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Antimicrobial silica and sand particles functionalized with an *N*-halamine acrylamidesiloxane copolymer

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ABSTRACT: The monomer 2-acrylamido-2-methyl-1-(5-methylhydantoinyl)propane (HA) was copolymerized with 3-(trimethoxysilyl)-propyl methacrylate (SL) and covalently attached onto silica gel and sand particles. As a result HASL copolymer-grafted silica gel and sand particles (HASL SGPs and SPs) were obtained. These two types of HASL SGPs and SPs provided excellent biocidal efficacy against Gram positive *S. aureus* and Gram negative *E. coli* O157:H7 bacteria when the copolymer-grafted particles were exposed to dilute sodium hypochlorite (household bleach) solution. In a flowing water application, seven logs of bacteria were inactivated within 10 s of contact time with the particles packed into a column. The treated particles also exhibited good washing and storage stabilities. The chlorine loss during extensive flow could be recovered by further exposure to dilute bleach solution. The antimicrobial particles have potential application for use in inexpensive disinfecting water filters for slow water flows. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43413.

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INTRODUCTION

It is well documented that water contamination has become a major problem in the world because a growing number of contaminants such as pathogens, ie. helminthes, protozoa, fungi, bacteria, rickettsiae, viruses, and prions are entering water systems.[1] Waterborne bacteria and viruses have caused many diseases, in some cases terminal ones.[1] To provide safe and clean water, much research is being devoted to water disinfection methods. Disinfectants such as free halogen, ozone, chlorine dioxide, and *N*-halamines, are being used in the treatment of water and wastewater. However, water-soluble compounds have drawbacks such as short-term stability in aqueous solution and reactivity with organic impurities in water to form undesired byproducts, which strongly limit their application.[2–5] As a result, further research is being done to provide safer and more stable water disinfection. Insoluble polymeric disinfectants, such as quaternary ammonium salts, phosphonium salts, and N-halamines, have been widely applied in the disinfection of hygienic areas, water purification, and food packaging.[4–9] Among these polymeric compounds, *N*-halamines have attracted much attention because of their unique properties, such as effective antimicrobial efficacy, stability in aqueous solution, durability, regenerability upon exposure to extensive water contact, lack of corrosion, low toxicity, and relatively low expense.[10–13]

N-halamines contain one or more nitrogen-halogen covalent bonds, and their positive oxidative halogen can be transferred directly to bacterial cells leading to the inactivation of the bacteria through destruction or inhibition of metabolic processes in the microorganisms.[10,14–17] In past decades a variety of *N*-halamine compounds have been investigated and applied in medical devices, textiles, hospitals, water purification systems, food packaging, food storage, and household sanitation to produce antibacterial materials.[10] Some of these N-halamine compounds, which contain reactive agents such as epoxide rings,[17–19] 2,4,6-trichloro-s-triazine,[20] vinyl groups,[21–23] and siloxanes,[24,25] could be attached to substrates with covalent bonds. They effectively inactivated bacteria and demonstrated good stability in aqueous solution and in dry storage. Among these reactive N-halamine compounds, *N*-halamine siloxanes were widely used because the siloxane group has a high reactivity with a wide variety of substrates, such as cellulose,[12,26–28] silica gel[29,30] sand,[31] paper,[32] polyurethane paint,[32] and aluminum.[33] It was found that *N*-

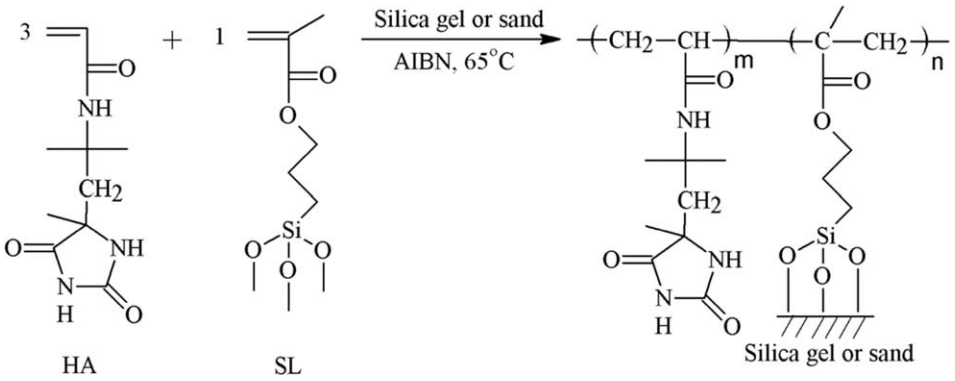


Figure 1. Preparation of HASL-grafted silica gel and sand.

halamine siloxane compounds and polymers were very useful in providing biocidal surface coatings.

