

Biocidal Hydantoinylsiloxane Polymers. IV. *N*-Halamine Siloxane-Functionalized Silica Gel

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ABSTRACT: The monomer 5,5-dimethyl-3-(3'-triethoxysilylpropyl)hydantoin and its hydrolysis product polymer poly[3-(5,5-dimethylhydantoinylpropyl)hydroxysiloxane] were employed to functionalize the surfaces of silica gel particles in order to produce an adhered film that becomes biocidal upon chlorination with dilute sodium hypochlorite bleach. The biocidal efficacy of the functionalized silica gel was demonstrated in a cartridge filter experiment against the bacterial pathogens *Staphylococcus aureus* and *Escherichia coli* O157:H7. Complete 6 log inactivations of the two bacte-

rial species were observed within 30 s of contact. Moreover, upon loss of biocidal activity due to depletion of bound chlorine, the coated silica gel particles could be recharged by further exposure to dilute bleach. Potential uses of the biocidal silica gel include disinfection and odor control in water treatment facilities and recirculating baths. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3448–3454, 2006

Key words: biocidal applications of polymers; biopolymers; *N*-halamine polymers; polysiloxanes; biocidal silica gel

INTRODUCTION

Our laboratory work for the past decade has focused on the preparation and testing of novel *N*-halamine biocidal polymers to be used in coatings that are capable of inactivation of pathogenic microorganisms upon direct contact.¹ The *N*-halamine biocidal polymers contain either nitrogen–chlorine or nitrogen–bromine covalent chemical bonds that are stable toward hydrolyses, that is, toward release of free halogen into aqueous solution. The *N*-halamine polymers developed in our laboratories function as biocides by the direct contact of the cells of microorganisms with the oxidative halogen atom. Advantages inherent in the polymeric *N*-halamine biocides are the capabilities of preparation *in situ* by exposure of the precursor polymers to free chlorine or free bromine, regeneration following loss of the halogen by simple reexposure of the polymers to additional free halogen, and rapid inactivation of a broad spectrum of pathogens.

Research has shown that *N*-halamine groups such as *N*-halo hydantoins, oxazolidinones, and imidazolidinones can be covalently attached to polymers and used in a variety of disinfection applications.^{2–19} In this work we will demonstrate that a novel hydantoi-

nylsiloxane, in either a monomeric or polymeric form, can be used to functionalize particles of silica gel, which become effectively biocidal upon exposure to dilute household bleach. We recently showed that similar chemistry could be used to produce biocidal sand particles.²⁰ However, silica gel, having a much larger surface area, will be shown to produce much more effective biocidal efficacy. Efficacy data for *N*-halogenated hydantoinyl siloxane monomers and polymers were presented recently.^{21,22} Prior work elsewhere showed that quaternary ammonium salt derivatives of siloxanes could be used to create biocidal surfaces,^{23,24} although the poly-quats are comparatively weakly biocidal relative to analogous *N*-halamines.⁷ In addition, it was recently reported using similar technology that an imidazole moiety can be attached through a siloxy tether to polysaccharides to create a weakly biocidal surface, which helps to prevent corrosion on aluminum substrates.^{25,26} In regard to silica gel, there is quite a bit of research being performed on modification of the particles of the material to extend its range of applications.^{27–29} Thus, imparting a biocidal function should be of broad interest.

EXPERIMENTAL

Preparation of 5,5-dimethyl-3-(3'-triethoxysilylpropyl)hydantoin Monomer (I)

The triethoxysilylpropylhydantoin derivative was prepared using 5,5-dimethylhydantoin and 3-chloro-

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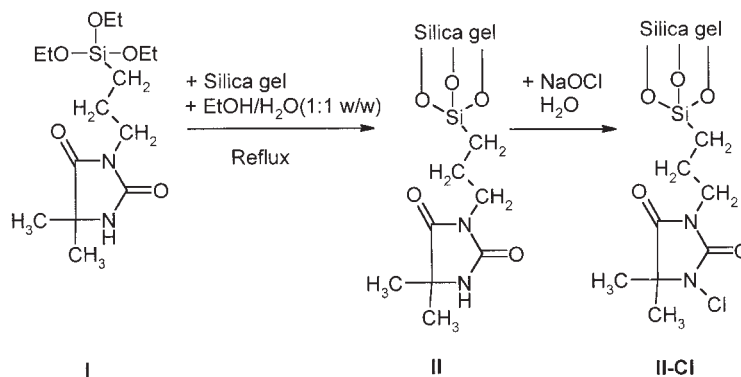


Figure 1 The preparation scheme for producing biocidal silica gel from monomer I.

propyltriethoxysilane (Aldrich Chemical Company, Milwaukee, WI) according to a procedure similar to that outlined in a U.S. Patent,³⁰ which was presented in detail elsewhere along with characterization data.^{20,21} Its structure, designated as I, is shown in Figure 1.

