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Treatment of melamine formaldehyde fibers for decontaminating biological and chemical warfare agents

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ABSTRACT: The demand for protection against biological and chemical warfare agents has increased the need for unique protective materials. *N*-halamines are superior candidates for this task by having rapid inactivation rates against a broad range of microorganisms and the ability to oxidize some pesticides and warfare agents to reduce their toxicity to humans. Thus, the design of *N*-halamine materials having fibrous structure, high halogen loading capacity with enhanced stability, and being relatively inexpensive is very important. This study investigated the effect of acid treatment on the chlorine loading and stability of a commercial flame retardant melamine formaldehyde (MF) fiber to introduce biocidal and detoxifying properties. The fibers formed into a web were treated with diluted sulfuric acid (H_2SO_4) under various conditions. The fiber webs were chlorinated with household bleach, and the stability of bound chlorine was investigated. The treated fabrics have been tested against a Gram-negative bacterium and a warfare stimulant.
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INTRODUCTION

Protection of civilians and defense personnel against biological pathogens spread in air as aerosols and chemical warfare agents is very important in reducing panic and chaos during terror attacks. Respiratory protection is the most important protection and often the only protection people require.[1,2] In this regard, filter facepiece respirators having antimicrobial properties are among the most useful protection devices. Since there is very limited time to inactivate pathogens or chemicals during the filtration pathway, antimicrobial agents such as *N*-halamine compounds are superior candidates due to their fast action mechanism. *N*-halamine chemistry has been employed to provide antimicrobial properties on fibers, filters, and other solid surfaces,[3–9] due to their biocidal activity against a full spectrum of microorganisms including Gram-negative and Gram-positive bacteria, fungi, viruses, and spores. Briefly, *N*-halamines contain covalent bonds (N—X, X═Cl, Br, I) with the oxidative halogen transferred to cell membranes leading to cell inactivation by an oxidation mechanism. This oxidative property has also been employed in detoxifying warfare agents such as organic sulfides.[10,11] However, *N*-halamine technology should be relatively inexpensive for large-scale applications. An *N*-halamine is defined as a compound containing one or more nitrogen–halogen covalent bonds.[12] Similar precursor functional groups (N—H) can be found in various commercial polymer structures in the amine, amide or imide form. Therefore, chlorination of N—H sites contained in commercial polymers might provide cost effective protective materials. *N*-chlorination of polymers (such as polyamides and polyurethanes) have been extensively studied.[13–15] Some of these polymers are available in fiber form, others as resins, and still others as prepolymers which are further polymerized into products.

Antimicrobial melamine compounds are widely known and have been used as water disinfectants and cleaning disinfectants in soluble form, or as slowly dissolving tablets in water.[8,16,17] Structurally, chloromelamines belong to the class of amine *N*-halamines. However, because of the strong electron withdrawing effect of the triazine rings, their chemical environments are similar to those of amide *N*-halamines, and their biocidal activities are expected to lie between amine and amide *N*-halamines.[17] In this regard, chloromelamine can provide both strong biocidal activity and good stability.

A commercial fiber, used in flame retardant applications, produced from melamine formaldehyde (MF) resin has very limited ability to absorb and retain halogen (0.1 wt % of chlorine) and therefore has limited biocidal activity. However, a portion of the

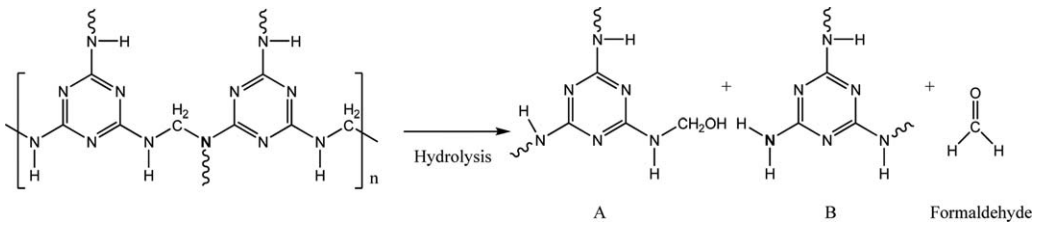

Figure 1. Hydrolysis of a melamine formaldehyde resin.

formaldehyde can be hydrolyzed away to increase the number of primary amino groups causing greater accessibility to chlorine absorption (Figure 1). The acid treatment removes a portion of the methylene/methylene-oxy crosslinks between melamine units leaving exposed N—H functional groups.

