



Potential evaluation and perspectives on using sponge-like superabsorbent cryogels for onsite water treatment in emergencies

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ABSTRACT

This paper reports and discusses the prospects of a novel approach for emergency water treatment using antibacterial PSA/Ag cryogels. The approach involves allowing the cryogel to swell in contaminated water after which the disinfected water can be recovered by a simple squeezing step. Employing this process allowed the cryogels to achieve enhanced disinfection compared to other Ag-modified materials. The cryogels could achieve more than two logs (99%) bacterial inactivation in natural water samples. The cryogels were robust and showed stable disinfection performance over 10 cycles indicating that they were highly reusable. These results indicate that the PSA/Ag cryogels offer excellent potential for applications requiring potable water production in response to emergencies or disasters.

Keywords: Cryogels; Disaster-relief; Disinfection; Emergency; Hydrogels; Potable water

1. Introduction

Providing a potable water supply to the affected population is among the first priorities after the occurrence of disasters that impact the infrastructure required to supply basic needs [1]. However, treating water in emergencies is challenging as it might be constrained by the absence of electrical power, skilled

personnel, and limited ingress and egress [2]. In light of the increasing frequency and intensity of global natural disasters [3], there is interest in developing compact and easily deployable emergency water technologies with simple and relatively low-energy operation.

This paper reports a new strategy for emergency water treatment enabled by the fabrication of superabsorbent cryogels. Cryogels are macroporous hydrogels that are capable of absorbing a large

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amount of water. Due to their high porosity, most of the absorbed water exists as free water that can be released via manual compression [4–7]. Cryogels can be further functionalized with antimicrobial agents such as silver nanoparticles (AgNPs) to impart antimicrobial properties [8–11]. These unique properties of cryogels inspired us to apply them as a sorbent to disinfect water. The present method offers the simplicity of allowing the cryogel to swell in contaminated water after which the disinfected water can be recovered by a simple squeezing step. In addition, these cryogels are lightweight allowing them to be rapidly deployed for emergency drinking water response.

The first part of this paper provides some background on the rationale for using cryogels for emergency water treatment. In particular, a substantial portion of this section is devoted to a review of existing Ag-modified composite materials for point-of-use water disinfection to provide the context for the novel approach for water treatment using cryogels. In the subsequent section, new findings regarding the use of the cryogels for treatment of natural water samples and their reusability are presented. Lastly, the potential use of the cryogels in disaster-relief applications and insights into their end-of-life handling as well as future work are discussed.

2. Rationale for using cryogels for emergency water treatment

In order to apply the as-synthesized materials as water sorbents and disinfectants, they must exhibit the following properties (in addition to having effective bacterial inactivation) for practical applications involving emergency drinking water response: (i) fast swelling, (ii) significant swelling degree, (iii) mechanical robustness, and (iv) high recovery rate of absorbed water. Note that a fast swelling rate is desirable because it reduces the treatment time required while a significant swelling degree and a high water recovery allow a greater amount of water to be recovered per unit dry mass of the material that reduces the freight requirement. Furthermore, the material should be robust so that it can be reused in multiple cycles to provide a sustainable water supply to the affected population.

Cryogels are macroporous polymeric networks formed in semi-frozen systems in which the ice crystals (for aqueous systems) function as the porogens [12–14]. They can meet all the aforementioned criteria due to their unique pore structure. Cryogels can typically reach their equilibrium swollen state in less than a minute, while conventional hydrogels (non-porous) take hours [15,16]. The fast swelling behavior of cryogels is attributed to their open interconnected

pores that allow convective transport of water molecules into and out of the cryogel. Furthermore, cryogels can withstand extensive deformation due to the cryo-concentration effect that results in dense pore walls. Cryo-concentration is the accumulation of dissolved solutes in the unfrozen liquid microphase (UFLP) as water molecules start to freeze. Note that there is a fraction of the water that is not frozen below the bulk freezing point due to the freezing-point depression as the consequence of the dissolved solutes being concentrated in the UFLP [17]. Cryogelation can be used to fabricate gels having various shapes and sizes [18]. However, the mode of gelation must be “freezing before gelation” in order to obtain robust cryogels that swell rapidly and substantially [19,20].

