation in the dyeing solution, liberating more individual dye molecules to enter the fiber. So the exhaustion will increase under higher temperature. Besides, the dye adsorption on the fiber is exothermic,[11] which will cause reduced adsorption when the temperature is increased to a certain degree. Thus, the maximum exhaustion temperature of the dye was observed.

Effect of salt concentration

Interestingly, Figure 2 also shows that the dye exhaustion without addition of a salt (0 g/L Na_2SO_4) was higher than the dye exhaustion at 30 g/L Na_2SO_4, which is totally different from regular fiber reactive dyes in dyeing cotton fabrics. The effect of salt concentration on dyeing behavior of the cationic reactive dye at 80°C was further studied. The results (Fig. 3) indicate that the salt concentration had a very noticeable effect on the dye exhaustion and fixation on cotton fabrics. The exhaustion and fixation yield of the dye decreased considerably with the increase of salt Na_2SO_4 concentration from 0 to 60 g/L.

Electrolytes in the dyeing bath promote the exhaustion of traditional anionic reactive dyes on cotton cellulose since dissociated sodium ions (Na^+) can neutralize and shield the surface negative charges of the fiber and thus reduce static repulsion between anionic dye molecules and negatively charged cellulose. This reduction of repulsion allows the anionic dye molecules to approach the fiber and exhaustion of the dye on the fiber. While the cationic reactive dye contains a positive charge in aqueous solution, it has inherent interaction with the fiber. Addition of the electrolyte could only provide adverse effect, leading to reduced dye exhaustion and fixation. Besides, the salt in the dyebath may increase the degree of aggregation of the dye molecules and reduce its solubility in water, which also could further lower exhaustion of the dye.

Effect of dyeing time

Dyeing time will affect dye exhaustion and fixation, which was investigated with a cationic reactive dye concentration of 1% (owf) under different salt Na_2SO_4 concentration (0 and 30 g/L) at 70°C and Na_2CO_3 concentration (30 g/L) at 80°C. The results are shown in Figure 4. It can be seen that all the

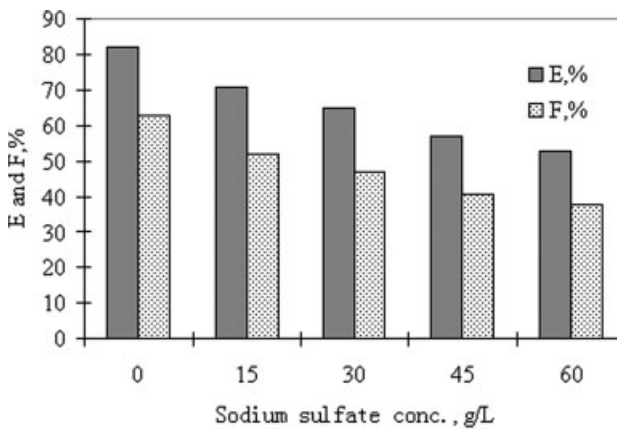


Figure 3 Salt effects on exhaustion E(%) and fixation F(%) of cationic reactive dye (dye conc. = 2.0% owf; liquor ratio = 50 : 1; Na_2CO_3 conc. = 30 g/L).

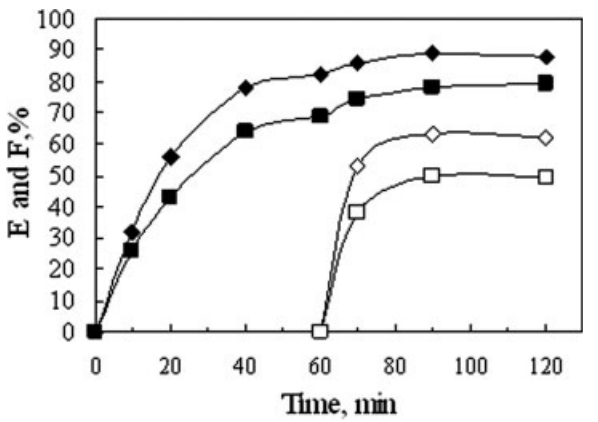


Figure 4 Effect of dyeing time on exhaustion and fixation of the dye (Symbols: ◆ E% and ◇ F% for 0 g/L Na_2SO_4; ■ E% and □ F% for 30 g/L Na_2SO_4).

