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Cytocompatible and Regenerable Antimicrobial Cellulose Modified by N-Halamine Triazine Ring

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ABSTRACT: This study reports the formation of cyanuric chloride hydrolysate and its attachment onto cellulose fibers though covalent bonding. The hydrolysis product, 2,4-dichloro-6-hydroxy-1,3,5-triazine, is prepared in water solution at ambient temperature, and directly used as a treatment solution for the treatment of cotton fabrics without any prior work-up. The triazine treated fabrics are rendered antimicrobial through exposure to chlorine bleach. The oxidative chlorine bonded to the triazine-treated cotton is very stable and regenerable to standard washing tests and UVA irradiation test. The N-halamine modified cotton fabrics demonstrate excellent antimicrobial efficacy against *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 with 7-logs reductions within the contact time of 10 and 5 min, respectively. In addition, the results of *in vitro* cell viability test suggested that the N-halamine modified fabrics have excellent cytocompatibility to mammalian cells. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40627.

KEYWORDS: biocompatibility; coatings; fibers

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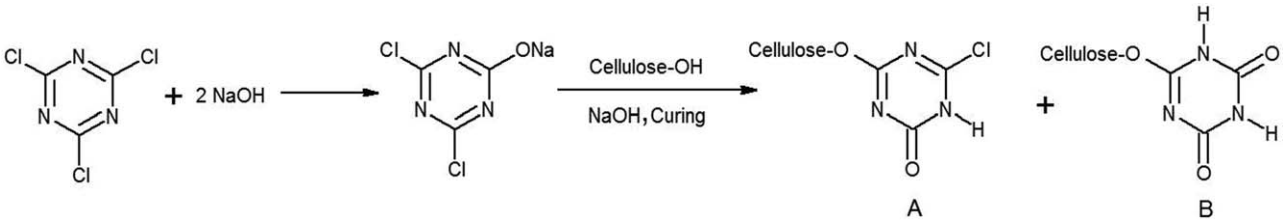
INTRODUCTION

Antimicrobial treatment of medical textiles has been extensively studied for applications in prevent of healthcare-associated infections. Quaternary ammonium salts,[1–3] metal ions,[4] light-activated coatings,[5] phosphonium salts,[6] and N-halamines[7–16] have been immobilized onto fabric surfaces to reduce the risk of cross-infections. Among these antimicrobial agents, N-halamines are the most promising candidates for preparing antimicrobial textiles due to their long-term stability, broad-spectrum antibacterial activity and being nontoxic and environmental friendly. In addition, their antibacterial properties are regenerable, and the lost active halogen on the surface of fabrics, which may be lost during wash and wear, can be recharged by simple exposure to household bleach during the washing process.

Various N-halamine compounds with heterocyclic structures such as hydantoins, oxazolidinones, and imidazolidinones have been employed to produce antimicrobial textiles. N-halamine precursors containing two hydroxyl groups were synthesized and coated onto cotton fabrics with the assistance of cross-linking agent 1,2,3,4-butanetetracarboxylic acid (BTCA).[13,14] Antimicrobial fabrics were developed by covalently bonding hydantoin or oxazolidinone rings to cotton fabrics with dimethylol-5, 5-dimethylhydantoin (DMDMH) and 3-Methylol-2,2,5, 5-tetramethyl-imidazolidin-4-one (MTMIO).[7–10] The treated fabrics rendered antibacterial properties after chlorination with household bleach. Series of hydantoin derivatives were coated on the surfaces of cotton and polyester swatches via siloxanes[11,16] and epoxides[12,17,18] as tethering groups. Admicellar polymerization technique was used to coat 3-(4′-vinylbenzyl)-5,5-dimethylhydatoin onto the surface of the cotton, and the chlorinated cotton showed excellent washing stability against repeat laundering.[15] Among these N-halamine precursors mentioned above, an imide or amide of the heterocycle is substituted by reactive groups with the ability to attach precursors to cellulosic fibers by grafting, cross-linking, tethering, or copolymerization methods. However, there are inherent disadvantages in coating these compounds onto fabrics. Because of their poor solubility in water, organic solvents are needed during the preparation of coating solutions used for coating the siloxane N-halamine precursors.