In previous works in these laboratories, it was demonstrated that 3-triethoxysilylpropyl-5,5-dimethylhydantoin as a monomer or as a polymer could be grafted on to silica gel[29] and sand particles[31] to produce antimicrobial efficacy in a flowing water application. In this work, a siloxane compound, 3-(trimethoxysilyl) propyl methacrylate (SL), copolymerized with *N*-halamine precursor 2-acrylamido-2-methyl-1-(5-methylhydantoinyl)propane (HA) and reacted with the silanol groups (hydroxyl groups) present on the surface of silica gel or sand particles was studied for the same application. It was rationalized that since HA contains three nitrogen sites for chlorination, enhanced antimicrobial efficacy might be expected as compared with the previous work in which the N-halamine precursor only contained one nitrogen site. Also, the monomer 3-(trimethoxysilyl)-propyl methacrylate (SL) contains two types of reactive sites: methoxy and vinyl groups, where SL can be covalently bonded with the silanol groups existing on the silica gel or sand surface. The reaction scheme is shown in Figure 1. HASL-grafted silica gel and sand particles (HASL SGPs and SPs) were rendered antimicrobial after being exposed to dilute sodium hypochlorite solution. It will be shown that these biocidal particles exhibited high chlorine stability in flowing water. In addition, they inactivated bacteria within a brief contact time, which indicates that they may be useful in water treatment applications.

EXPERIMENTAL

Materials and Instrumentation

Diacetone acrylamide was purchased from Tokyo Chemical Industry, Co., LTD (Tokyo, JP). 3-(Trimethoxysilyl)propyl methacrylate (SL), potassium cyanide, and ammonium carbonate were obtained from Acros Organics (NJ). Silica gel (6-12 mesh) and 2,2′-Azobis(2-methylpropionitrile) (AIBN) were obtained from Sigma-Aldrich, Inc. (St. Louis, MO). Ottawa sand standard (20-30 mesh) was provided from Fisher Chemicals, Inc. (Fair Lawn, NJ).

Bacteria cultures of *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895) were purchased from American Type Culture Collection (Rockville, MD), and Trypticase soy agar was obtained from Difco Labo- ratories (Detroit, MI). All chemicals were used without further purification.

ATR-IR data recorded with 32 scans at 4 cm^{-1} resolution were obtained with an ATR-FT-IR spectrometer (Model Spectrum400, Perkin Elmer Co., Waltham, MA). The morphology of the samples was observed using a SU1510 scanning electron microscope (SEM) (Hitachi, Inc., Tokyo, JP). UV degradation studies were performed with an Accelerated Weathering Tester (The Q-Panel Co., Cleveland, OH).

Synthesis of HA

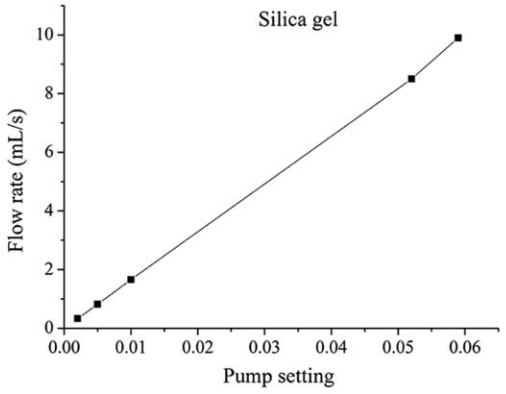
2-Acrylamido-2-methyl-1-(5-methylhydantoinyl)propane (HA) was synthesized according to a protocol described previously.[34] Briefly, diacetone acrylamide (0.1 mol), potassium cyanide (0.2 mol), and ammonium carbonate (0.6 mol) were added into a round-bottom flask and reacted at room temperature for 5 d in a water/ethanol (1:1, v/v) solvent mixture. After evaporating ethanol and adjusting the pH to 7 with 6*N* hydrochloric acid, a crude white product was obtained by filtration. The product was purified by recrystallization from acetonitrile. The purified HA was obtained by filtration and dried at 45° C overnight. The spectral parameters for the purified HA were the same as reported previously[34]; the melting point was 178 °C.

Grafting Procedure

In previous research different mole ratios of HA to SL were used to synthesize HASL copolymers to coat onto cotton fabrics. Stability of the fabrics coated with different mole ratios of HA to SL towards washing was determined. It was found that the chlorine loading increased, but the stability toward washing decreased by increasing the amount of HA in the copolymer.[34] In this study, silica gel and/or sand particles were reacted with HA and SL together, ie. the HASL copolymer was formed *in situ*, which yielded a higher chlorine loading than reacting the particles with preformed copolymer. Several molar ratios of HA to SL were used to react with the silica gel and sand. It was found that when a 3:1 molar ratio of HA to SL was used in the grafting process, ideal chlorine loading and satisfactory stability of the chlorine on the particles were obtained.

