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Antimicrobial Modification of Cotton by Reactive Triclosan Derivative

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Abstract: 4-(4-chloro-6-(5-chloro-2-(2,4-dichloro-phenoxy)phenoxy)-1,3,5-triazin-2-ylamino)-benzenesulfonic acid sodium (CPTB), an antimicrobial agent, was synthesized from cyanuric chloride, sulfanilic acid and triclosan. The synthesized compound was coated on cotton fabrics by covalent bonds through a reactive dyeing process. The cotton fabrics coated with CPTB were characterized by FTIR and SEM. The antimicrobial properties against *S. aureus* and *E. coli* O157:H7 and the breaking strength of the treated cotton fabrics were examined before and after chlorination. The unchlorinated coated fabrics containing triclosan inactivated 95.88 % of *S. aureus* and 79.65 % of *E. coli* O157:H7 within 30 min, while the chlorinated coated samples enhanced the efficacy significantly and inactivated all *S. aureus* and *E. coli* O157:H7 within 10 min. The novel coating process in this study only caused a small degree of breaking strength loss compared with traditional pad-dry-cure coating. Washing tests and UV light tests showed that CPTB attached to cotton fabrics was very stable toward repeated washing and UVA irradiation.

Keywords: Antimicrobial, N-halamine, Triclosan, Cotton fabric, Bacteria

Introduction

Natural textile materials provide a suitable circumstance for the growth of microorganisms and are more susceptible to microorganisms than synthetic textiles, especially to the drug-resistant bacteria [1-4]. In order to prevent the cross-infection of disease in the public arena, antimicrobial textiles have attracted great attention in recent years [5-11]. Chemical finishing of fabrics with quaternary ammonium salts [12-14], triclosan [15-17], chitosan [18,19], and N-halamine [11,20-25] have been widely used to produce antimicrobial textiles.

Triclosan (2,4,4'-Trichloro-2'-hydroxydiphenyl ether) is a broad spectrum antimicrobial agent with notably high chemical stability and persistent activity, and is commonly used in household and industrial products, such as hand soaps, surgical scrubs, shower gels, toothpastes, mouthwashes, surgical drapes and children's toys [15-17]. The studies on the toxicity of triclosan have shown that triclosan has acute and chronic toxicity to aquatic organisms such as algae, daphnids, and fish [16,26,27]. However, investigators have found that triclosan is nontoxic orally and shows no mutagenic, carcinogenic, or teratogenic properties [17,28]. The pad-dry-cure process was one of the common methods used to incorporate triclosan onto fabrics with 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA) as crosslinking agent [1]. Acidic solution and high curing temperature in the process would have a significant negative effect on the physical properties of cotton fabrics. Synthesizing polymers and/or making nanoparticles with triclosan are other ways to produce antimicrobial materials [17,29]. However, the experimental processes of these methods might be complicated and inconvenient in practical applications.

To make the coating process simple to operate, chemicals with reactivity such as cyanuric chloride could be introduced to react with hydroxyl groups of triclosan and cellulose. In addition, because of poor water solubility and mild antimicrobial efficacy of triclosan, substances with good water solubility and powerful antimicrobial efficacy could also be attached into the desired compound to improve these properties of triclosan. In this study, cyanuric chloride was chosen as the linking agent. Its three chlorines could be substituted at different temperatures. The first and second chlorines of cyanuric chloride were substituted by triclosan

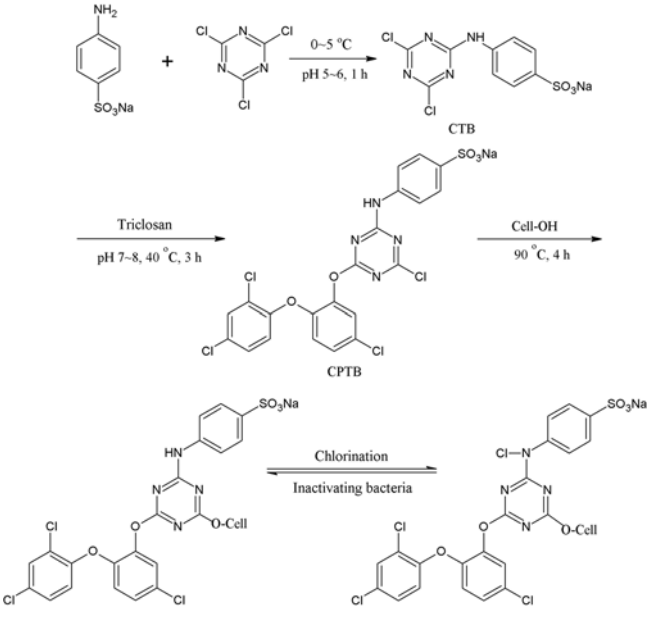

Figure 1. Preparation of antimicrobial cotton fabrics.