We have previously found that by systematically tuning the synthesis conditions, cryogels with tailored properties could be prepared. Robust cryogels having high elasticity were prepared; they could withstand oscillatory swelling–deswelling cycles while maintaining their integrity. In addition, these cryogels could swell up to 200 g/g (i.e. grams of water per gram of dry cryogel) within 15 s [19]. This means that about 3 g of the cryogel are sufficient to produce 500 mL of water in a single squeeze cycle.

The excellent mechanical and water absorption properties of these cryogels in combination with the antibacterial AgNPs allow them to be used in a sponge-like manner that offer a simpler approach for emergency water treatment in contrast to existing methods (Table 1). In particular, operation in the column mode requires the use of sophisticated pumping systems for operational control that may be challenging under limited conditions. Filtration-based systems (such as those using filters or membranes) tend to have long treatment times due to difficulty in controlling percolation time and the lack of porosity of the materials used. Furthermore, our poly(sodium acrylate) (PSA) cryogels decorated with AgNPs show substantially improved disinfection efficiency in comparison to other Ag-modified composite materials that is thought to be largely attributed to their high porosity and fast water absorption/desorption properties. Further details on the comparison of other Ag composites materials with our PSA/Ag cryogels can be found in Table 1.

3. Experimental details

3.1. Fabrication of poly(sodium acrylate) (PSA) cryogels

PSA cryogels were synthesized according our previously reported protocol [19]. Briefly, a degassed

Table 1

Summary of the performance of Ag-modified materials for point-of-use water disinfection

Material	Operation mode	Bacterial inactivation efficiency (LRV/min) ^a	Advantages	Disadvantages	Reference
Polymeric spheres containing AgNPs	Batch	0.04	Easy to deploy due to its lightweight	Need filtration to recover the polymeric spheres after treatment; low antibacterial efficiency	[38]
Ceramic filters impregnated with AgNPs	Filtration (gravity)	0.04	Ceramic filter is inexpensive and robust	Low water throughput; filter prone to clogging; low antibacterial efficiency	[39]
Carbon foams impregnated with AgNPs	Filtration	0.1	Easy to deploy due to its lightweight; can achieve high water throughput	Need pumping system and good operational control; relatively low antibacterial efficiency—several recirculation cycles may be required to achieve the desired disinfection level	[40]
Magnetized nanoscavengers containing AgNPs	Batch (recovery using magnetic trapping)	0.2	Capping layer can be functionalized to degrade organics or adsorb heavy metal ions	Need magnetic field and additional time to recover nanoscavengers after treatment; relatively low antibacterial efficiency	[41]
Fibrous ion-exchange polymer containing AgNPs	Column	0.5	Easy to deploy due to its lightweight; can have high Ag-content due to its high ion-exchange capacity	Need pumping system and good operational control; relatively low antibacterial efficiency—several recirculation cycles may be required to achieve the desired disinfection level	[23,42,43]
AgNPs coated resin gel beads	Column	0.5	Good antibacterial activity during initial use; easy to deploy due to its lightweight	Need pumping system and good operational control; antibacterial properties deteriorate substantively after breakthrough	[44]
Activated carbon impregnated with AgNPs	Batch	0.7	Easy to deploy due to its lightweight	Activated carbon is expensive; need filtration to recover the activated carbon after treatment	[45]
AgNPs-impregnated paper	Filtration (gravity)	0.8	Low-cost support material; easy to deploy and highly portable	Relatively long treatment time (10 min of average percolation time); reusability may be limited by the durability of the papers used	[46]
AgNPs-coated polyurethane foam	Batch and column	1.2	High water throughput; robust support material; easy to deploy and highly portable	Stability of the AgNPs incorporated unclear	[47]
Silica beads	Column	1.2	Easy to deploy due to its lightweight	Need pumping system and good operational control	[48,49]
Fiberglass mats impregnated with Ag/Fe ₂ O ₃	Batch and column	2	Easy to deploy due to its lightweight	Need pumping system and good operational control for column operation	[50]