HASL silica gel particles (SGPs) were prepared according to the protocol described below. Typically, 4.78 g (20 mmol) HA were dissolved in 30 mL of methanol in a 50 mL round bottom flask. After all of the HA was dissolved, 15 g of silica gel (6-12 mesh) was added into the flask. The mixture was stirred for 1 h to allow the absorption of HA and methanol into the silica gel. Then, 1.65 g (6.7 mmol) SL and 0.1 g AIBN were added into

Pump setting	v (mL/s)
0.002	0.33±0.00
0.005	0.82±0.00
0.010	1.66±0.01
0.052	8.47±0.09
0.059	9.90±0.08



Pump setting	v (mL/s)
0.001	0.17±0.00
0.002	0.33±0.00
0.003	0.49±0.00
0.004	0.66±0.00
0.005	0.81±0.00
0.023	3.85±0.01

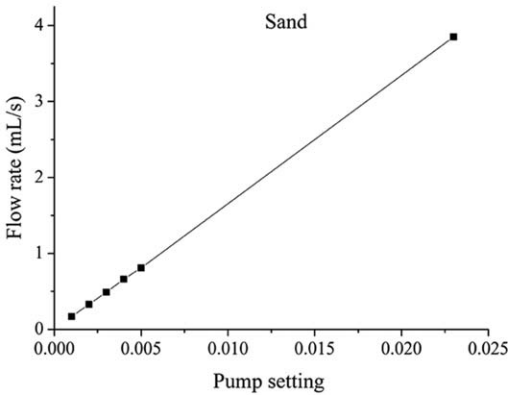


Figure 2. The relationship between the flow rate and pump setting.

the mixture, and nitrogen was bubbled through the solution for 20 min to remove any dissolved oxygen. The reaction took place at 65 °C for 8 h under reflux conditions. After the reaction, HASL SGPs were washed several times with methanol and obtained by vacuum filtration.

HASL sand particles (SPs) were prepared by a similar method with a slight modification. The reactants [4.78 g (20 mmol) of HA, 1.65 g (6.7 mmol) of SL, and 0.1 g AIBN] were placed in the reaction vessel with 30 mL methanol and 30 g of sand (20-30 mesh). The mixture was reacted at 65 °C in an oven overnight to provide co-condensed functionalization. To remove the unreacted molecules, the HASL SPs were washed in an ethanol/water (3:1, v/v) mixture for 1 h. Then HASL functionalized sand was washed two times in a 1% detergent solution for 30 min. Finally, the product was rinsed several times with copious amounts of water and was dried at 45 °C.

Chlorination and Titration

To provide antimicrobial properties, HASL SGPs and HASL SPs were soaked in a 10 wt % Clorox solution at pH 7 for 1 h with the addition of one drop of Triton-X 100 surfactant. Upon completion of the chlorination process, the sample was collected by vacuum filtration, washed with copious amount of water, and finally dried at 45 °C for 1 h. The amount of active chlorine loading of the chlorinated HASL-grafted silica gel and sand particles (HASL-Cl SGPs and SPs) was measured by standard iodometric/thiosulfate titration. The Cl^+ wt % and total active chlorine content (atoms/g) of the particles were calculated using the following equations:

$$Cl^+\ \% = \frac{35.45 \times N \times V}{2 \times W} \times 100\% \quad (1)$$

$$\text{Total chlorine content (atoms/g)} = \frac{Cl^+\ \%}{35.45} \times 6.02 \times 10^{23} \quad (2)$$

where N and V are the normality (equiv./L) and volume (L) of the titrant ($Na_2S_2O_3$), respectively, and W is the weight of the sample (g) used for the titration.

Calibration of the Pump Flow Rate

To measure the antimicrobial efficacies of the HASL-grafted particles for a water filtering application, a column (20 cm length, 1.6 cm inside diameter) packed with chlorinated HASL-grafted particles was used, and then a bacterial suspension with a known inoculum population was pumped through the column.