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and 4-amino-sulfanilic acid, which can be converted to an N-halamine structure with good antimicrobial properties, through a nucleophilic substitution reaction to synthesize the novel antimicrobial agent (CPTB). The third chlorine on the synthesized CPTB could react with cellulose to produce antimicrobial cotton fabrics (Figure 1).

N-halamines are organic and inorganic compounds containing nitrogen-halogen covalent bonds (N-X). These bonds include amine, amide and imide [30-40]. Previous research shows that amine is more stable than amide and imide [24,41]. CPTB contains one amine group (N-H) and should be stable when N-H is converted to N-X. Much attention has been paid to N-halamines owing to their stabilities, regenerabilities, and efficacies for inactivating bacteria [20,42-50]. Our previous study synthesized two kinds of N-halamine antimicrobial precursors using cyanuric chloride as the reactive agent, and the coated cotton after chlorination showed good antimicrobial properties against *Staphylococcus aureus* and *E. coli* O157:H7 [51]. The biocidal efficacy of the antimicrobial cotton coated with CPTB could be further improved upon exposure to diluted household bleach providing additional N-halamine structures (Figure 1). The coated cotton samples were characterized by FTIR and SEM. The antimicrobial activity of the coated cotton fabrics before and after chlorination against *Staphylococcus aureus* and *E. coli* O157:H7 were evaluated. In addition, other properties including breaking strength, stability, and regenerability were investigated.

Experimental

Materials

Bleached cotton fabric (Zhejiang Guandong Textile Dyeing Garment Co., Ltd. China), Triclosan (97 %, J&K Chemical Co., Ltd., China) and cyanuric chloride (99 %, J&K Chemical Co., Ltd., China) were purchased and used as received. Other chemicals were bought from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

Instruments

An AVANCE III 400 MHz digital NMR spectrometer was used to characterize the synthesized product (CPTB). Fourier transform infrared spectra of cotton and treated cotton fabrics were recorded on a Nicolet Nexus spectrometer using the attenuated total reflectance (ATR) method. Surface morphologies (SEM) of uncoated and coated cotton fabrics were investigated by a SU1510 spectrometer.

Synthesis of CPTB

4-amino-benzenesulfonic acid (0.02 mol, 3.47 g) and sodium carbonate (0.01 mol, 1.06 g) were dissolved in distilled water (20 m*l*), and then added into a solution of cyanuric chloride (0.02 mol, 3.69 g) in acetone (30 m*l*). The reaction was carried out at 0-5 ^{o}C for 1 h, and pH was maintained at 5-6 by the addition of 20 % (w/w) aqueous sodium carbonate. Then, triclosan (0.02 mol, 5.79 g) dissolved in acetone (10 m*l*) was added to the mixture, and the temperature was increased to 40 ^{o}C. The reaction was carried out at 40 ^{o}C and pH 7-8 (adding 20 %wt aqueous sodium carbonate) for 3 h. The desired product was isolated via filtration and washed with water and acetone (Yield: 85.3 %). The product exhibited the following spectral data: ^{1}H-NMR (DMSO) δ6.95 (d, 2H), δ7.08 (d, 1H), δ7.17 (d, 2H), δ7.27 (s, 1H), δ7.36 (d, 1H), δ7.51 (s, 1H), δ7.72 (d, 2H).

Application of CPTB onto Cotton Fabrics

An aqueous solution containing CPTB (15 g/*l*) and Na_2SO_4 (100 g/*l*) was prepared, and cotton swatches were soaked in the solution for 30 min at room temperature. The temperature of the mixture slowly increased to 90 ^{o}C, and then NaOH (0.3 g/*l*) was added to the solution. After 4 h of treatment, the sample was isolated and washed with water to remove unfixed CPTBs and dried at room temperature.