(Continued)

Table 1
(Continued)

Material	Operation mode	Bacterial inactivation efficiency (LRV/min) ^a	Advantages	Disadvantages	Reference
Alginate beads containing AgNPs	Column	6	Simple synthesis of alginate beads; high water throughput; can be easy to deploy due to the lightweight of dried gels; rapid bacterial disinfection	Need pumping system and good operational control; washing of excess reagent may be difficult due to the nonporous structure; dried gel beads may take a long time to re-swell to equilibrium for column operation	[51]
Polyurethane sponge or cotton textile coated with carbon nanotubes and Ag nanowires	Filtration (with electric field)	360	Low-cost support materials; rapid bacterial disinfection; easy to deploy due to its lightweight	Need electricity to achieve high rate of disinfection (electroporation); need pumping system and good operational control; relatively low water throughput	[52,53]
PSA/Ag cryogels	Batch (with squeezing)	26	Rapid bacterial disinfection; easy to deploy due to its lightweight; high water throughput; washing of excess reagents is easy due to the porous network and elasticity of cryogels	More tests are being carried out to study the durability and disinfection of contaminated water collected from lakes, wells, and rain run-off	[54]

^aThe bacterial inactivation efficiency was calculated by normalizing the highest bacterial (*E. coli*) inactivation reported in the papers with respect to their average contact time or time taken to achieve the log reduction value (the longer time was used for calculation).

and chilled reaction mixture containing sodium acrylate (SA, 97%, Sigma–Aldrich) and *N,N'*-methylenebis (acrylamide) (MBA, 99%, Sigma–Aldrich) were mixed with ammonium persulfate (APS, 98% purity, Sigma–Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, ≥99%, Sigma–Aldrich). The concentrations of APS and TEMED in the final reaction mixture were 1.75 mM and 0.125% (v/v), respectively. The total monomer (SA + MBA) concentration used was 8% at a crosslinker ratio of 0.05 (mol MBA/mol SA). The resulting reaction mixture was transferred into several 3-mL poly(propylene) syringes that were then placed into a bath fluid (−20°C, 1:1 mixture of ethylene glycol/MilliQ water) and incubated in an ultra-low temperature freezer (Eutra ED-FU4100). After 24 h, the PSA cryogels were thoroughly washed in MilliQ water (18.2 MΩ·cm at 25°C) and dehydrated in *t*-butanol followed by drying in a freeze-dryer (Alpha 1-4LD, −45°C). The dried cryogels were subsequently cut into cylindrical disks of 5 mm in diameter and length.

3.2. Fabrication of PSA cryogels and PSA/Ag cryogels

PSA/Ag cryogels were prepared using the intermatrix synthesis method [21]. For the preparation of PSA/Ag cryogels used in this study, 1 g of the dried PSA cryogel was allowed to swell in a 250 mL solution of 10 mM AgNO₃ (≥98%, Merck) during which the suspension was shaken at 120 rpm on an orbital shaker for 24 h in the dark. The cryogels were then immersed in a 250 mL solution of 100 mM NaBH₄ (Alfa Aesar) to form AgNPs. The resultant nanocomposites were thoroughly washed by immersion in MilliQ water followed by vacuum filtration. After three repetitions of the washing step, the nanocomposites were dried using the same procedure that was used for the PSA cryogels. This formed a PSA/Ag cryogel having an Ag content of 167 mg/g.

3.3. Characterization of cryogel nanocomposites

An energy-dispersive X-ray spectroscopy detector (EDX) attached to a field emission scanning electron

microscope (FESEM, JEOL 6340F) was used to conduct a line-scan analysis for the determination of the elemental Ag distribution along a PSA/Ag cryogel cross-section. The morphology and size of the AgNPs were studied using a transmission electron microscope (TEM, Carl Zeiss Libra 120 Plus) at an accelerating voltage of 120 kV. ImageJ software was used to analyze the TEM images for determination of the AgNP-size distribution.