Different columns were packed with un-chlorinated and chlorinated HASL-grafted particles. The weight of silica gel (15 g) and sand (11 g) particles were utilized to pack each column with about the same total chlorine content. The total number of active chlorine atoms of the chlorinated particles in each column was measured as 2×10^{21} Cl^+ atoms for 15 g of silica gel particles and 11 g of sand particles, respectively. The empty-bed volumes (V) of each column packed with 15 g of silica gel and 11 g of sand particles were measured as 8.5 mL and 3.8 mL, respectively. A peristaltic pump (MasterFlex L/S, Cole Palmer Inc., Vernon Hills, IL) was used to control the flow rate.

Before the biocidal test was performed, the pump flow rate was calibrated in order to obtain a calibration curve of the pump

Table I. Contact Times Used for the Biocidal Test and the Corresponding Pump Setting and Flow Rate Values

Silica gel			Sand		
Pump setting number	Flow rate (mL/s)	Contact time (s)	Pump setting number	Flow rate (mL/s)	Contact time (s)
0.002	0.33	25	0.001	0.17	22
0.005	0.82	10	0.002	0.33	11
0.01	1.66	5	0.004	0.66	5
0.052	8.47	1	0.023	3.85	1

setting vs. flow rate. Distilled water was pumped through the column packed with HASL-Cl SGPs and SPs at a certain setting number of the pump, and the time (T) taken to collect 100 mL of water was measured. Then the flow rate (v) and contact time (t) were calculated as follows (the results are shown in Figure 2):

$$v\,(\mathrm{mL/s}) = 100/T$$
$$t\,(\mathrm{s}) = V/v$$

where v is the flow rate of the water that passes through the packed column (mL/s), T is the time to collect 100 mL distilled water, V is the empty-bed volume of the column packed with particles (mL), and t is the contact time between the particles and water at a certain flow rate.

Antimicrobial Testing

The antimicrobial testing protocol was adopted from a previous study[27] and used with only slight modifications. To avoid any subsequent inactivation of the bacteria by any free oxidative chlorine remaining on the particles after the chlorination process, all of the chlorinated silica gel and sand particles were packed into the columns and rinsed with 3 L of distilled water and then dried at 45 °C for 2 h before the antimicrobial testing.

After extensive washing, HASL-Cl SGPs and SPs and unchlorinated HASL SGPs and SPs were challenged with *S. aureus* and *E. coli* O157:H7 bacteria, each being packed in different columns. The un-chlorinated HASL SGPs and SPs were used as controls. The bacterial suspension was pumped through each column with a peristaltic pump. The inoculum populations of the *S. aureus* and *E. coli* O157:H7 were 2.80 x 10^7 CFU/mL and 2.00 x 10^7 CFU/mL, respectively. Contact times were determined and varied by using corresponding flow rate values from the calibration curve chart shown in Table I. After a determined contact time of flow, approximately 2 mL of effluent was collected in a sterile tube at specified time intervals. Then, a 1 mL aliquot of the effluent was taken and immediately quenched with 1 mL of 0.05 N sodium thiosulfate to prevent any subsequent inactivation of the bacteria by any free chlorine that could be leached from the HASL-Cl SGPs and SPs in the column. Serial dilutions of the quenched effluent solutions were made (0.1 mL quenched solution mixed with 0.9 mL phosphate buffer), and an aliquot of 25 μL of each dilution was plated onto Trypticase soy agar. The plates were incubated at 37 °C for 24 h, and viable bacterial colonies were recorded for biocidal efficacy analysis.

Stability Testing

The chlorine bond stability of the chlorinated particles under flowing water conditions was studied. To investigate the stability of the chlorine bound in the *N*-halamines, two columns (each being 20 cm length, 1.6 cm inside diameter) were packed with HASL-Cl SGPs and SPs, respectively. The weights of silica gel (15 g) and sand (11 g) were controlled to ensure that they had the same total chlorine content (2 × 10^{21} Cl^+ atoms). About 3 L of distilled water were pumped through each column packed with chlorinated samples at a rate of 6 mL/min. After pumping 1 L of water through the sample, the first and last 100 mL portions of the effluent were collected and titrated. In addition, after each 1 L of water was flowed through the particles, a small amount of particles were removed and titrated to measure the remaining active chlorine on them. Moreover, the same sampled particles were also re-chlorinated and titrated.

UVA light stability of the bound chlorine on HASL-Cl SGPs and SPs were determined by exposure to UV light in the UV chamber for different exposure times, ranging up to 24 h. After a given time, particles were removed from the chamber and titrated. In addition, particles that were exposed to UV light for 24 h were re-chlorinated and titrated.