This study investigated the effect of acid treatment on the chlorine loading and stability of a commercial flame retardant MF fiber to introduce biocidal and detoxifying properties. The acid treatment increased the number of N—H sites on the fiber causing the fiber to become more accessible (about 100 times) to chlorine absorption. This procedure allowed the production of cost effective protective fibers and filters. The stability of bound chlorine on the fibers towards fluorescent light and shelf-storage was remarkable, and the remaining chlorine loadings after 120 days were sufficient for biocidal activity. The biocidal performance of the chlorinated-treated fibers was notable and was improved by a hydrophilic *N*-halamine surface coating. The produced fibers were also very effective against detoxification of the warfare agent stimulant paraoxon. The commercial fiber meets regulatory specifications and is used especially for flame retardant applications. In this regard, the chlorinated-treated MF fibers can be used in various applications such as water/air filters and disposable facepiece respirators.

EXPERIMENTAL

Materials and Instrument

Melamine formaldehyde (MF) fibers, sold under the Basofil® trade name, were provided by Basofil Fibers, LLC. The MF staple fibers were opened in a fiber opener/blender and vacuum deposited on a screen to form a web of fibers. The fiber webs were consolidated by needle-punching for facile handling and testing. IR data were obtained with a Nicolet 6700 FT-IR spectrometer with an Attenuated Total Reflectance (ATR) accessory. The tensile properties of the fibers were investigated with an Instron 5565 Universal Tester according to ASTM D1774-94; 20 specimens were tested for each sample.

Acid Treatment

The MF fibers were hydrolyzed with 1*M* sulfuric acid (H_2SO_4) aqueous solution at various temperatures for various time intervals. After the treatments, samples were washed vigorously with distilled water and then retained in distilled water. The pH of the water was monitored to confirm the complete removal of H_2SO_4 from the samples.

Chlorination and Analytical Titration Procedures

The acid-treated fibers were dried in air for one day before chlorination and then were chlorinated with 10% household bleach at pH 8.2, buffered with sodium bicarbonate, for 1 h. The chlorinated-treated fibers were rinsed with distilled water and then dried at 45°C for 1 h to remove any unbonded chlorine. The active chlorine content of the chlorinated fibers was determined by a modified iodometric/thiosulfate titration.[18] The chlorinated fibers (about 0.15 g) were suspended in a solution of 90 mL of ethanol and 10 mL of 0.1 *N* acetic acid. After addition of 0.2 g of potassium iodide, the mixture was titrated with 0.0375 *N* sodium thiosulfate until the yellow color disappeared at the end point. The weight percent Cl^+ on the samples was calculated by the following equation:

$$\% \ Cl^+ = (35.45NV)/(2W) \times 100$$

where N and V are the normality (meqv/mL) and volume (mL), respectively, of the sodium thiosulfate consumed in the titration, and W is the weight of the sample (g).

Stability Testing

Fluorescent light stability of the bound chlorine was measured under laboratory fluorescent lighting at ambient conditions. Shelf-storage was performed in a dark place at ambient conditions. After a specific time of light exposure or shelf-storage, the samples were titrated to determine the stabilities of the bound chlorine, or rechlorinated and titrated to determine the stabilities of the chlorinated polymers.

Hydrophilic *N*-Halamine Coating Procedure

High chlorine loadings produced a hydrophobic character on the surface of fibers. An *N*-halamine precursor, 3-triethoxysilylpropyl-5,5-dimethylhydantoin, previously synthesized by our group[19] was used to reduce the hydrophobic surface character of the treated fibers. The acid-treated MF fiber webs were coated with the *N*-halamine coating at 5% concentration in ethanol/water (1 : 1 v/v). The coated webs were cured for 1 h at 95°C and then washed with 0.5 wt % detergent solution for 15 min. New Fourier Transform Infrared (FTIR) bands, carbonyl stretching of the hydantoin ring at 1773 cm^{-1} and 1696 cm^{-1} indicated the attachment of the coating.