3.4. Disinfection tests

Two raw water samples representing turbid and clear water were obtained from a freshwater pond on the campus of Nanyang Technological University and a dechlorinated tap water, respectively. The raw water quality metrics were characterized using a pH meter (Cyberscan 6000, Eutech Instruments), total organic carbon (TOC) analyzer (TOC-V_{CSH}, Shimadzu), and turbidity meter (Hach 2100N). For the TOC determination, samples were filtered through a 0.45 μm syringe filter (Pall) prior to analysis. At least triplicate experiments were conducted for the measurements. Table 2 summarizes the key raw water quality metrics of the samples.

The raw water samples were spiked with 10⁴ colony-forming units per mL (cfu/mL) of *Escherichia coli* (ATCC[®] 25922TM) to increase their bacterial loading. A 0.02 g cryogel sample was added into 10 mL of the spiked raw water samples. After 15 s of swelling in the bacterial suspension, the swollen cryogels were immediately collected and squeezed to obtain the treated water. 100 μL samples of both the raw and treated water were spread on agar plates after appropriate dilution followed by a 24-h incubation at 37°C before enumeration. Six replicates were conducted for the disinfection experiment.

3.5. Analytical methods for Ag determination

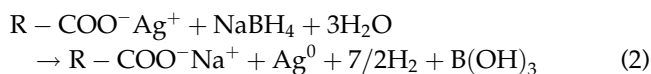
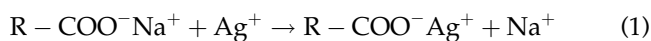
Samples were digested in HNO₃ (67%, Merck) at 150°C for 30 min in a digester unit (Hach DRB 200)

prior to total Ag analyses using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Perkin Elmer Optima 2000DV). Triplicate experiments were conducted.

4. Results and discussion

4.1. Intermatrix synthesis and characterization of PSA/Ag cryogels

As shown in Fig. 1 the preparation of the PSA/Ag cryogels is simple and highly scalable. Intermatrix synthesis of the PSA/Ag cryogels involves sequential equilibration of pre-formed PSA cryogels in AgNO₃ solution followed by *in situ* borohydride reduction as represented by the equations below [21]:



This synthesis method formed AgNPs that are mostly located near the surface of the cryogels as evidenced by the EDX line-scan profile of a PSA/Ag cryogel cross-section that shows the Ag peak having a significantly higher intensity on the edges of cryogels (Fig. 2(a) and (b)).

It is unlikely that diffusional processes limited the penetration depth of Ag⁺ or BH₄⁻ into the cryogel in view of the high porosity of the cryogel. A more likely explanation for this observation could be the Donnan exclusion effect [22]; the presence of a large number of negative charges (due to carboxylate groups) on the PSA cryogels could have impeded a deep diffusion of the negatively charged borohydride ions into the polymer matrix that preferentially form AgNPs on the surface of the cryogels [23–25]. Impregnation of the AgNPs on the external surface is desirable because it allows enhanced contact with the bacterial cells

Table 2
Summary of water quality metrics of the two raw water samples

Water quality metric	Turbid water ^a	Clear water ^b
Turbidity (NTU)	36.9 ± 4.6	0.5 ± 0.2
Total organic carbon (mg-C/L)	3.3 ± 0.3	1.6 ± 0.1
pH	6.3 ± 0.2	6.6 ± 0.2
Bacterial count (cfu/mL)	260 ± 70	Not detectable

^aWater sample collected from a freshwater pond on the campus of Nanyang Technological University.

^bDechlorinated water sample collected from water tap in our laboratory.