TABLE II
Antimicrobial Efficacy of the Dyed Cotton Fabrics

Washing times	Bacteria	0.5%		1.0%		2.0%	
		0 g/L	30 g/L	0 g/L	30 g/L	0 g/L	30 g/L
0	*E.coli*	98.9%	97.4%	99.9%	99.6%	99.9%	99.9%
	S.aureus	97.6%	93.2%	99.9%	99.5%	99.9%	99.9%
1	*E.coli*	70.8%	64.5%	76.6%	68.3%	72.3%	70.9%
	S.aureus	72.6%	55.9%	75.1%	70.7%	77.4%	73.2%
5	*E.coli*	11.4%	7.9%	10.3%	12.1%	17.8%	14.5%
	S.aureus	12.6%	10.5%	15.6%	9.4%	14.8%	15.5%
10	*E.coli*	0%	0%	0%	0%	0%	0%
	S.aureus	0%	0%	0%	0%	0%	0%

Dye concentrations were 0.5%, 1.0%, 2.0% (owf). Exhaustion phase of dyeing: Na_2SO_4 concentrations = 0 g/L or 30 g/L; time = 60 min; liquor ratio = 50 : 1. Fixation phase of dyeing: Na_2CO_3 30 g/L; time = 60 min; liquor ratio = 50 : 1. *E. coli* and *S. aureus* concentrations: 10^5–10^7 CFU/mL. Contact time: 5 h.

exhaustion and fixation showed increased values over the exhaustion and fixation time. On the other hand, dyeing without salt always demonstrated higher exhaustion and fixation yields compared with dyeing with 30 g/L Na_2SO_4 over the range of dyeing time studied. It is believed that during the primary exhaustion process, equilibrium is established between the dye in the fiber and the dye in solution. This equilibrium is disturbed when the alkali is added since a dye molecule in the fiber reacts with cellulose; its place has to be taken by another dye molecule being transferred out of the bath and into the fiber, in an attempt to re-establish the equilibrium. Thus, increasing the dyeing time would lead to an increase of dye exhaustion and fixation values.

The cationic reactive dye has a long alkyl chain which increases the hydrophobicity, suggesting that the dyes may become less favorable to remain in the dye bath. On the other hand, the long alkyl chain will also increase Van der Waals interactions between the dye and the fiber. The large dye size and the strong interactions with cellulose may increase difficulty of the dye moving from solution to fibers and inside fibers. Thus, there is less diffusion of the dye into the fibers, i.e., low mobility of the dye within the cellulose matrix. The low diffusion rate will lower exhaustion E(%) of the dyeing. Therefore, even after the addition of alkali, the exhaustion E(%) was not enhanced very much due to the poor migration property of the cationic reactive dye. Figure 4 also shows the fixation behaviors of the reactive dyes on cotton fiber. The differences between the fixation F(%) and exhaustion behaviors were small, which implies that once the dyes are exhausted, the fixation ratios of the exhausted dyes on the cotton fibers were similar.

Antimicrobial properties of dyed fabric

Antimicrobial function of the dye treated cotton fabrics was evaluated against *E. coli* and *S. aureus* following AATCC Test Method 100. The results are shown in Table II. It can be seen that with the increase of dyeing concentrations, the antimicrobial activities of fabrics increase before Launder-Ometer washing. When dye concentration is higher than 1.0%, the treated fabrics show the highest antimicrobial efficacy after 5 h of contact. However, Table II also shows that the washing durability of the treated fabrics was low. For example, after the first washing, the fabric dyed in 2.0% (owf) dyeing bath could only kill 72.3% of *E. coli*. But after five times washing, its antimicrobial activities almost disappeared. It is believed that the low washing durability of the dyed cotton fabric may be caused by the loss of dyes on the fiber surface during washing. The loss of dyes on surfaces of fibers may not have significant impact on color of the product. The washed fabrics did not show significant color changes (Table III). To confirm this assumption, Ma and Sun measured the surface resistivity of Orlon fabrics treated with antimicrobial cationic dyes before and after washing.[9] The results indicated that the decrease of antimicrobial activities of Orlon fabrics possibly caused by the loss of dyes on fiber surfaces during washing. In the antimicrobial testing, only the bacterial accessible dyes can come into with the bacteria and thus kill them. The bacteria accessible dyes mainly locate on the surface

TABLE III
CIELAB Color Difference of Dyed Cotton Fabrics After Repeated Washing

Times	L	a^*	b^*	c^*	h^0	K/S
0	85.74	3.81	52.97	53.11	85.89	1.662
1	86.43	3.45	52.28	51.22	85.96	1.604
5	86.65	3.27	52.16	50.87	86.02	1.583
10	87.12	3.09	51.03	49.51	86.23	1.521

Dye concentrations was 1.0% (owf); Na_2SO_4 concentrations = 0 g/L; time = 60 min; liquor ratio = 50 : 1. Fixation phase of dyeing: Na_2CO_3 30 g/L; time = 60 min; liquor ratio = 50 : 1.

of the fabrics. During washing, these bacteria accessible dyes may be washed away and dissolved in the water. After washing, the fixed dyes inside the fibers and fabrics may not be in sufficient contact with bacteria and consequently kill them, leading to the antimicrobial activities of the treated fabrics dropping significantly.