Scheme 1. Alkali hydrolysis of cyanuric chloride and the attachment of triazine rings to cellulose.

In addition, the siloxane N-halamines coated onto fabrics decompose when exposed to UV light. Though fabrics modified with N-halamine diols can improve UV light stability to a certain extent; however, fabric strength decreases dramatically due to intramolecular crosslinking in the fibers and depolymerization of the cellulose macromolecules caused by BTCA acidity.

In this study, a novel method was used to form N-halamine precursors through controlled hydrolysis of cyanuric chloride, and attach them onto cellulose by covalent bonds. When compared to ordinary alkyl halides, the C-Cl groups in cyanuric chloride are quite active because of triazine ring's strong electron withdrawing effect.[19–21] The first chlorine atom of cyanuric chloride can be replaced by a hydroxyl group in an alkali aqueous solution forming water soluble compounds in the form of sodium salts (Scheme 1).[21] The second C-Cl bond can react with cellulose through nucleophilic substitution and the triazine ring is attached to cellulose via an ether bond by using a regular pad-dry-cure finishing process. The third C-Cl bond may partially hydrolyze under curing and basic conditions, and enol structures in triazine ring transforms to amide and imide structures by tautomerism (Scheme 1).[22,23] The two forms of the N-halamine precursor are demonstrated by XPS analysis in this article.

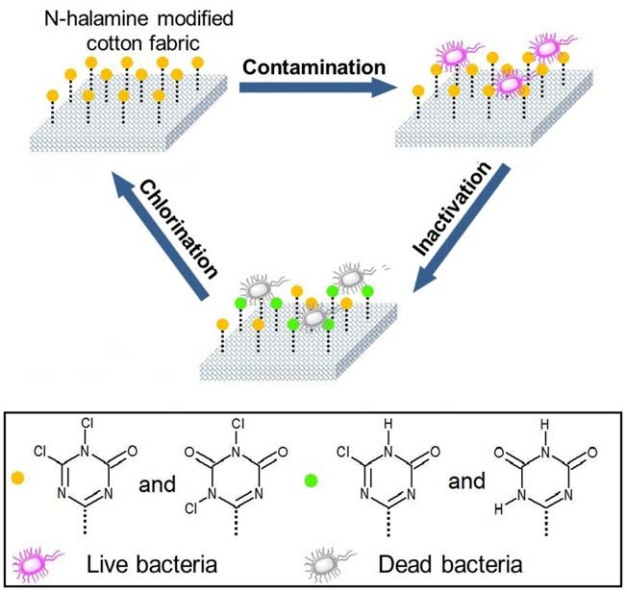


Figure 1. Schematic illustration of the biocidal function and regeneration process of N-halamine–modified cotton fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The hydrolysate of cyanuric chloride was prepared under ambient temperature, and the water solution from the final reaction could be directly used as a treatment solution for the treatment of cotton fabrics without any prior work-up. Lower curing conditions were employed in the treatment of fabrics, which could avoid dramatic strength damage to the fabrics, which occurs in the traditional high temperature curing. The amide and imide of triazine rings immobilized on cotton fibers were transformed to amide and imide N-halamines after bleach treatment, which have efficient and renewable antibacterial property as shown in Figure 1. The chemical structures of the treated cotton were characterized by FTIR and XPS. Breaking strength, washing stability, and UV stability of the chlorinated cotton fabrics modified by triazine rings were investigated. The biocidal efficacies of chlorinated modified cotton fabrics against *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 were evaluated according to a modified AATCC 100 method. The biocompatibility of the N-halamines modified cotton swatches was assessed by a cell viability test.