Chlorination and Analytical Titration

Diluted commercial aqueous sodium hypochlorite solution (10 %) was adjusted to pH 7 by the addition of 10 % sulfuric acid, and the CPTB coated cotton fabric was immersed in the solution for 1 h at room temperature. Then the chlorinated cotton samples were washed thoroughly with distilled water and dried at 45 ^{o}C for 1 h to remove free chlorine from the surface of the cotton fabrics.

The chlorine contents of the fabric samples were analyzed by using an iodometric titration method. Each fabric sample of 0.2 g was immersed in water for a few minutes, and then KI and a few drops of starch solution were added as indictors. The mixture was titrated with 0.001 N sodium thiosulfate solution immediately. The amount of active chlorine on the cotton swatches was calculated according to the following equation:

$$[Cl^{+}]\,\% = (35.45NV) / (2W) \times 100\,\%$$

where $[Cl^{+}]$ % is the wt% of oxidative chlorine on the samples, N and V are the normality (equiv/*l*) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight of the cotton samples (g).

Antimicrobial Test

According to AATCC Test Method 100-1999, control fabric swatches and unchlorinated and chlorinated treated fabric swatches were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC 43895) using a sandwich test [2-11,20-25]. Bacteria were suspended in pH 7, 100 mM phosphate buffer, and 25 μl of the bacterial suspensions were added to the middle of two pieces of one inch square cotton swatches. The contact times were 1, 5, 10, and 30 min.

Then the samples were quenched with 5.0 m*l* of sterile 0.02 N sodium thiosulfate solutions to remove all oxidative chlorine. The bacteria were rinsed off the swatches, and serial dilutions of the bacteria suspensions were made using pH 7, 100 mM phosphate buffer. The bacteria were then plated on trypticase soy agar plates. The plates were incubated at 37 °C for 24 h, and bacterial colonies were recorded for antimicrobial efficacy analysis. Data were analyzed by using analysis of variance (ANOVA) of the Statistical Analysis System (Version 9.3 for Windows) with significance level of P=0.05.

Breaking Strength Test

An electronic fabric strength tester was used to evaluate the breaking strength of untreated cotton fabrics and unchlorinated and chlorinated treated cotton fabrics according to the GB/T3923-1997 method. The measurement was carried out at ambient temperature. Five replicates (5 cm × 20 cm) were prepared for each sample, and the average value was recorded for analysis.

Washing Test

Durability and stability of chlorine on the cotton swatches against repeated standard washing were evaluated according to American Association of Textile Chemists and Colorists (AATCC) test method 61-1996. Stainless steel canisters, containing 0.15 % AATCC detergent water solution (150 m*l*) and 50 stainless steel balls, were fixed in a Launder-Ometer and rotated at 42 rpm and 49 °C. The cotton swatches were subjected to the equivalent of 5, 10, 25, and 50 washing cycles in the test. Each washing cycle was rotated for 45 min, which was equivalent to five machine washings. Each test sample was washed with distilled water and then dried in air at ambient temperature. The remaining chorine on the samples was determined by the titration method discussed previously.

UV Light Stability Test

An Accelerated Weathering Tester (The Q-panel Company, USA) was used to measure the UVA light stability of cotton fabrics coated with CPTB. The chlorinated cotton fabrics coated with CPTB were placed in the UV light chamber for exposure times ranging from 1 to 24 h. After a specific time of UV irradiation, the cotton swatches were removed from the UV chamber and titrated, or rechlorinated and titrated, to measure the chlorine concentrations for analyzing the stability of CPTB.

Results and Discussion

Preparation of Antimicrobial Cotton Fabrics

As a broad-spectrum bactericide and fungicide, triclosan has high chemical stability, persistent activity and extensive use in consumer goods and textile products. The main limitation of its application is the low solubility in aqueous solution [15,16]. The hydroxyl group in the ring gives triclosan relatively high reactivity with other active substances. In this study, cyanuric chloride reacts with 4-amino-sulfanilic acid to produce 4-(4,6-dichloro-1,3,5-triazin-2-ylamino)-benzenesulfonic acid sodium (CTB) at 0-5 °C. Then, the synthesized intermediate CTB reacts with triclosan to produce the desired product CPTB at 40 °C. The introduction of 4-amino-sulfanilic acid into CPTB improves the water solubility of triclosan significantly. The synthesized CPTB was bound to cotton fabrics by nucleophilic substitution at 80-90 °C similar to the dyeing process of a reactive dye. The antimicrobial efficiency of cotton fabrics achieved could be further enhanced upon chlorination in dilute sodium hypochlorite solution.