Preparation of poly[3-(5,5-dimethylhydantoinylpropyl)hydroxysiloxane] (Poly-I)

The monomer 3-chloropropyltriethoxysilane (Aldrich) was polymerized by a method described previously.²¹ The resulting poly(3-chloropropylhydroxysiloxane) was then converted into **Poly-I** (Fig. 2) by reacting the potassium salt of 5,5-dimethylhydantoin (Aldrich) with an equimolar quantity of poly(3-chloropropylhydroxysiloxane) in DMF at 100°C for 6 h, followed by removal of the KCl precipitate and DMF solvent.²¹

Coating procedures

In the case of monomer I, typically 5.0 g of 30–60 mesh silica gel (Sigma–Aldrich, St. Louis, MO) were placed in a 100-mL flask with 20.0 g of ethanol/water (1:1, w/w) and 0.5 to 1.5 g of I. The mixture was

refluxed for 1–6 h. The coated silica gel (**II**, Fig. 1) was removed by filtration, rinsed 3 times with 100-g portions of ethanol/water (1 : 1, w/w), and dried in air at ambient temperature. For **Poly-I** a similar procedure was employed except that the ethanol/water mixture was generally made either acidic with 1N HCl or basic with 0.1–1.0N NaOH. For example, a mixture of 0.75 g of **Poly-I**, 2.5 g of silica gel, and 10.0 g of ethanol/0.1N NaOH (1 : 1, w/w) were refluxed for 1–10 h to produce **Poly-II**, as shown in Figure 2.

A form of the polymer-coated silica gel (**Poly-III**) could also be produced by direct polymerization of monomer I on the particles of the silica gel. In this case, typically 2.5 g of silica gel were placed in a 50-mL beaker, to which was added 0.25–1.25 g of I and 5.0 g of 0.1N HCl. The mixture was allowed to stand at ambient temperature without stirring for 4–28 h and then filtered, rinsed with distilled water, and dried as described above.

Chlorination of coated samples to render them biocidal

The various forms of coated silica gel (**II**, **Poly-II**, and **Poly-III**) were chlorinated by simply exposing them to

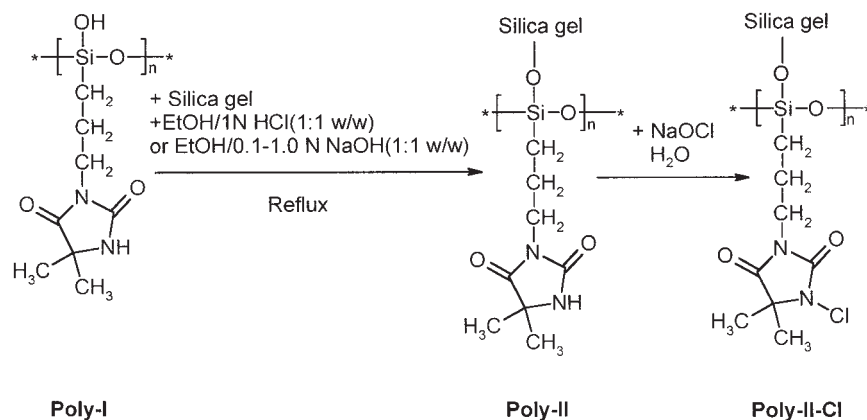


Figure 2 The preparation scheme for producing biocidal silica gel from polymer **Poly-I**.