Antimicrobial Efficacy Testing

Control and chlorinated fibers were challenged with *Escherichia coli* O157:H7 (ATCC 43895) using a "sandwich test". About 25 μL of bacterial suspension in pH 7 buffer, were deposited in the center of a 6.5 cm^2 fiber swatch, and a second identical swatch was laid on top of the first swatch. A sterile weight was used to ensure sufficient contact of the swatches with the inocula. After determined contact times, the samples were quenched with 5.0 mL of sterile 0.02 *N* sodium thiosulfate solution to remove any oxidative chlorine that could cause extended disinfection. Serial dilutions of the solutions contacting the surfaces were plated on Trypticase agar and incubated for 24 h at 37°C,

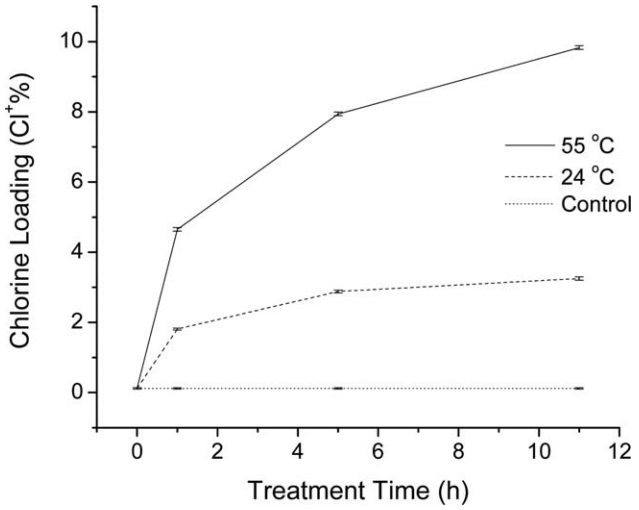

Figure 2. Chlorine loadings (Cl^+%) of acid-treated MF fibers.

and colony counts were made to determine the presence of viable bacteria.

Warfare Stimulant Testing

The information was obtained using a CV-50W (a voltammetric analyzer) with a flow injection apparatus. About 10 m*M* phosphate buffered saline (PBS) was used in the flow injection system. The treated fiber webs were retained for 30 min, 90 min, and 24 h in a $2.5 \times 10^{-3} M$ solution of paraoxon in de-ionized water. Injections were made in 50 μL increments from each sample. The sample dimensions were 0.5 cm on a side (0.25 cm^2).

RESULTS AND DISCUSSION

The acid-treated MF fibers became more accessible (about 100 times) to chlorine absorption, as shown in Figure 2. The chlorine loading of the untreated fibers was 0.12%, and the acid treatment at 55°C for 11 h increased the chlorine loading to 9.83%. The effectiveness of the treatment was increased by elevating the treatment temperature (55°C) and by extending treatment times. Chlorine loadings of around 8–10% are tremendously high for fibrous structures and would be very useful as long-term sources of oxidative chlorine (Cl^+) for antimicrobial and detoxification applications.

Scanning Electron Microscopes (SEM) micrographs (Figure 3) show the modification of the surfaces of the MF fibers after the acid treatment. In addition to increasing the number of primary amino groups in the structure, the treatment caused the formation of scales on the surface of the fibers contributing to high chlorine loadings due to increased surface area. Also, even after the severest acid treatment, the fiber tensile strengths only decreased from 1.99 g/den to 1.28 g/den which is still sufficient for textile processing and filtration applications.

The acid-treated MF fibers chlorinated at pH 8.2 were exposed to stability tests for 120 days. The fluorescent light and shelf-storage stabilities of the bound chlorine were very good, and the shelf storage stability was superior as expected (Table I). The remaining chlorine loadings even after 120 days were sufficient for biocidal activity.[18,20] However, rechlorination of the 120 days-aged samples could not reach their initial chlorine loadings (9.83% at pH 8.2) indicating the loss of N—H sites during storage. More acidic chlorination condition at pH 7.0 (adjusted with HCl) exhibited better rechlorination results, but still not to the initial chlorine loading level (11.97% at pH 7.0).

MF fibers itself and product A (Figure 1) have alpha hydrogens (the hydrogen atom bonded to the carbon atom next to nitrogen atom) which can lead to an alpha dehydrohalogenation reaction.[21] This reaction liberates molecular hydrochloric acid (HCl) having potential to catalyze the hydrolysis of diaminotriazine end groups (Figure 4) into aminohydroxytriazine (ammeline-type) and dihydroxytriazine end groups.[22]

The FTIR spectra of MF fiber, acid-treated MF fiber, chlorinated-treated MF fiber, and aged-chlorinated-treated MF fiber are shown in Figure 5. The N—H stretching band at 3318 cm^{-1} [Figure 5(A)] broadened toward lower frequency 3188 cm^{-1} [Figure 5(B)] after the acid treatment indicating an increase in the number of hydroxyl groups and hydrogen bonding. The band lost its intensity after chlorination related to decreasing number of hydrogen bonds due to the