MATERIALS AND METHODS

Materials

Hundred percent bleached cotton fabrics was provided by Zhejiang Guandong Printing and Dyeing Company, China. Cyanuric chloride was purchased from JandK Chemicals, Shanghai. Other chemicals used in the research were purchased from Sinopharm Chemical Reagent, Ltd., Shanghai. The bacteria employed in the tests were *S. aureus* ATCC 6538 and *E. coli* O157:H7 ATCC 43895 (American Type Culture Collection, Rockville, MD). NIH mouse 3T3 fibroblasts were purchased from ATCC (Manassas, VA). Dulbeco's modified eagle media (DMEM), fetal bovine serum (FBS), and Penstrip (Penicillin and streptomycin) were obtained from Sigma-Aldrich (St. Louis, MO).

Instruments

FTIR spectra of cotton and modified cotton were performed with a NICOLET NEXUS 470 spectrometer. X-ray photoelectron spectroscopy (XPS) of the samples was obtained using an ESCALAB 250Xi (Thermo Scientific, USA). Breaking strength of the cotton fabrics was measured with an electronic fabrics strength tester (YG(B)026D, China). UV light stabilities of chlorinated cotton fabrics were measured using an Accelerated Weathering Tester (The Q-panel Company, USA).

Preparation of Cotton Fabrics Modified with N-Halamine Precursors

A predetermined amount of cyanuric chloride and sodium hydroxide with a mole ratio of 1 : 2 were added to distilled water and stirred for 10 min to obtain a clear solution. Two

percentage sodium hydroxide (based on the predetermined weight of above solution) was added into the above solution. Then, cotton swatches were soaked in baths of 2–4% triazine aqueous solutions for 15 min and padded with a wet pick-up of 100%. The fabrics were dipped and padded twice, then dried at 80°C for 5 min, followed by curing at 120°C for 10 min. The treated cotton swatches were soaked in 0.5% detergent solution for 15 min, washed with distilled water, and dried in air.

Chlorination and Titration

The treated cotton fabric swatches were soaked in a 10% commercial aqueous sodium hypochlorite solution at pH 7 at room temperature for 1 h to produce biocidal materials. The chlorinated cotton samples were washed thoroughly with distilled water and dried at 45°C for 1 h to remove all unbonded chlorine from the surface of the fabric. The concentration of loaded chlorine on the samples was determined by the iodometric/thiosulfate titration method. The Cl^+% on the cotton swatches were calculated using the following equation:

$$Cl^+(\%) = \frac{N \times V \times 35.45}{W \times 2} \times 100$$

where N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight (g) of the samples.

Breaking Strength Testing

The breaking strengths of untreated cotton fabrics and treated cotton fabrics with/without chlorination were measured using an electronic fabric strength tester [YG(B)026D, China] according to the GB/T3923-1997 method. The testing was performed at ambient temperature. The loading rate of the testing machine was set as 200 mm/min. Five replicates (5×20 cm^2) were produced for each sample, and their averages were reported.

Standard Washing Testing

The stability and rechargeability of chlorine on the samples were evaluated using a standard washing test according to AATCC Test Method 61. The N-halamine modified cotton samples were washed for the equivalents of 5, 10, 25, and 50 machine washes in a Launder-Ometer. Then the chlorine loadings of the samples after the washings with and without rechlorination were determined by the titration procedure.

UVA Light Stability Testing

UVA light stabilities of chlorinated cotton fabrics modified with triazine were investigated using an Accelerated Weathering Tester (The Q-panel Company, USA) according to ASTM D4587 standards. The chlorinated modified cotton fabrics were placed in the UV light chamber (0.89 W/m^2, 60°C) for contact times ranging from 1 to 24 h. After a specific time of exposure to UVA light, the cotton samples were removed from the UV chamber and titrated immediately, or rechlorinated, and titrated.

Antimicrobial Testing

Unchlorinated and chlorinated fabrics were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) using a modified AATCC Test Method 100–1999. Bacterial suspensions (25 μL) made with pH 7 phosphate buffer were added to the center of two pieces of 1 inch^2 cotton swatches. A second swatch was sandwiched over the first to ensure contact between the suspension and the fabric. After contact times of 1, 5, and 10 min, the samples were quenched with 5.0 mL of sterile 0.02 N sodium thiosulfate solution to remove all oxidative chlorine. The sodium thiosulfate employed in these studies in a control experiment did not cause a reduction of either bacterium. Serial dilutions of the quenched samples were made using pH 7 phosphate buffer and plated on Trypticase soy agar. The plates were incubated at 37°C for 24 h and then counted to determine the presence or absence of viable bacteria. Three repeats were performed for each test, and their averages were reported in this article.