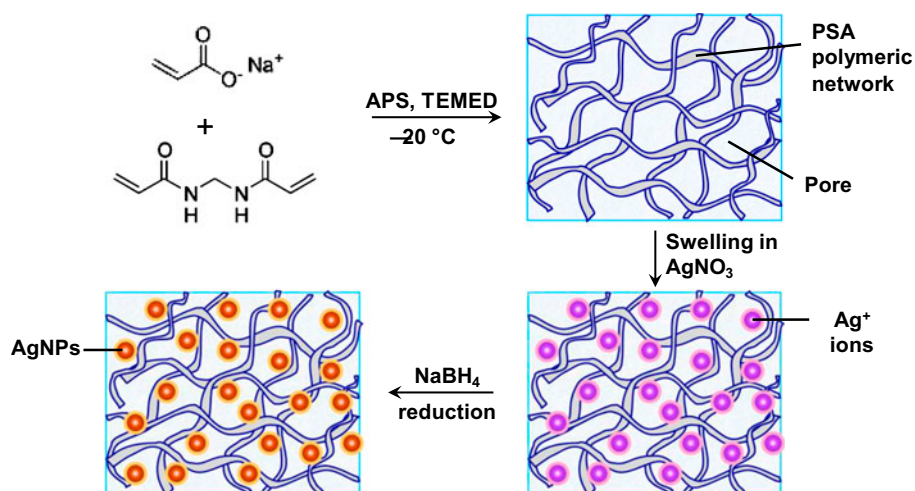


Fig. 1. Schematic summarizing the synthesis of PSA/Ag cryogels.

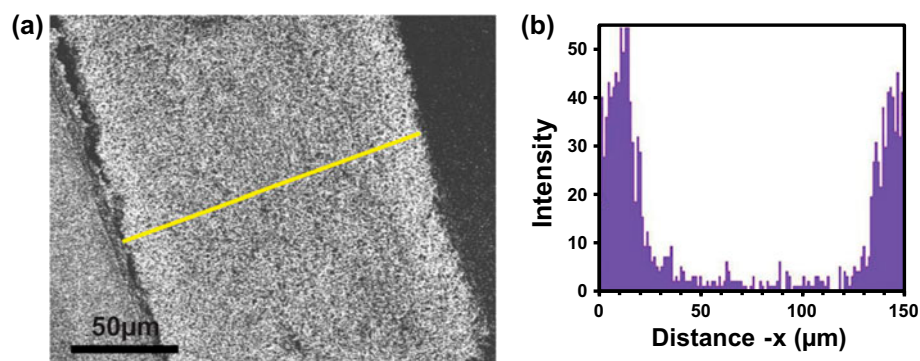


Fig. 2. (a) FESEM image of a longitudinal cross-section of a PSA/Ag cryogel. (b) EDX line-scan profile of Ag in the cryogel cross-section as indicated by the yellow line in (a).

thereby improving the disinfection efficacies of the cryogels.

The TEM image in Fig. 3 shows the morphology of the PSA cryogel impregnated with the AgNPs. This method formed well-dispersed and fine AgNPs most of which are smaller than 10 nm (Fig. 3(b)). This in combination with the highly interconnected porous network of the cryogels and surface distribution of the AgNPs results in the exposure of a high surface area of bioactive Ag species that would enhance the contact between the bacterial cells and bioactive Ag species for their effective inactivation.

4.2. Disinfection efficacies and reusability of PSA/Ag cryogels

Fig. 4(a) shows the proposed approach in which the cryogels can be used in a sponge-like manner to produce potable water under difficult circumstances.

We have previously found that employing the process in Fig. 4(a) enabled the cryogels to substantively reduce the turbidity (by 80–90%) of the feed by selectively absorbing/desorbing water [19]. With the PSA/Ag cryogels, the process involves (i) allowing the cryogel to swell in contaminated water during which the bacterial cells are inactivated after getting into close contact with the bioactive Ag species that are densely decorated on the cryogel pore surfaces, and (ii) recovering the disinfected water by squeezing the swollen cryogel (Fig. 4(a)). This process allowed the PSA/Ag cryogels to achieve enhanced disinfection because the bacterial cells get into close contact with the Ag species on the cryogel; note that it was recently found that intimate surface contact between bacterial cells and AgNPs led to enhanced toxicity [26].