TABLE I
Coating Efficiency of Monomer I on Silica Gel as
Function of Reaction Time

Reaction time (h) ^a	Titrated Cl ⁺ (wt %)
1	0.34
2	0.59
3	1.00
4	1.09
5	1.15
6	1.16

^a The weights of silica gel, I, and ethanol/water (1 : 1, w/w) in each case were 5.0, 1.5, and 20.0 g, respectively. The reaction was run under reflux conditions.

commercial household bleach (Clorox Company, Oakland, CA). Typically, 25.0 g of a form of coated silica gel were soaked in 300 mL of a 50% aqueous solution of sodium hypochlorite bleach buffered to pH 7.0 for 1 h at ambient temperature. The chlorinated silica gel samples (**II-Cl**, **Poly-II-Cl**, and **Poly-III-Cl**) were removed by filtration, rinsed with three 100-mL portions of distilled deionized water, and dried at 45°C for 2 h to remove any occluded free chlorine. The chlorine loadings on the silica gel particles (wt %) were determined by standard iodometric/thiosulfate titration. Some experiments were performed to determine the stability of the chlorine on the silica gel particles over time under flow conditions and the regeneration capabilities upon reexposure to additional free chlorine.

Biocidal efficacy evaluation

Glass columns (25.0-cm length, 1.0-cm inside diameter) were packed to about 18.0 cm with the various forms of silica gel including uncoated silica gel, and unchlorinated, but coated silica gel to serve as controls. The empty-bed volumes of the columns were measured to be about 3.50 mL, such that a controlled flow rate of 3.50 mL/s would give a contact time of 1.0 s for bacteria in the columns. A peristaltic pump (Gelman Sciences, Ann Arbor, MI) was used to control the flow rate of 50-mL portions of inoculum (buffered to pH 7.0) through the columns. The contact times could be varied by repeated recirculation of the inoculum through the columns. Measured portions of effluent (25 µL) were collected at specific time intervals in sterile tubes; they were immediately quenched with 0.02N sodium thiosulfate to prevent any subsequent inactivation of the bacteria by any free chlorine that might have leached out of the biocidal silica gel. Then, serial dilutions of the quenched effluents were plated onto trypticase agar and colony counts were performed after incubation at 37°C for 24 and 48 h. The two bacterial pathogens employed were Gram-positive *Staphylococcus aureus* (ATCC 6538) and Gram-negative *Escherichia coli* O157:H7 (ATCC 43859). The cell

density of the *S. aureus* was about 1.2×10^5 colony forming units (CFU)/mL and that of the *E. coli* was about 1.9×10^5 CFU/mL.

RESULTS AND DISCUSSION

Preparation of biocidal silica gel coated with I

Compound I is hydrolyzed in the ethanol/water solution to form hydantoinyltrihydroxysiloxane, which chemically bonds readily to the silica gel particles through a condensation reaction with the OH groups on the silica gel particles. This is in contrast to the observation reported previously for sand particles, for which a surface polymerization of hydrolyzed I was necessary to induce adhesion because of lower surface area and much fewer exposed OH groups. Chlorination of **II** then occurs via direct contact of the oxidative chlorine in aqueous sodium hypochlorite with the amide nitrogen on the hydantoin ring to form the biocidal silica gel particles (**II-Cl**, Fig. 1). The efficiency of the chemical bonding process can be assessed by analytical determination of the weight percentage of bound oxidative chlorine on the silica gel particles.

Table I shows the effect of varying the reaction time. In this experiment 5.0 g of silica gel were mixed with 1.5 g of I in 20.0 g of ethanol/water (1 : 1 w/w), and the mixture was refluxed for 1–6 h before chlorination. The data show that the chlorine loading became almost constant after a 5-h reaction of I. The data also illustrate a significant enhancement of chlorine binding (>1.1 wt % Cl⁺) relative to sand particles of similar mesh²⁰ (only 0.27 wt % Cl⁺). Table II shows the effect of varying the concentration of I relative to that of the silica gel. In this case the weight of the silica gel was held constant at 5.0 g, whereas the amount of I in 20.0 g of ethanol/water (1 : 1 w/w) was varied from 0.5 to 1.5 g at a fixed reaction time of 5 h. As can be seen in Table II, the weight percentage of titratable chlorine (Cl⁺) increased dramatically as the concentration of I was increased until the surface reaction sites on the silica gel particles were exhausted. Economics will dictate the loading concentration of I to

TABLE II
Coating Efficiency of Monomer I on Silica Gel as
Function of Concentration of I

I (g) ^a	Titrated Cl ⁺ (wt %)
0.50	0.66
0.75	0.89
1.00	1.08
1.25	1.12
1.50	1.15

^a The weights of silica gel and ethanol/water (1 : 1, w/w) in each case were 5.0 and 20.0 g, respectively. The reaction was run under reflux conditions for 5 h.