To measure the storage stability of chlorinated silica gel and sand particles, HASL-Cl SGPs and SPs were introduced into transparent glass vials. Some of the vials were wrapped with aluminum-foil to provide dark storage conditions; whereas others were placed under lab-lighting to provide exposure to florescent light. Samples were kept at both dark and lab-lighting

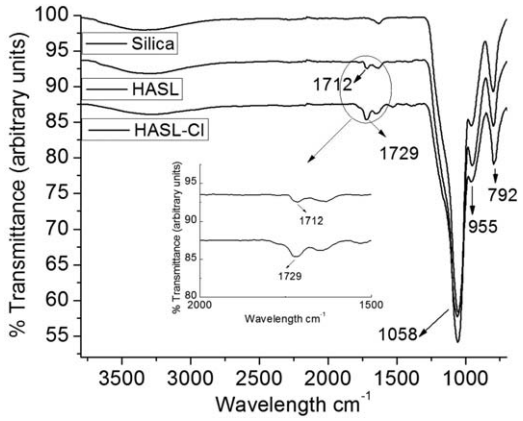


Figure 3. FTIR spectra of silica (non-grafted), HASL (un-chlorinated), and HASL-Cl (chlorinated) silica particles.

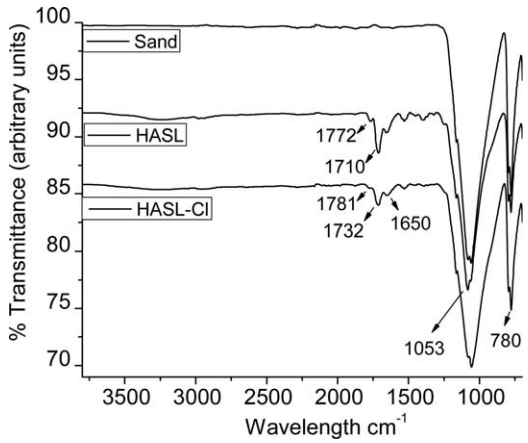


Figure 4. FTIR spectra of sand (non-grafted), HASL (un-chlorinated), and HASL-Cl (chlorinated) sand particles.

conditions for 30 d. At specific time intervals, a small amount of the samples were removed and titrated. Also, samples which were stored for 30 d were re-chlorinated and titrated.

RESULTS AND DISCUSSION

Characterization of Antimicrobial HASL-Grafted Silica Gel and Sand Particles

Silica and sand particles contain of silanol (Si-O-H) groups on their surfaces. Synthesized HASL copolymer also contains siloxane groups (Si-O-H) on which a grafting process was possible between the silica gel or sand surface and the copolymer. After exposure to dilute sodium hypochlorite solution, the HASL-grafted particles containing numerous amide and imide groups were rendered antibacterial.

As previously mentioned, a similar approach was followed and HASL copolymer was used to coat cotton fabrics, for which siloxane groups of the copolymer could bind with the hydroxyl groups located on the surface of the cotton fabrics.[34]

FTIR spectra of non-grafted, HASL-grafted (chlorinated and un-chlorinated) silica, and sand particles are shown in Figures 3 and 4. The FTIR spectra of the silica and sand particles exhibited similar structure and had a distinctive Si-O-Si and Si-O-H bands at about 1058/1053 $cm^{-1}$and 792/780 cm^{-1}, respectively. Compared with non-grafted particles, the spectra of HASL silica and sand particles showed new characteristic vibrational bands at 1712 cm^{-1} and 1710 $cm^{-1,}$ respectively, which correspond to the amide carbonyl groups stretching vibrational modes of the hydantoin ring.[35] This vibrational band shifts to 1729 cm^{-1} and 1732 cm^{-1} observed for HASL-Cl spectra, after chlorination of silica and sand particles, respectively, due to electron-withdrawing effect of the chlorine atoms. This result has also been observed in previous N-halamine studies.[34]

SEM micrographs of the non-grafted and HASL-grafted silica gel and sand particles surfaces are shown in Figure 5 and 6.