Cell Culture and *In Vitro* Cytocompatibility Evaluation

NIH 3T3 mouse fibroblasts were cultured in DMEM media with 10% FBS and 1% Pentrip at 37°C and 5% CO_2. All fabric samples were cut into round shapes to fit into 96 well tissue culture plates and sterilized by UV exposure for 20 min on each side. Then, ~8000 cells/well were seeded onto each sample. After 4 and 24 h incubation, MTS assay was performed to quantify the cell viability by reading the absorbance at 490 nm according to manufacturer's instruction. Blank tissue culture plates (TCPS) and unmodified cottons were served as controls. The cell viability was determined as the percentage to the TCPS control. Statistical analysis of all data was conducted by 1-way ANOVA (StatView) whereas $p < 0.05$ were considered statistically significant ($n = 6$).

RESULTS AND DISCUSSION

Preparation and Characterizations of Modified Cotton Fabrics

In this study, we presented a method to form N-halamine precursor through controlled hydrolysis of cyanuric chloride in water solutions under ambient temperature. A mixture of mole ratio 1 : 2 of cyanuric chloride and NaOH was used to prepare a uniform water solution by forming 2,4-dichloro-6-hydroxy-1,3,5-triazine sodium salt. Cyanuric chloride reacts with equimolar of sodium hydroxide through nucleophilic reaction by substituting one chlorine of cyanuric chloride with hydroxyl to form 2,4-dichloro-6-hydroxy-1,3,5-triazine. Another equimolar of sodium hydroxide in the solution was used to form salt and make a clear solution. Excess alkali was added in the finishing solution to neutralize the acid generated by the nucleophilic substitution reactions between cellulose and triazine ring. The produced N-halamine precursor (2,4-dichloro-6-hydroxy-1,3,5-triazine) in water solution could be used directly to treat cellulose fibers by a regular pad-dry-cure technique without the incorporation of organic solvents. The water solution treatment of the cotton is a big advantage by avoiding using the flammable solvent ethanol during N-halamine siloxanes coating.[16] The curing temperature (120°C) applied in this study is much lower than the curing temperature in our previous reports (170–180°C).[13,14] The agents used in this study are very cheap and easily available. Furthermore, this method is very easy to scale up and attractive for practical applications by using the available equipment in textile mill.

The FTIR spectra of cotton and cotton treated with triazine are shown in Figure 2. The resolution of the NICOLET NEXUS 470 spectrometer used in FTIR experiments is 2 cm^{-1}. Compared

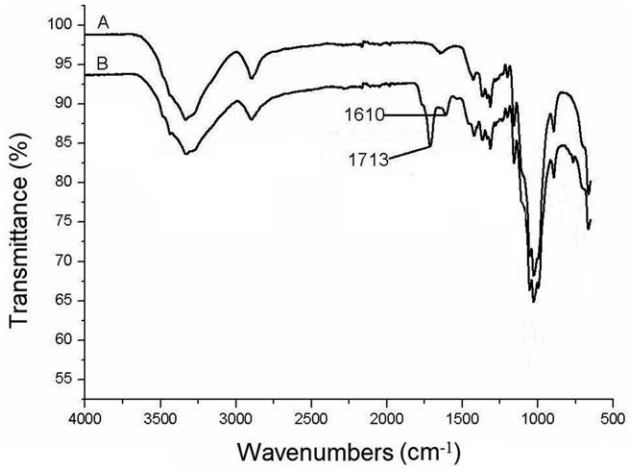


Figure 2. FTIR spectra of (A) untreated cotton, (B) cotton treated with 4% triazine.