Table 1. Chlorine contents of fabrics under various finishing conditions

CPTB (g/*l*)	Na_2SO_4 (g/*l*)	NaOH (g/*l*)	Reaction temp. (°C)	Cl^+%
15	100	0	80	0.05
15	100	0.3	80	0.12
15	100	0.5	80	0.11
15	100	1	80	0.05
15	200	0.3	40	0.02
15	200	0.3	60	0.05
15	200	0.3	80	0.10
15	200	0.3	90	0.14

The structure of CPTB is similar to a high-temperature reactive dye, and the dying process of a reactive dye could be used in the antimicrobial finishing of cotton fabrics. The reaction between CPTB and cellulose is mainly decided by alkalinity and temperature. Table 1 shows active chlorine contents on cotton fabrics under different concentrations of NaOH and various temperatures. The addition of NaOH in the finishing is to dissolve CPTB and favor the chemical reaction between CPTB and cellulose by increasing more cellulose anions. However, excessive alkali may cause the hydrolysis of the triazine ring which leads to the decrease of chlorine loadings [41,52]. The third chlorine of triazine ring could be substituted at high temperature, and the higher temperature favors the substitution reaction resulting in the increase of active chlorine content. Besides alkalinity and temperature, neutral salt also acts an important role in the finishing process. Neutral salt in the finishing process reduces the static repulsion between CPTB molecules and negatively charged cellulose and promotes the exhaustion of CPTB on cotton fabrics since the dissociated sodium ions (Na^+) can neutralize and shield the surface negative charges of the fibers [11,41].

Characterization of Treated Cotton Fabrics

FTIR spectra of cyanuric chloride, CPTB, cotton and

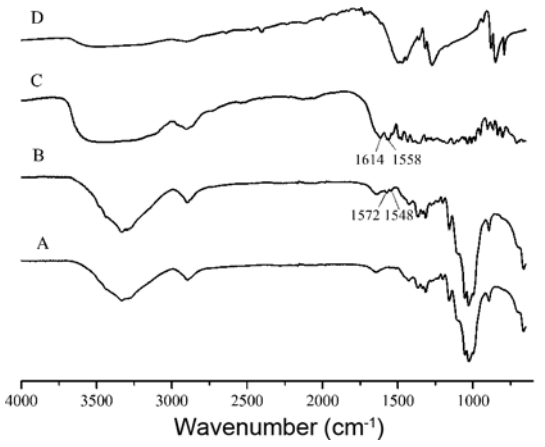

Figure 2. FTIR spectra of (A) cotton fabric, (B) cotton coated with CPTB, (C) CPTB, and (D) cyanuric chloride.

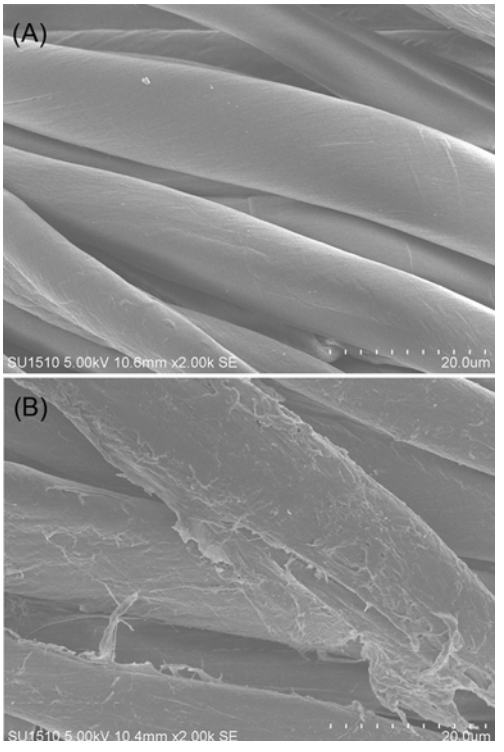

Figure 3. SEM micrographs of (A) untreated cotton and (B) cotton coated with CPTB.

cotton coated with CPTB are shown in Figure 2. Compared to cyanuric chloride (Figure 2(D)), CPTB has more than two distinctive characteristic vibrational bands at 1614 cm^{-1} and 1558 cm^{-1} (Figure 2(C)), which should be attributed to the benzene rings [53]. Accordingly, these characteristic peaks in the CPTB coated cotton fabrics appeared at 1572 cm^{-1} and 1548 cm^{-1} (Figure 2(B)). These bands were not seen in the FTIR spectra of the untreated cotton fabrics (Figure 2(A)).