TABLE III
Coating Efficiency of Poly-I on Silica Gel under Acidic Conditions as Function of Reaction Time

Reaction time (h) ^a	Titred Cl ⁺ (wt %)
2	0.30
5	0.64
8	1.09
16	1.80
24	1.85
32	1.90

^a The weights of silica gel, **Poly-I**, and ethanol/1N HCl (1 : 1, w/w) in each case were 2.5, 0.75, and 10.0 g, respectively. The reaction was run under reflux conditions.

achieve the desired biocidal performance. A 10 wt % starting concentration of **I** relative to the weight of the silica gel may be the maximum feasible, but a 0.66 wt % loading of chlorine at that concentration is certainly adequate to produce efficacious biocidal performance.

Preparation of biocidal silica gel coated with Poly-I

Whereas compound **I** has three hydroxyl groups available for a condensation reaction with surface hydroxyl groups on silica gel particles, **Poly-I** only has one such site (Fig. 2). Consequently, the attachment process becomes less efficient in the ethanol/water solvent system than was the case for monomer **I**. However, the addition of either an acid or base catalyzes the reaction for attachment of **Poly-I**. Table III presents the data pertaining to varying reaction times in the presence of 1N HCl. In this case 2.5 g of silica gel was reacted with 0.75 g of **Poly-I** in 10.0 g of ethanol/1N HCl (1 : 1, w/w). Reflux times of 2–32 h were employed. The reaction required much longer times for completion (16–32 h) than was the case for monomer **I**, but at the longer times the biocidal chlorine loading (1.8–1.9 wt % Cl⁺) was higher for the particles coated with **Poly-I** than achieved for particles coated with monomer **I**. Because of the rather slow reaction in the presence of 1N HCl, it was deemed unnecessary to

TABLE V
Coating Efficiency of Poly-I on Silica Gel as Function of Concentration of Poly-I in 0.1N NaOH

Poly-I (g) ^a	Titred Cl ⁺ (wt %)
0.25	0.93
0.50	1.66
0.62	1.96
0.75	2.07
1.00	2.10

^a The weights of silica gel and ethanol/0.1N NaOH (1 : 1, w/w) in each case were 2.5 and 10.0 g, respectively. The reaction was run under reflux conditions for 8 h.

explore lower concentrations of HCl. However, in the case of base catalysis, the reaction became more rapid as shown by the data in Table IV. Using the same proportions of reactants as for the acid-catalyzed reaction, it was observed that 0.1N NaOH led to a weight percentage of Cl⁺ loading of 2.1 after an 8-h reaction. In contrast, a higher concentration of NaOH (1N) gave a maximum loading of only 1.0 wt % Cl⁺, which was independent of time over 5 h of reaction. Basic conditions are known to decompose the hydantoin ring, so it is recommended that the concentration of NaOH be kept low (0.1–0.2N) for the coating procedure. Clearly, base catalysis is preferable to acid catalysis in producing a coating capable of maximum chlorine loading in a relatively brief reaction time. Table V shows that as the amount of **Poly-I** relative to silica gel [2.5 g in 10.0 g ethanol/0.1N NaOH (1 : 1, w/w) reacting for 8 h] was increased, the obtainable Cl⁺ weight percentage loadings increased as expected to a constant value of 2.1 when the surface sites were exhausted.

Polymerization of **I** directly on silica gel particles

Monomer **I** can be readily polymerized in acidic solution, and the resulting oligomer is not soluble in the acidic solution such that it precipitates onto the silica

TABLE IV
Coating Efficiency of Poly-I on Silica Gel under Basic Conditions as Function of Reaction Time

Reaction time (h) in 0.1N NaOH ^a	Titred Cl ⁺ (wt %)	Reaction time (h) in 0.2N NaOH ^a	Titred Cl ⁺ (wt %)	Reaction time (h) in 1.0N NaOH ^a	Titred Cl ⁺ (wt %)
1	0.45	1	0.86	1	1.03
2	0.87	2	1.31	2	1.04
3	1.36	3	1.79	3	1.03
4	1.58	4	1.81	4	1.04
5	1.85	5	ND	5	1.02
8	2.07	8	ND	8	ND
10	1.97	10	ND	10	ND

ND, no determination.