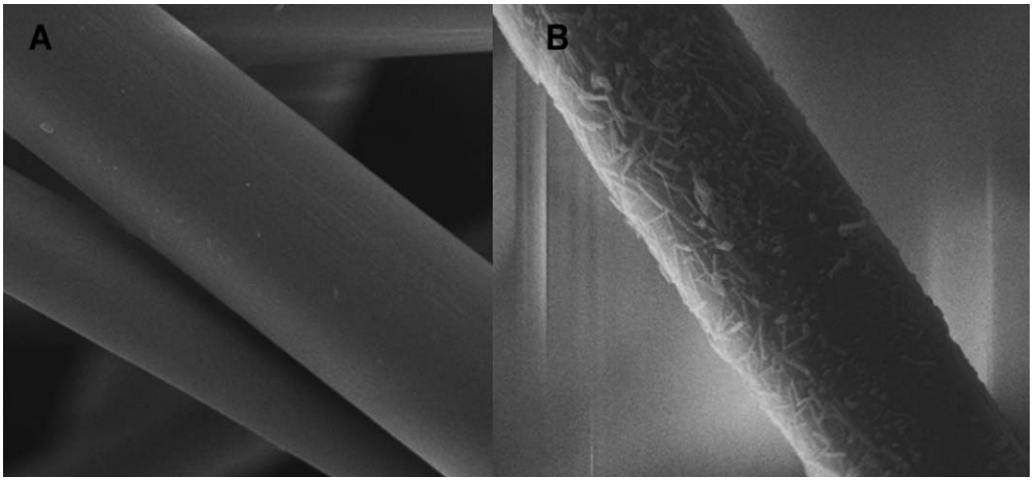

Figure 3. SEM micrographs (at 4000×) of as-spun (A) and acid-treated (B) MF fibers.

Table I. Stability of Bound Chlorine on MF Fibers Toward Fluorescent Light Exposure and Shelf-Storage Conditions (Cl^+% Remaining)

Days	Fluorescent light	Shelf-storage
0 (Chlorination at pH 8.2)	9.83	9.83
7	7.95	8.39
14	7.15	8.11
30	4.85	7.23
75	1.87	6.16
105	0.82	5.19
120	0.76	4.15
Rechlorination at pH 8.2	4.48	6.40
Rechlorination at pH 7.0	9.95	9.77

transformation from the N—H to the N—Cl bond. The band broadened further toward lower frequency 3119 cm^{-1} [Figure 5(D)] after aging for 120 days indicating an additional increase in the number of hydroxyl groups. The increase in the number of hydroxyl groups supports the hydrolysis of diaminotriazine end groups. The new band at 1745 cm^{-1} [Figure 5(D)] can be carbonyl stretching of the carbonyl tautomer of ammeline-type intermediate (Figure 4).[23] We performed a rechlorination at pH 7.0 (Table I) to prove that the formation of aminohydroxytriazine end groups during the aging and these end groups can be chlorinated better at acidic conditions. The more acidic nitrogen atom in the carbonyl tautomer can be chlorinated better under acidic conditions explaining the higher chlorine loadings at lower pH (pH 7.0) for the rechlorination of 120 days-aged samples.

In general, the biocidal characteristic of a fiber depends on the concentration of the biocidal sites.[3] However, for *N*-halamine compounds an increase in Cl^+ active sites may cause an increase in hydrophobicity of the material, which may lead a poorer biocidal performance due to a decrease in contact with microbial cells.[19,24] To evaluate this hypothesis, three different samples were prepared by using the treatment conditions resulting in different chlorine loadings (Table II). The MFA sample was treated with acid for 5 min at 24°C, the MFB sample was treated with acid for 11 h at 55°C, and the MFC sample was coated with an *N*-halamine precursor after the acid treatment of 11 h at 55°C. The treated MF fibers were challenged with *Escherichia coli* at a concentration of 2.80×10^7 CFU/sample (7.45 log). The unchlorinated control samples (MFA, MFB, and MFC) provided only about 1 log reductions, due to the adhesion of bacteria to the swatches within 30 min contact time intervals.

All of the chlorinated samples showed excellent antimicrobial activity by inactivating all bacteria within 30 min. The MTC-Cl sample inactivated bacteria relatively faster than MFA-Cl and MFB-Cl samples. The coating compound is relatively more hydrophilic than the MF polymer, and thus increased the surface wetting characteristic of the treated MF fibers.