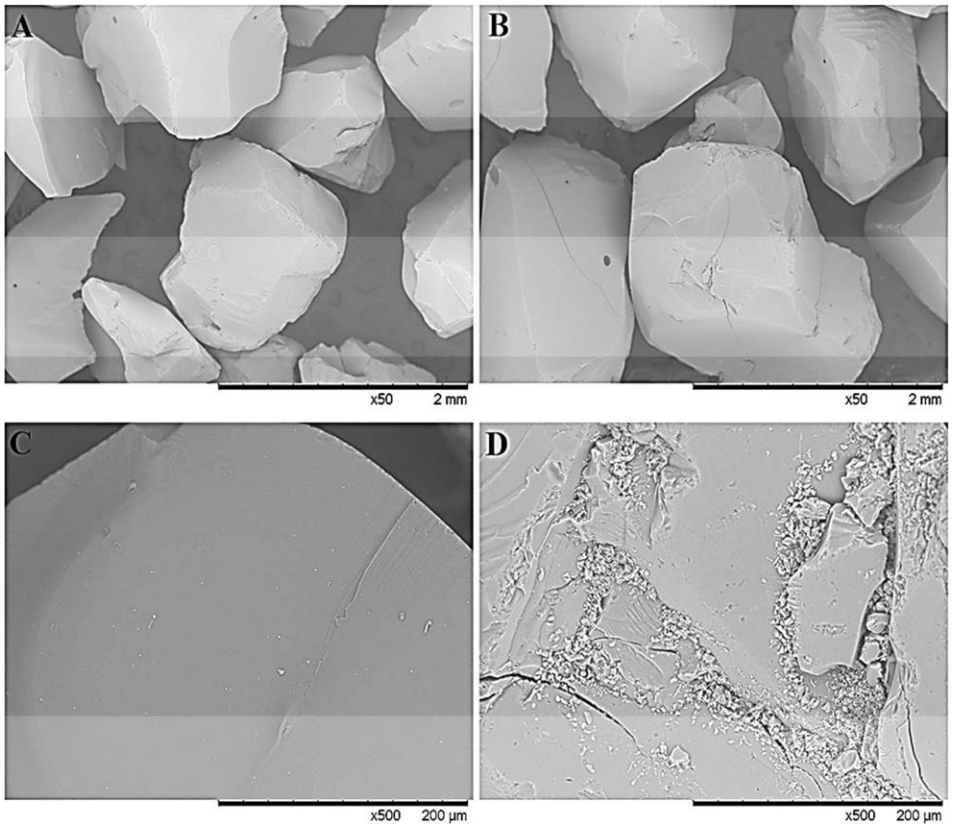


Figure 5. The surface morphology of non-grafted (A) and (C) and HASL-grafted (B) and (D) silica gel particles; (A) and (B) 50 magnification and (C) and (D) 500 magnification.

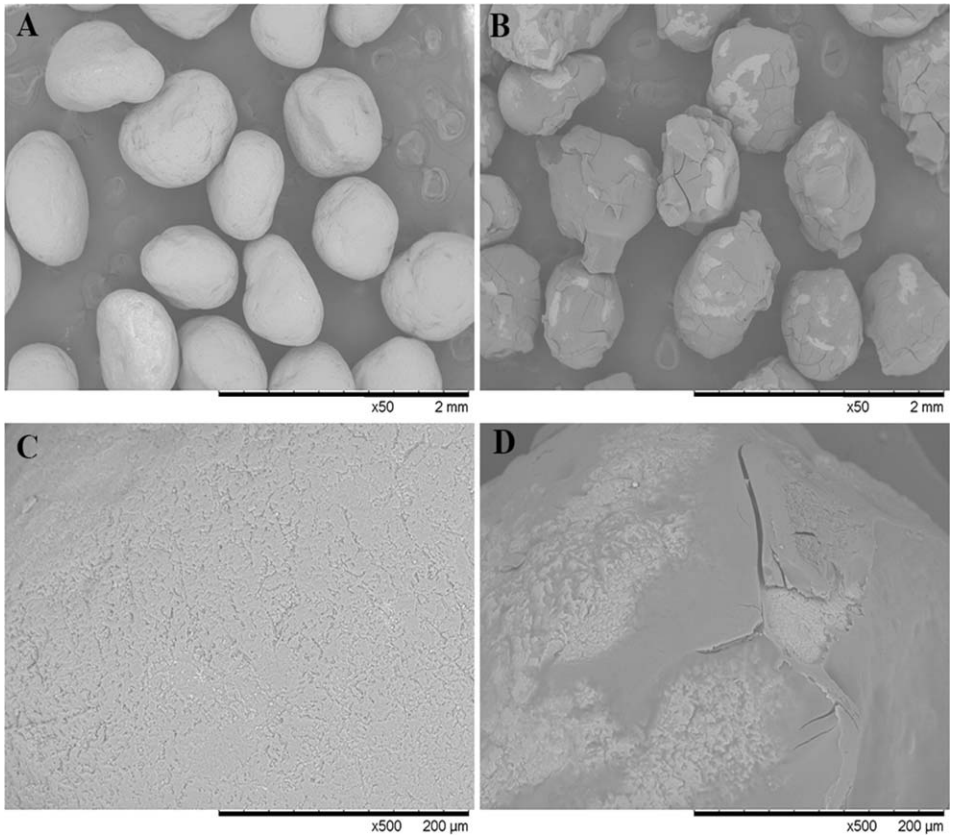


Figure 6. The surface morphology of non-grafted (A) and (C) and HASL-grafted (B) and (D) sand particles; (A) and (B) 50 magnification and (C) and (D) 500 magnification.