^a The weights of silica gel, **Poly-I**, and ethanol/0.1–1.0N NaOH (1 : 1, w/w) in each case were 2.5, 0.75, and 10.0 g, respectively. The reaction was run under reflux conditions.

TABLE VI
Polymerization Efficiency of Monomer I on Silica Gel as
Function of Concentration of I

I (g) ^a	Titrated Cl ⁺ (wt %)
0.25	0.68
0.50	1.26
0.75	1.61
1.00	1.90
1.25	2.12

^a The weights of silica gel and 0.1N HCl in each case were 2.5 and 5.0 g, respectively. The reaction was run at ambient temperature for 20 h.

gel particles if they are present during the polymerization. This presents a second means of reaction of a form of **Poly-I** with the silica gel. Tables VI and VII present data concerning polymerization of **I** in the presence of silica gel. For Table VI the concentration of **I** was varied from 0.25 to 1.25 g in the presence of 2.5 g silica gel in 5.0 g of 0.1N HCl with a fixed time of reaction of 20 h at ambient temperature. For Table VII 0.75 g of **I** was polymerized in 5.0 g of 0.1N HCl in the presence of 2.5 g of silica gel at ambient temperature for 4–28 h. The data in both tables are consistent with the results for prepolymerization of **I** to form **Poly-I** before coating on silica gel as in Table III. It should be noted that polymerization of **I** in the presence of silica gel and NaOH does not work well because **Poly-I** itself does not form efficiently in the presence of a base.

Stability of chlorinated coatings under flowing water conditions

The adhesions of the hydantoinylsiloxane coatings and the stabilities of chlorine upon them, as well as chlorine regeneration capabilities, were evaluated in flowing water experiments. For columns packed identically to the ones described in the biocidal efficacy section, about 50 L of distilled deionized water were flowed through continually for a period of about 168 h

TABLE VII
Polymerization Efficiency of Monomer I on Silica Gel as
Function of Reaction Time

Reaction time (h) ^a	Titrated Cl ⁺ (wt %)
4	1.11
8	1.38
12	1.46
16	1.61
20	1.74
24	1.69
28	1.74

^a The weights of silica gel **I**, and 0.1N HCl in each case were 2.5, 0.75, and 5.0 g, respectively. The reaction was run at ambient temperature.

TABLE VIII
Stability of Coated Silica Gel Particles under Flowing
Water Conditions

Coating material ^a	Time of flow (h)	Titrated Cl ⁺ (wt %) ^b	Titrated Cl ⁺ (wt %) ^c
II-Cl	0	1.05	
	168	1.02	1.04
Poly-II-Cl	0	2.05	
	168	1.98	2.03
Poly-III-Cl	0	1.72	
	168	1.64	1.68

^a The material was packed into a glass column (see text).

^b The chlorine loadings were measured before and after flowing distilled, deionized water through the column at a rate of about 5 mL/min.

^c The chlorine loadings were measured after recharging the material in the column with household bleach (see text).

by gravity feed (5 mL/min). Iodometric/thiosulfate titration was used to measure the weight percentages of Cl⁺ at the beginning and the end of the experiment, as well as after a rechlorination procedure for each of the columns. The concentration of free chlorine measured as Cl⁺ in the effluent water was always below 0.2 mg/L. The results of the experiment are presented in Table VIII. As can be seen, very little Cl⁺ was lost from the coated silica gel particles during the 168-h period (about 4%), and the fact that much of the Cl⁺ could be replaced upon rechlorination indicates that the coatings remain well adhered to the silica gel particles in the presence of flowing water, at least at the flow rate employed.

Biocidal efficacy evaluation

Typical data for the efficacy of the coated silica gel samples against *S. aureus* in pH 7.0 buffered distilled deionized water are presented in Table IX. Although the control silica gel columns (uncoated, coated with **II**, coated with **Poly-II**, and coated with **Poly-III**) did produce some filtration of the bacteria (e.g., 0–1.6 log reductions over the first 10 s), it is clear that the chlorinated coatings were efficacious at inactivation within 10 s of contact for **Poly-II-Cl** and **Poly-III-Cl**, because complete log reductions of greater than 6 were obtained. Only the monomer **II-Cl** coated silica gel that contained only 1.03 wt % Cl⁺ was unable to achieve a complete inactivation within 10 s; it required 10–30 s for a 7.1 log reduction of *S. aureus*. Live bacteria could be recovered from the control columns, but not the chlorinated ones, so a true inactivation phenomenon was observed for the chlorinated silica gel particles. In contrast, in the previous work for coated sand, contact times on the order of 1 min were required for complete inactivation.²⁰ As expected, the increased surface area, exhibiting more chlorine binding sites for the silica gel than for sand, leads to greater