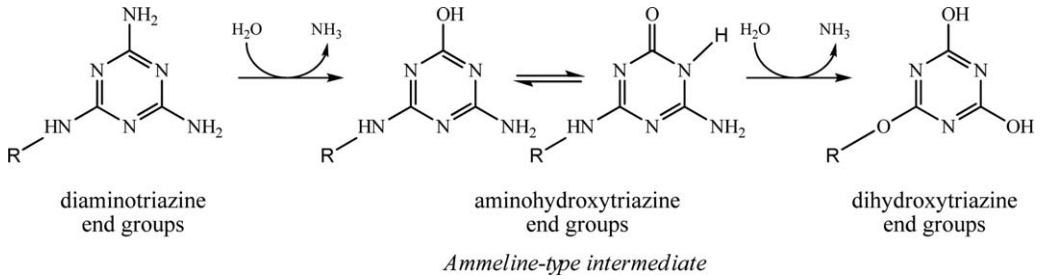

Figure 4. Hydrolysis of diaminotriazine end groups.

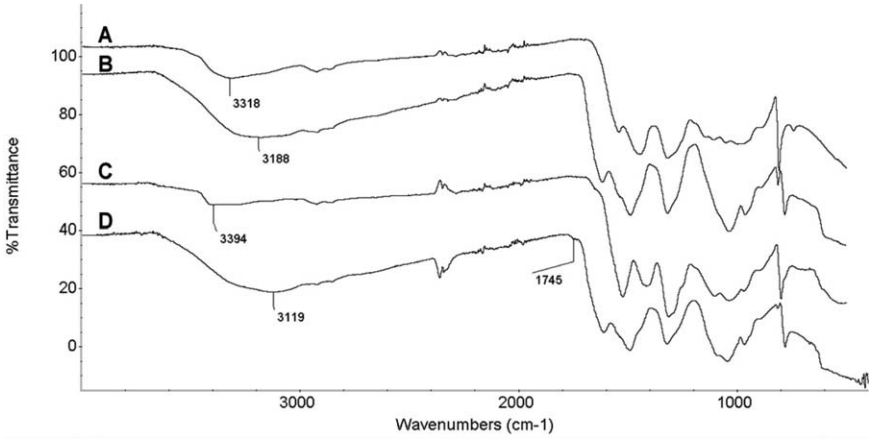

Figure 5. FTIR spectra of as-spun MF fiber (A), acid-treated fiber (B), chlorinated-treated fiber (C), and aged-chlorinated-treated MF fiber (D).

Table II. Biocidal Test

Sample/ chlorine loading (Cl^+%)	Contact time (min)	Bacterial reduction (log)
MFA	30	0.86
MFA-Cl	5	0.96
0.98	10	2.30
	30	7.45
MFB	30	0.66
MFB-Cl	5	0.13
9.56	10	1.43
	30	7.45
MFC	30	0.39
MFC-Cl	5	2.42
4.46	10	5.14
	30	7.45

SEM micrographs (Figure 6) show the modification of the surface of MF fibers after the acid-treatment and coating procedures. There were some island type depositions of the *N*-halamine coating on the fiber web.

N-halamine compounds are also useful for the neutralization of various chemical warfare agents and some pesticides.[10,11] The stored chlorine can easily oxidize the reactive chemicals. In this study, MF (control), MFB-Cl (chlorinated-treated), and MFC-Cl (chlorinated-coated-treated) samples were exposed to an aqueous solution of paraoxon (2.5×10^{-3} *M*), and then the destruction (hydrolysis)[25] of paraoxon was monitored in the time intervals of 30 min, 90 min, and 24 h. Paraoxon is chemically similar to the nerve agents sarin and soman,[26] and a good stimulant in terms of its hydrophilic/hydrophobic balance.[27,28]

Figure 7 displays the change in concentration of paraoxon after exposure to control (A), chlorinated-treated (B), and chlorinated-coated-treated (C) samples for specific time intervals. The chlorinated-treated (B) and the chlorinated-coated-treated samples (C) decreased the paraoxon concentration in all time intervals of exposure. The chlorinated-treated sample (B) decreased the paraoxon concentration by 20%, 34%, and 60% compared to the control sample within time intervals of 30 min, 90 min, and 24 h; whereas, the chlorinated-coated-treated sample (C) decreased about 31%, 54%, and 69%. Overall the chlorinated-coated-treated sample exhibited better destruction of (or faster reaction with) the paraoxon than the uncoated chlorinated sample.