to the FTIR spectrum of cotton, the spectrum of cotton treated with triazine before chlorination (without adding bleach) showed characteristic absorption bands at 1713 cm^{-1} for C=O bonds and at 1610 cm^{-1} for C=N bonds, which indicated that triazine was successfully attached to cellulose through covalent bonds, because unreacted water-soluble triazine could be easily washed off from the surface of cotton fabric.[24]

Further confirmation of triazine rings grafted onto cotton fabric was observed by XPS spectra. The XPS spectra of cotton and triazine-treated cotton are shown in Figure 3. The resolution of the ESCALAB 250Xi used in XPS studies is 0.8 eV. The spectrum of the cotton modified with triazine shows two new peaks at binding energies of 399.8 and 199.1 eV, indicating the existence of nitrogen and chlorine atoms on the surface of cotton treated with triazine.[25,26] The nitrogen and chlorine content on the surface of triazine-treated cotton calculated from the XPS peaks are 2.28% and 0.64%, respectively. It clearly demonstrated that triazine rings were covalently bonded onto cellulose because unreacted water-soluble 2,4-dichloro-6-hydroxy-1,3,5-

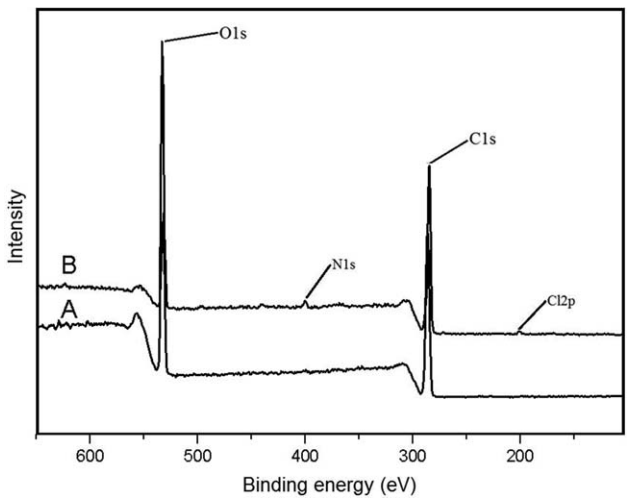


Figure 3. XPS spectra of (A) untreated cotton, (B) cotton treated with 4% triazine.

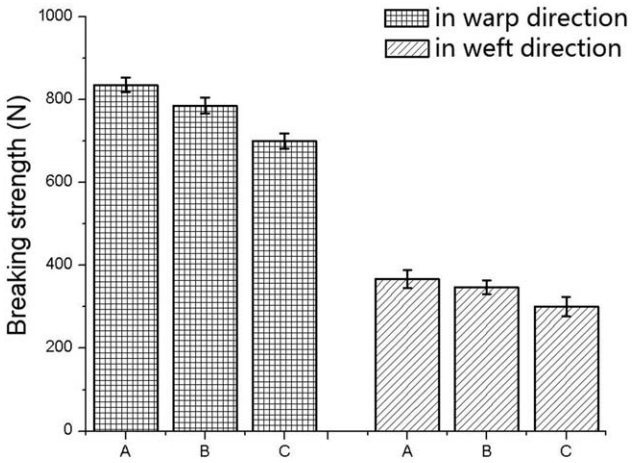


Figure 4. Breaking strength of (A) untreated cotton fabrics, (B) treated but unchlorinated cotton fabrics, and (C) treated and chlorinated cotton fabrics.

triazine could be easily washed off. The molar ratio of nitrogen and chlorine, based on the calculation from the XPS peaks, is 3.6 : 1 and differs from theoretical ratio of 3 : 1. The discrepancy might be due to the loss of third chlorine atoms on the triazine ring immobilized on cotton fibers under baking and basic finishing processes, resulting in two types of N-halamine precursors (A and B shown in Scheme 1). The molar ratio of form A and form B, calculated from molar ratio of nitrogen and chlorine is 5 : 1.