Although we have shown the high antibacterial efficacies of the PSA/Ag cryogels in our previous work, their disinfection of natural water samples

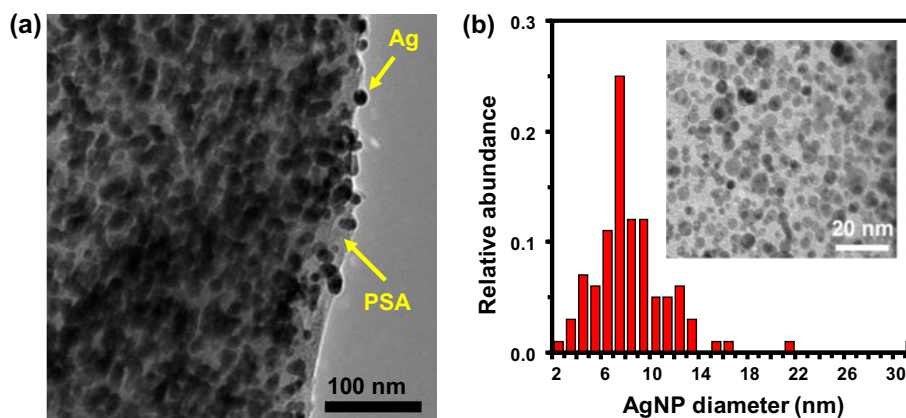


Fig. 3. (a) TEM image of a thin section of a PSA/Ag cryogel. (b) AgNP-size distribution with inset showing a typical TEM image used for analysis.

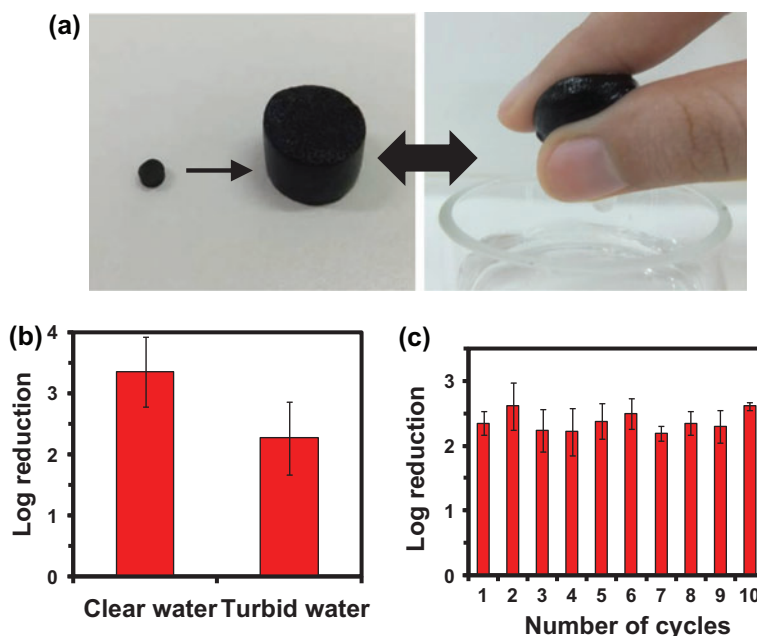


Fig. 4. (a) Photographs depicting the novel approach of using PSA/Ag cryogels to disinfect water: (i) water absorption by a cryogel and (ii) recovery of treated water via squeezing. (b) Bacterial inactivation in turbid and clear water samples. (c) Disinfection of turbid water samples by PSA/Ag cryogels over ten cycles.

needs to be studied due to potential complication by complex solution chemistry. For the disinfection tests, two types of water samples namely, pond water and tap water were used to represent turbid and clear water in the natural environment. Both the raw water samples were spiked with 10^4 cfu/mL of *E. coli* to study the disinfection efficacies of the PSA/Ag cryogels in the two water samples under high bacterial loadings. Fig. 4(b) shows that the PSA/Ag cryogels, after being allowed to swell in the contaminated water

for 15 s, could achieve more than two logs (99%) bacterial inactivation of both the raw water samples. This shows that the PSA/Ag cryogels have good potential for treatment of contaminated water. However, the presence of natural organic matters (NOMs) and suspended solids apparently had an adverse effect on the antibacterial activity of the cryogel as evidenced by the lower bacterial inactivation in the turbid water relative to the clear water (Fig. 4(b)). Note that in addition to having a higher turbidity, the “turbid water”

also has a higher TOC value indicating the presence of a greater amount of NOMs (Table 2).