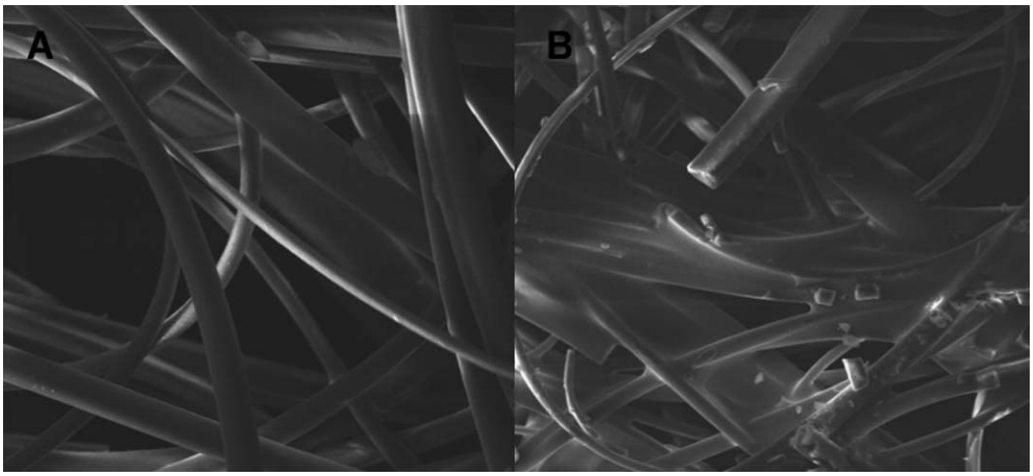

Figure 6. SEM micrographs (at 750×) of the treated MF fibers before (A) and after (B) coating.

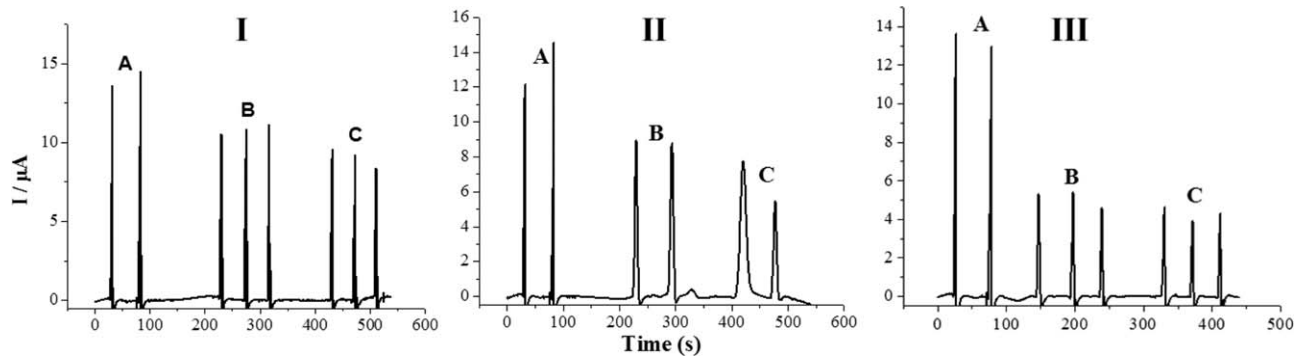

Figure 7. Current versus elution time plot for detection of paraoxon after 30 min (I), 90 min (II), and 24 h (III). A: unchlorinated (control), B: chlorinated-treated (MFB-Cl), and C: chlorinated-coated-treated (MFC-Cl).

CONCLUSIONS

After acid treatment, some formaldehyde was released from the MF fiber structure, which made the fiber more accessible (100 times) to chlorine absorption. The treatment also increased the surface area of the fibers. On the other hand, the strength loss caused by the treatment was less than 35% even after the severest treatment conditions. This procedure allowed the production of cost effective protective filter materials. The alpha dehydrohalogenation reaction liberates molecular hydrochloric acid during storage which hydrolyze the melamine parts (diamino end groups) into an ammeline-type intermediate (aminohydroxy end groups) reducing the rechlorination ability of the fibers. The biocidal performance of the chlorinated-treated fibers was notable and was improved by a hydrophilic *N*-halamine surface coating. The produced fibers were also very effective in the detoxification of paraoxon, a warfare agent stimulant.

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