There was not any significant difference between non-grafted and HASL-grafted silica particles at 50 magnification [Figure 5(A,B)]. However, clear differences were observed for the non-grafted and HASL-grafted sand at the same magnification [Figure 6 (A,B)]. Lighter color spots were observed on the surface of HASL-grafted sand SEM image indicating HASL attachment on the sand particles surface. This obvious distinction was also detected at 500 magnification between non-grafted and HASL-grafted silica gel [Figure 5(C,D)] and sand [Figure 6(C,D)] particles.

Antimicrobial Efficacy

After the 3 L water rinsing of the packed columns before the antimicrobial testing described in the Experimental Section, the remaining Cl^+ % loadings of the silica gel and sand particles were 0.81 and 1.06, respectively. HASL-Cl SGPs and SPs were challenged with *S. aureus* and *E. coli* O157:H7 at concentrations of about 2×10^7 CFU/mL, as shown in Table II. Unchlorinated HASL SGPs and SPs, used as controls, showed less than 0.3 log of bacterial reduction. This may be due to the adhesion of the bacteria onto HASL-grafted but un-chlorinated particles. Both of the chlorinated particles (HASL-Cl SGPs and SPs) showed excellent biocidal activities. HASL-Cl SGPs inactivated the 7 logs of the *S. aureus* and *E. coli* O157:H7 within a contact time of 10 s and 5 s, respectively. And the chlorinated sand inactivated all of the *S. aureus* and *E. coli* O157:H7 bacteria (2.80×10^7 CFU/mL and 2.00 x 10^7 CFU/mL, respectively) within 11 s.

The chlorinated HASL SG's and SP's provided enhanced inactivation of both bacteria at much lower contact times at

Table II. Biocidal Testing of HASL-Grafted Silica Gel and Sand Particles

Samples	Contact time (s)	Bacterial log reduction	
		S. aureus[a]	*E. coli* O157:H7[b]
Control	25	0.289	0.083
Silica gel-Cl	1	5.043	3.761
	5	5.720	7.301
	10	7.447	7.301
	25	7.447	7.301
Control	22	0.129	0.127
Sand-Cl	1	0.430	1.167
	5	3.778	1.796
	11	7.447	7.301
	22	7.447	7.301

[a] The bacterial population was 2.80×10^7 CFU/mL.
[b] The bacterial population was 2.00×10^7 CFU/mL.

Table III. Stability of HASL-Grafted Particles under Flowing Water Conditions

Samples	Water volume (L)	First 100 mL (ppm)	Last 100 mL (ppm)	Remaining Cl^+%	Rechlorination (Cl^+%)
Silica gel	0	-	-	0.82	1.03
	1	2.40	1.19	0.74	0.94
	2	0.93	0.72	0.68	0.94
	3	0.63	0.34	0.64	0.91
Sand	0	-	-	0.61	0.66
	1	0.35	0.23	0.58	0.65
	2	0.22	0.14	0.57	0.59
	3	0.09	0.08	0.55	0.60

comparable chlorine loadings than did the treated silica gel and sand particles reported previously.[29,31]

Stability of Chlorinated HASL-Grafted Particles under Flowing Water Conditions

N-halamine functionalized particles were packed into columns and measured amounts of distilled water were passed through with the effluent water being collected for chlorine analyses. The remaining chlorine amounts on the *N*-halamine functionalized silica gel and sand particles (HASL-Cl SGPs and SPs) after washing with the distilled water, the oxidative chlorine amount released into effluent water, and the chlorine regeneration capability of the functionalized particles after extensive washing were determined. The results are shown in Table III. It was observed that a small amount of oxidative chlorine was released into the effluent water. However, the amount of free chlorine in the effluent (ppm) decreased when the volume of the water that passed through the chlorinated particles was increased. When only 1 L of water was flowed through the HASL-Cl SGPs, a higher amount of free chlorine (2.4 ppm) was detected in the initial portion of 100 mL of effluent. After 3L of DI water flowed through the chlorinated particles, the release of free chlorine was decreased substantially, and only 0.34 ppm free chlorine was measured in the effluent. As a result of free chlorine release, the initial oxidative chlorine percentage of the HASL-Cl SGPs was decreased from 0.82 to 0.64 Cl^+ wt %. Compared to silica gel, the chlorine on the sand was more stable, and less free chlorine was leached out from the chlorinated sand particles. In fact, most of the chlorine could be recovered after exposing subsequently to dilute bleach solution. The loss of oxidative chlorine refers to N-Cl bond dissociation, not to the dissociation of the siloxane tethering groups due to the hydrolysis.[34] After re-chlorination of the particles, a higher chlorine loading was obtained than for the initial chlorine amount present in the particles, especially for silica gel. Two possible explanations for this observation are: one, in the first chlorination cycle all of the N-H functional groups present in the HASL structure were not chlorinated; whereas, in the second chlorination cycle (after re-chlorination), the remaining un-chlorinated N-H groups could be chlorinated to form N-Cl bonds, and two the particles swelled upon exposure to flowing water providing better access to binding sites for the chlorination solution.[27,28,34] This swelling would be expected to be greater for the SGs than for the SPs in accord with the observations noted in Table III.