The reduced disinfection efficacies in the presence of NOMs and suspended solids is probably due to their interactions with the bioactive Ag species (both AgNPs and Ag⁺) that consequently limit the contact between bacterial cells and the Ag species preventing the inactivation of the bacterial cells to take effect [27–30]. It is envisaged that deactivation of the Ag species in the presence of NOMs and suspended solids occur via: (i) shielding of the pathogenic microbes from the Ag species due to sorption of the NOMs or suspended solids on the surface of the bacterial cells, (ii) sorption of NOMs and suspended solids on the surface of AgNPs that would lower the reactivity of the nanoparticle surface to a variety of reactions (e.g. reactive oxygen species generation, oxidative dissolution of Ag⁺, or specific interaction with bacterial cells) that are believed to be the possible biocidal mechanisms of AgNPs, and/or (iii) adsorption or partitioning of Ag⁺ by NOMs that reduces the amount of Ag that is bio-available to the bacterial cells in the solution. More detailed work is planned to further understand the effect of solution chemistry on the antibacterial properties as well as the Ag release behavior of the PSA/Ag cryogels.

The reusability of PSA/Ag cryogels was tested over ten disinfection cycles. Indeed, the cryogels showed stable disinfection performance over ten repetitions that indicates their high reusability. The AgNPs in the cryogels are highly stable that prevents uncontrolled release of Ag species into the treated water. The total Ag consumed in one disinfection cycle was ca. 0.1% of the Ag content in a fresh cryogel. A mass balance analysis indicates that the cryogel can be used up to 1,000 cycles provided that there is no mechanical degradation during squeezing to recover the treated water; this is equivalent to 150 L/g production capacity. Preliminary tests indicate that the cryogels have the ability to undergo multiple cycles of compression (data not shown). Detailed mechanical fatigue tests will be conducted in the future to investigate the limiting factor for repeated usage of the cryogel.

Disposal of used PSA/Ag should be avoided because Ag is a precious metal, and to avoid the potential of ecotoxicological impact on the environment [31]. The limiting factor for repeated use of the cryogel may either be deterioration in bacterial inactivation as a result of Ag loss or physical damage during squeezing. The disinfection efficacies of the cryogels can be restored by re-loading them with AgNPs if they remain mechanically robust. However, for physically damaged cryogels the residual Ag can be recovered by burning off the polymer scaffolds.

Future research can be directed at exploring alternative inorganic- or organic-based disinfectants [32–35]. In particular, antimicrobial polymers are advantageous due to their potential low-cost and high stability that minimizes the release of harmful species into treated water [36,37]. Finally, for practical applications, these cryogels can be incorporated into a portable and simple device that can be used for efficient recovery of treated water.

5. Conclusions

In this study we demonstrated a novel process for the use of superabsorbent cryogels decorated with silver nanoparticles for water disinfection. The cryogels were used to disinfect water by absorbing contaminated water after which the disinfected water was recovered via squeezing. The cryogels could inactivate more than two logs (99%) of the bacteria in the natural water samples and maintain their performance over ten repetitions. Furthermore, the cryogels have the robustness to be used in multiple cycles while maintaining their performance. Based on these results, we believe that the PSA/Ag cryogels have the potential to be deployed for emergency drinking water response. They can offer a simple alternative to treat water under limiting conditions. Furthermore, these cryogels are lightweight and highly portable allowing them to be easily deployed for emergency response.

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