Breaking Strength Testing

The mechanical testing results of the untreated cotton fabrics and treated cotton fabrics before and after chlorination are shown in Figure 4. When compared to the control samples, the treated cotton fabrics with triazine showed a small degree of tensile strength loss, and over 84% of the original breaking strength could be maintained after chlorination both in warp and weft directions. In our recent report, the tensile strength loss of the cotton fabric modified with GTT after chlorination was over 30%,[18] which is much higher than that of the modified cotton fabric in this study. The small decrease in breaking strength shows this treating method has an advantage over previous studies to produce antimicrobial N-halamine fabrics in practical applications. The use of mild curing temperature (curing at 120°C) and basic curing conditions might avoid dramatic decrease of tensile strength caused by high curing temperature and acidic curing conditions.[17,18] The reduction of breaking strength caused by the chlorination process was due to oxidation of cellulose by sodium hypochlorite, which was also reported in other research.[12,13] In addition, the treatment does not change handle of the cotton fabrics.

Washing Testing

The data pertaining to the stability and rechargeability of chlorine on the fabric treated with triazine during washing according to AATCC Test Method 61–2001 are shown in Table I. The retained weight percent of oxidative chlorine on the prechlorinated cotton fabrics decreased rapidly with the increase of washing cycles during the first 10 washing cycles, primarily due

Table I. Stability Toward Washing of Chlorinated Cotton Fabrics Modified by Triazine Rings

Washing cycles	A (Cl^+ % wt)	B (Cl^+ % wt)
0	0.35	
5	0.12	0.33
10	0.05	0.30
25	0.03	0.30
50	0.01	0.28

A, chlorinated before washing.
B, chlorinated before washing and rechlorinated after washing.

to the hydrolysis of the N-Cl bond and some small degree release of the triazine rings with the elongation of washing times. However, 85% of the chlorine content was retrieved after 50 washing cycles and rechlorination, indicating that most of the precursor remained on the fabric and the ether bond linking cellulose and triazine ring was quite stable. 0.28 wt % Cl^+ remained on fabrics after 50 washing cycles and rechlorination indicating the triazine modified cotton fabrics still effective in inactivating microorganisms. The fabric could be recharged during each machine washing cycle by adding aqueous dilute household bleach in practical process. The washing stability of the fabrics modified with triazine is another significant improvement over the cotton modified with N-halamine siloxanes.[28] Only 23% of chlorine could be recovered after 50 washing cycles and rechlorination for the siloxanes modified samples. The washing stability data indicated that the covalent bonds between cotton and triazine are much more stable than the bonds between cotton and siloxanes.

UVA Light Stability Testing

Another finding in this research is the excellent UVA light stability and rechargeability of the oxidative chlorine in the treated fabrics. As shown in Table II, about 71% of the chlorine remained on the modified cotton fabrics after 24 h of UVA light irradiation with possibility of recovering all of the lost chlorine. However, after 24 h of UVA irradiation, almost all the chlorine lost for the cotton modified with GTT, and 88% of the lost chlorine for GTT recovered after rechlorination.[18] The excellent UVA light stability of cotton treated with cyanuric chloride is a significant improvement as compared to that of cotton fabrics modified with N-halamine siloxanes[16,27,28] and GTT.[18] Kocer et al. have studied the stability and mechanism of photolytic decomposition of N-halamine antimicrobial siloxane coatings.[27,28] When the fabrics modified with N-halamine siloxanes exposed to UVA irradiation, the N-Cl bonds break down, followed by a Cl radical migration to the propylidene chain connected to the siloxane tethering group. Then alpha or beta scission occurs leading to partial loss of the biocidal moiety from the surface of the modified materials, thus precluding complete rechlorination.[27,28] However, in this study, triazine rings are directly attached to the cellulose molecule by ether bonds, and there are no alkyl side chains in triazine rings, which disfavor the UVA photo degradation process.