CONCLUSIONS

Antimicrobial cationic reactive dye was synthesized successfully by reacting alkyl halide with 1-aminoanthraquinoe derivatives, and characterized by using FTIR and NMR analyses. It was found that the dye exhibited adequate antimicrobial activities against both Gram positive and Gram-negative bacteria at a concentration of 10 ppm. The hydrophobic characteristics may increase the antimicrobial function of the cationic reactive dye. This cationic dye also can react with cellulose to dye cotton without using any electrolyte as dyeing assistant. The dye exhaustion and fixation rates on cotton were reasonably high without significant hydrolysis, and the dyed cotton exhibited good color washfastness. However, the washfastness of the antimicrobial functions of dyed fabrics was unreasonably low.

References

1. Liu, S.; Sun, G. Durable and regenerable biocidal polymers: Acyclic *N*-halamine cotton cellulose. Ind Eng Chem Res 2006, 45, 6477.
2. Sun, G.; Worley, S. D. Chemistry of durable and regenerable biocidal textiles. J Chem Educ 2005, 82, 60.
3. Sun, G.; Xu, X. Durable and regenerable antibacterial finishing of fabrics: Chemical structures. Text Chem Color 1999, 31, 31.
4. Sun, G.; Xu, X. Durable and regenerable antibacterial finishing of fabrics: Fabric properties. Text Chem Color 1999, 31, 21.
5. Vigo, T. L.; Danna, G. F.; Goynes, W. R. Affinity and durability of magnesium peroxide-based antibacterial agents to cellulose substrates. Text Chem Color 1999, 31, 29.
6. Zhao, T.; Sun, G. Antimicrobial finishing of wool fabrics with quaternary aminopyridinium salts. J Appl Polym Sci 2007, 103, 482.
7. Zhao, T.; Sun, G. Antimicrobial finishing of cellulose with incorporation of aminopyridinium salts to reactive and direct dyed fabrics, J Appl Polym Sci 2007, 106, 2634.
8. Ma, M.; Sun, Y.; Sun, G. Antimicrobial cationic dyes, Part 1: Synthesis and characterization. Dyes Pigments 2003, 58, 27.
9. Ma, M.; Sun, G. Antimicrobial cationic dyes, Part 3: Simultaneous dyeing and antimicrobial finishing of acrylic fabrics. Dyes Pigments 2005, 66, 33.
10. Ma, M.; Sun, G. Antimicrobial cationic dyes, Part 2: Thermal and hydrolytic stability. Dyes Pigments 2004, 63, 39.
11. Johnson, A. The Theory of Coloration of Textiles, 2nd ed.; Society of Dyers and Colorists, Bradford, UK, 1989.
12. Zhao, T.; Sun, G. Synthesis and characterization of antimicrobial cationic surfactants: Aminopyridinium salts. J Surfactants Detergents 2006, 9, 325.
13. Kaminski, J. J.; Huycke, M. M.; Selk, S. H.; Bordor, N.; Higuchi, T. N. Halo Derivatives. V. Comparative antimicrobial activity of soft *N*-chloramine systems. J Pharm Sci 1976, 65, 1737.
14. Silverstein, R. M.; Webster, F. X.; Kienle, D. J. Spectrometric Identification of Organic Compounds; Wiley: New York, 2005.
15. Zhao, T.; Sun, G. Comparison of the antimicrobial activities of four quaternary pyridinium salts. J Appl Microbiol, available online at: http://www.blackwell-synergy.com/doi/full/10.1111/j.1365-2672.2007.03616.x and should be published in hard copy soon.
16. Jawetz, E.; Melnick, J. L.; Adelberg, E. A.; Brooks, G. F.; Butel, J. S.; Ornston, L. N. Medical Microbiology; Prentice-Hall: London, 1989, p 46.
17. Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2nd ed.; Wiley: New York, 1980, p 14–17.