Table IV. Stability of HASL-Cl SGPs and SPs under UV Light Irradiation

	Chlorine loading (Cl^+%)	
Time (h)	Silica gel	Sand
0	0.90	0.28
1	0.65	0.13
2	0.41	0.08
3	0.30	0.07
4	0.27	0.05
8	0.18	0.03
12	0.11	0.03
24	0.04	0.02
24 (rechlorination)	0.48	0.22

Table V. Storage Stability of HASL-Cl SGPs and SPs under Lab-Light and Dark Conditions

	Chlorine loading (Cl^+%)			
	Lab-light		Dark	
Time (days)	Silica gel	Sand	Silica gel	Sand
0	0.90	0.28	0.90	0.28
5	0.79	0.26	0.88	0.28
10	0.78	0.24	0.87	0.26
15	0.75	0.20	0.83	0.21
20	0.72	0.21	0.76	0.21
25	0.66	0.19	0.70	0.23
30	0.62	0.19	0.69	0.20
30 (rechlorination)	0.88	0.24	0.89	0.28

Storage Stabilities in the Presence of Light and Darkness

The stabilities of the HASL-Cl SGPs and SPs toward UV light irradiation are presented in Table IV. The oxidative chlorine content (Cl^+ %) decreased significantly with the extension of UV light exposure time. After 1 h of UVA light exposure, silica gel, and sand particles lost about 28% and 53% of the bound chlorine remaining (0.65 Cl^+ % and 0.13 Cl^+ %) of the oxidative chlorine on the silica gel and sand particles, respectively. After 24 h of UVA light irradiation, most of the bound chlorine on the silica gel and sand was lost. A portion of the oxidative chlorine could not be recovered after exposing to dilute sodium hypochlorite. This could be due to the intermolecular rearrangement of the chlorine atom onto the carbon atoms, which are adjacent to the Si atom resulting in Si–carbon bond cleavage.[12]

Table V illustrates the storage stability of the HASL-Cl SGPs and SPs under ambient laboratory light and dark conditions. It was found that the chlorine on the silica gel and sand particles decreased slightly with the elongation of storage time. The chlorine loading of the samples was somewhat less stable when the samples were exposed to florescent light, rather than when stored in darkness. About 69% of chlorine on the silica gel and 68% of chlorine on the sand remained after exposure to lab-light for 30 d, and about 77% and 71% of chlorine remained on the silica gel and sand, respectively, under dark storage for 30 d. Notably, almost all of the chlorine loading was recovered after exposure to dilute bleach solution after 30 d.

CONCLUSIONS

Silica gel or sand particles have been functionalized with HASL copolymer in a one-step process. A siloxane monomer (SL) was copolymerized with *N*-halamine precursor (HA) by free radical polymerization while a concomitant attachment occurred onto silica gel or sand particles through the siloxane groups of the SL constituent. Antimicrobial silica gel or sand particles were obtained after exposure to dilute bleaching solution. The chlorinated HASL copolymer functionalized silica gel and sand particles inactivated 7-logs of *S. aureus and E. coli* O157:H7 within several seconds in a flowing water application. Available oxidative chlorine on the silica gel and sand particles was relatively stable and could be largely regenerated after 3 L of flow. The oxidative chlorine on the HASL-grafted silica gel and sand particles was very stable under both lab-light and dark storage conditions. Antimicrobial water filters containing chlorinated HASL SGPs and SPs have potential for practical use as inexpensive antimicrobial water filters, particularly for slow flowing water.

AUTHOR CONTRIBUTIONS

Z. Jiang, a graduate student, and B. Demir, a post-doctoral fellow, performed the sample preparation and flow testing experiments. R. M. Broughton, X. Ren, and S. D. Worley, Professors, supervised the work, and Professor T. S. Huang provided the microbiological analyses. All contributed to the manuscript preparation.

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