The SEM micrographs of the surfaces of the uncoated and CPTB coated cotton fabrics are shown in Figure 3. The surfaces of the untreated cotton fibers are smooth, but the surfaces of the cotton fabrics coated with CPTB become rough and have uneven coverage which indicates that CPTB was bounded to the cotton fibers.

Antimicrobial Properties

The antimicrobial testing results of the treated cotton fabrics challenged with *S. aureus* and *E. coli* O157:H7 at concentrations of about 10^7 CFU (colony-forming units/ sample) are shown in Table 2 and 3, respectively. It is evident that the control cotton fabrics caused some degree of bacterial reduction due to the adhesion of bacteria to the cotton fabrics. The reduction for *S. aureus* is more significant than for *E. coli* O157:H7 due to the shapes of the bacteria. The unchlorinated CPTB-coated cotton fabrics can inactivate 95.88 % of *S. aureus* and 79.65 % of *E. coli* O157:H7 within 30 min, and provide much more degree of bacterial reduction than the control samples owing to the existence of triclosan. The chlorination process converts N-H to N-Cl and enhances the antimicrobial efficacy significantly. The chlironated

Table 2. Antimicrobial properties against *S. aureus*[a]

Sample	Contact time (min)	Bacterial reduction	
		Average (%)	Average (log)
Cotton	30	81.58d	0.739d
Cotton-CPTB	1	90.62c	1.058d
	5	95.48b	1.345d
	10	95.61b	1.359d
	30	95.88b	1.385d
Cotton-CPTB-Cl	1	99.80a	3.193c
	5	100a	5.766b
	10	100a	7.301a
	30	100a	7.301a

[a]Inoculum was 2.0×10^7 CFU/sample.

Table 3. Antimicrobial properties against *E. coli* O157:H7[a]

Sample	Contact time (min)	Bacterial reduction	
		Average (%)	Average (log)
Cotton	30	38.00d	0.212e
Cotton-CPTB	1	66.76c	0.466d
	5	80.15b	0.705c
	10	79.40b	0.686c
	30	79.65b	0.691c
Cotton-CPTB-Cl	1	84.62b	0.814c
	5	100.00a	5.028b
	10	100.00a	7.431a
	30	100.00a	7.431a

[a]Inoculum was 2.7×10^7 CFU/sample.

samples inactivated almost all of *S. aureus* and *E. coli* O157:H7 within 1 min and 5 min, respectively. Obviously, the chlorinated fabrics can inactivate all the bacteria in shorter time than triclosan. However, triclosans are moderate biocides which can extend the shelf-life of the coated cotton when the oxidative chlorine is consumed during inactivating bacteria. The coated samples still have a certain antibacterial ability due to triclosan even if all the chlorines are lost.

Breaking Strength

The results of the breaking strength testing of the unchlorinated/chlorinated cotton fabrics coated with CPTB are shown in Figure 4. The antimicrobial coating leads to a small degree of breaking strength reduction. There are only 9 % of breaking strength loss in the warp (from 890 N to 807 N) and 2 % of breaking strength loss in the weft (from 380 N to 374 N), which might be due to the substitution of the hydroxyl group by CPTB and the breaking of intermolecular and intramolecular hydrogen bonds in cellulose. The chlorination treatment has little effect on the breaking strength of the CPTB-coated cotton fabrics, and the breaking strength loss after chlorination is 15 % in the warp and 13 % in the weft compared to the control cotton fabrics.

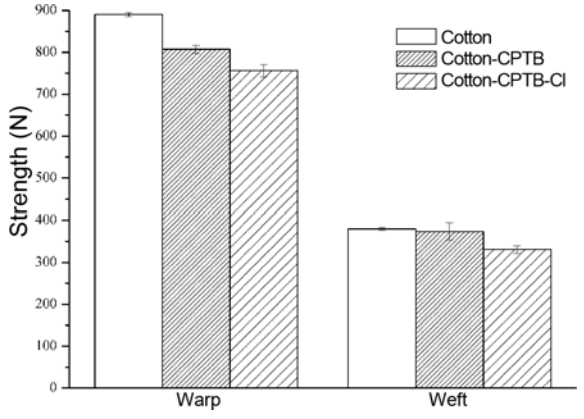

Figure 4. Breaking strength of cotton fabrics coated with CPTB.