Table II. UV Light Stability of Chlorinated Cotton Fabrics Modified by Triazine Rings

Time (h)	Cl^+ % wt	Cl^+ % wt after rechlorination
0	0.35	
1	0.33	
2	0.32	
4	0.29	
8	0.28	0.35
12	0.25	0.34
24	0.25	0.35

Antimicrobial Testing

Both unchlorinated and chlorinated cotton treated with triazine were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) at concentrations of about 10^7 CFUs (colony-forming units). The antimicrobial test results of the triazine treated cotton samples before and after chlorination are shown in Table III. The unchlorinated cotton samples treated with triazine was used as a control, and showed only 0.98 and 0.12 log reductions of *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) within 10 min of contact time, respectively, mainly due to adhesion of bacteria to the samples. The chlorinated modified cotton fabrics inactivated 99.999% *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) within 1 min of contact time. The chlorinated modified fabrics provide a total inactivation of *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) with 7-logs within the contact time of 10 and 5 min, respectively. The biocidal efficacy is comparable to amide N-halamine modified fabrics, but better than those amine N-halamines reported previously.[10–12,14]

In Vitro Cytocompatibility Evaluation

NIH 3T3 mouse fibroblasts were cultured on all cotton samples to study the cytotoxicity of the antibacterial fabric. As displayed in Figure 5, both triazine-treated cotton and chlorinated cotton showed no significant decrease of cell viability as compared to TCPS control and plain cotton after 4 and 24 h incubation ($p > 0.05$). This observation suggests that the bacteria-killing

Table III. Biocidal Efficacy Testing

		S. aureus[a]		*E. coli 0.157:H7*[b]	
		Bacterial reduction		Bacterial reduction	
Sample	Contact time (min)	%	Log	%	Log
Unchlorinated (control)	10	89.58	0.98	27.23	0.14
Chlorinated[c]	1	99.999	4.82	99.999	5.00
	5	99.999	5.13	100	7.43
	10	100	7.26	100	7.43

[a] Total bacteria: 1.80×10^7 (cfu/sample).
[b] Total bacteria: 2.67×10^7 (cfu/sample).
[c] 0.23% oxidative chlorine content.

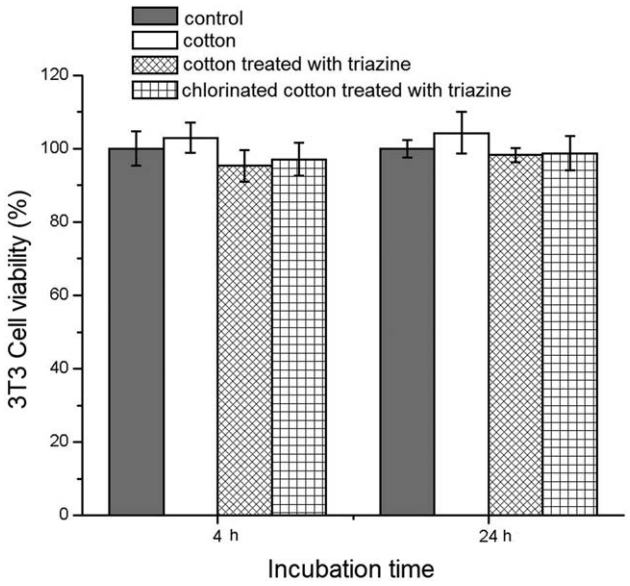


Figure 5. Cell viability of 3T3 fibroblasts on different fabrics and control (tissue culture plates) after 4 and 24 h incubation.

triazine treatment is not toxic. With comparable level of cytocompatibility as regular cotton, which is widely used in medical treatments, our triazine-treated cotton could further explore more biomedical applications with the antibacterial nature.

CONCLUSIONS

This study presents a novel method to form N-halamine precursor through controlled hydrolysis of cyanuric chloride in water solutions under ambient temperature. The produced N-halamine precursor water solution was used directly to treat cellulose fibers without the incorporation of organic solvents. The treated cellulose was converted into N-halamine structure after exposure to dilute household bleach, which showed excellent antimicrobial activity. The chlorinated cotton samples completely inactivated seven logs of *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC43895) at a contact time of 10 and 5 min, respectively. In addition, the N-halamine groups in the treated fabrics are stable and regenerable to laundering and UVA irradiation. More importantly, *in vitro* cell viability testing showed that treated cotton was nontoxic to mammalian cells, suggesting that this antibacterial fabric is biocompatible. The produced antimicrobial cellulose has considerable potential for practical applications in the healthcare industry.

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