efficacy in the inactivation of pathogens. The performance of materials coated with *N*-halamine monomers or polymers may be expected to be directly related to the surface area and chlorine binding-site concentration. Such materials should be designed with the application in mind, that is, cost, desired performance, and so forth.

Efficacy data for *E. coli* O157:H7 are provided in Table X. As for the case of coated sand controls,²⁰ the *E. coli* O157:H7 bacterial cells were filtered to a lesser extent by the controls than were the *S. aureus* organisms. This is probably attributable to the different sizes and shapes of the two bacteria. The chlorinated coatings all produced complete inactivations of *E. coli* O157:H7 within at least 30 s, with **Poly-II-Cl** being efficacious within 10 s. Prior work demonstrated that *E. coli* O157:H7 is slightly more difficult to inactivate by *N*-halamines than is *S. aureus*, probably because of the more complex cell wall structure for Gram-negative *E. coli* O157:H7 than for Gram-positive *S. aureus*.²⁰

CONCLUSIONS

We demonstrated that a hydantoinylsiloxane in either monomeric or polymeric form can be employed to

TABLE IX
Biocidal Efficacy Against *S. aureus*

Coating material/chorine loading	Contact time (s)	Log reduction ^a
Silica gel control 0 wt % Cl ⁺	10	0.02
	30	0.10
	60	0.15
II 0 wt % Cl ⁺	10	0.42
	30	1.72
	60	1.81
II-Cl 1.03 wt % Cl ⁺	10	3.52
	30	7.12
	60	7.12
Silica gel control 0 wt % Cl ⁺	10	1.13
	30	1.32
	60	1.34
Poly-II 0 wt % Cl ⁺	10	0.65
	30	1.28
	60	1.44
Poly-II-Cl 2.07 wt % Cl ⁺	10	6.52
	30	6.52
	60	6.52
Silica gel control 0 wt % Cl ⁺	10	0.82
	30	0.97
	60	1.56
Poly-III 0 wt % Cl ⁺	10	1.59
	30	1.62
	60	2.48
Poly-III-Cl 1.70 wt % Cl ⁺	10	6.22
	30	6.22
	60	6.22

^a The bacterial exposure to the columns varied from 1.7 × 10⁶ to 1.3 × 10⁷ colony forming units.

TABLE X
Biocidal Efficacy Against *E. coli* O157:H7

Coating material/chorine loading	Contact time (s)	Log reduction ^a
Silica gel control 0 wt % Cl ⁺	10	0.13
	30	0.09
	60	0.14
II 0 wt % Cl ⁺	10	0.03
	30	0.05
	60	0.06
II-Cl 1.03 wt % Cl ⁺	10	4.04
	30	7.17
	60	7.17
Silica gel control 0 wt % Cl ⁺	10	0.06
	30	0.15
	60	0.31
Poly-II 0 wt % Cl ⁺	10	0.26
	30	0.43
	60	0.60
Poly-II-Cl 2.07 wt % Cl ⁺	10	7.09
	30	7.09
	60	7.09
Silica gel control 0 wt % Cl ⁺	10	0.20
	30	0.31
	60	0.48
Poly-III 0 wt % Cl ⁺	10	0.16
	30	0.22
	60	0.58
Poly-III-Cl 1.70 wt % Cl ⁺	10	2.97
	30	6.27
	60	6.27

^a The bacterial exposure to the columns varied from 1.9 × 10⁶ to 1.5 × 10⁷ colony forming units.

coat particles of silica gel through covalent bonding. Upon chlorination with aqueous solutions of household bleach, the coated silica gel particles became biocidal. In a column experiment, three types of coatings were able to inactivate *S. aureus* and *E. coli* O157:H7 in contact times of 0–30 s. The coatings were quite stable to flowing water and could be rechlorinated upon loss of oxidative chlorine. Biocidal silica gel should find applications in disinfection of flowing water in industrial and medical applications.

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