Table 4. Washing tests of cotton coated with CPTB

Washing cycles[a]	A	B	C
0	0.12	0.12	
5	0.01	0.10	0.10
10	-	0.10	0.10
25	-	0.09	0.09
50	-	0.09	0.08

[a]Each washing cycle in this method is equivalent to five machine washings. A: chlorination before washing test, B: chlorination before and after washing test, C: chlorination after washing test, and the error in the Cl^+% was ±0.01.

Stabilities and Regeneration

One of the most significant advantages of N-halamine moieties over other antibacterial agents is that the antimicrobial activity of those with the structural feature such as CPTB can be regenerated by exposing to dilute sodium hypochlorite solution. Table 4 illustrates the chlorine stability and regeneration of the CPTB-coated cotton fabrics toward the repeated standard washing. Each washing cycle in the test is equivalent to five machine washings. Three types of samples are displayed: pre-chlorinated at the beginning of washing test (A), pre-chlorinated and rechlorinated after a given number of washing cycles (B), and unchlorinated until after a given number of washing cycles (C). For the pre-chlorinated samples, all of the chlorine was lost after 5 cycles due to the hydrolysis of the N-Cl bond, and 83 % of the chlorine could be recharged upon rechlorination. Although most of the oxidative chlorine was lost after 50 machine washes, the coated fabrics would still have the antimicrobial functionality due to the attached tricolsan on the cotton. The unchlorinated and chlorinated samples are very resistant against washing cycles which indicates that the CPTB bonded onto cotton fabrics was very stable toward hydrolysis during repeat washings.

Figure 5 exhibits the UVA light stability of the chlorinated CPTB-coated cotton fabrics. The active chlorine on the CPTB-coated cotton fabrics reduces quickly, and all of the chlorine was lost during the first hour of irradiation. The results indicate that the N-Cl bond is not very stable under UV light. However, 83 % of the lost chlorine can be recharged after chlorination within the first hour exposure. About 67 % of the chlorine on cotton fabrics could be recovered after 24 h irradiation and rechlorination, which indicates that the chemical bonds between CPTB and cellulose are relatively stable, and the UV stability of the cotton coated with CPTB increased significantly compared with the cotton fabrics coated with the N-halamine siloxanes [36]. The aromatic structure introduced into CPTB can absorb ultraviolet light and prevent the breaking of chemical bonds [54,55].

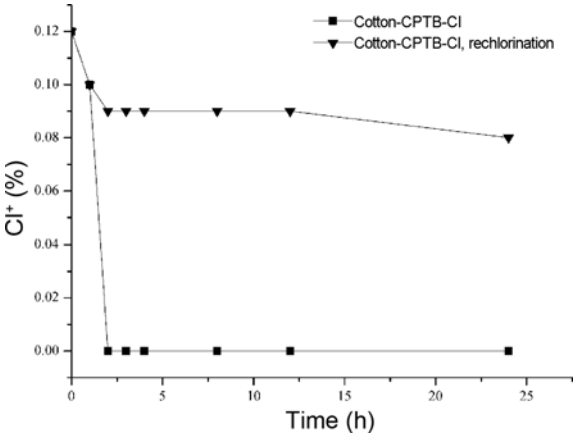

Figure 5. UV light stability of cotton fabrics coated with CPTB.

Conclusion

The antimicrobial agent containing N-halamine precursor and triclosan, 4-(4-chloro-6-(5-chloro-2-(2,4-dichloro-phenoxy) phenoxy)-1,3,5-triazin-2-ylamino)-benzenesulfonic acid sodium (CPTB), was synthesized and successfully coated onto cotton fibers via a dying process which is used to dye cotton with the reactive dyes. The application occurs in mild processing condition due to the low coating temperature. The finishing process only caused a small degree of breaking strength loss, which is one of the major advantages over the traditional pad-dry-cure technique. The unchlorinated CPTB-coated cotton fabrics demonstrated certain antimicrobial activities against *S. aureus* and *E. coli* O157:H7 within short contact time which is attributed to the efficacy from triclosan. The chlorination of CPTB-coated cotton fabrics could improve the antimicrobial efficacy significantly, and all of *S. aureus* and *E. coli* O157:H7 could be inactivated within 5 min. About 75 % of active chlorine could be recharged after 50 washing cycles, and 67 % for those after 24 h exposure to UVA light. The durability of the coated cotton fabrics is sufficient for practical application

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