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# Water disinfection with geopolymer–bentonite composite foam containing silver nanoparticles

Tero Luukkonen [a,*], Mohammad Bhuyan [b], Anna-Maria Hokajärvi [b], Tarja Pitkänen [b,c], Ilkka T. Miettinen [b]

[a] Fibre and Particle Engineering Research Unit, University of Oulu, Oulu, Finland
[b] Laboratory of Water Microbiology, Expert Microbiology Unit, Finnish Institute for Health and Welfare, P.O. Box 95, 70701 Kuopio, Finland
[c] Faculty of Veterinary Medicine, Department of Food Hygiene and Environmental Health, University of Helsinki, Helsinki, Finland

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ABSTRACT

Geopolymers resemble conventional ceramics but can be manufactured at near-ambient temperatures. In this work, geopolymer–bentonite composite foam with silver nanoparticles was prepared and applied for water disinfection, inspired by point-of-use ceramic water filters. The inactivation efficiency against *Escherichia coli* and intestinal enterococci bacteria was found to be promising (0.6–2.4 and 0.3–1.4 $\log_{10}$ reductions, respectively) for ~1 d. However, the inactivation efficiency against somatic coliphage viruses was poor (<0.05 $\log_{10}$). The geopolymer matrix did not alter the chemical water quality. Thus, the pH and the concentrations of Ag, Si, Al, and Na remained in compliance with drinking water guideline values, and the foam showed no physical disintegration. These results provide preliminary proof of concept of the suitability of geopolymer foam composites for point-of-use water disinfection.

## 1. Introduction

Ceramic silver-impregnated point-of-use drinking water filters are important for reducing the spread of waterborne pathogens in developing countries [1]. Ceramic filters can be prepared using abundantly available materials, commonly clay, water, and sawdust. Their manufacturing process is simple, and ceramic filters are relatively inexpensive (5–15 USD/filter) [2]. However, high-temperature firing of the filters contributes to smog formation and particulate matter emissions [3].

Geopolymers are ceramic-like materials formed by mixing an aluminosilicate precursor (e.g., calcined clays) with an alkali-activator solution (e.g., sodium hydroxide and/or silicate) and curing at near-ambient temperatures. Their nanostructure resembles that of zeolites but lacks long-range order [4]. Highly porous geopolymers can be obtained by introducing blowing agents (e.g., $H_2O_2$) and surfactants during preparation [5]. Furthermore, geopolymers can be modified to possess antimicrobial properties via, for example, an ion exchange of $Na^+/K^+$ to $Ag^+$ [6] or by preparing composites with nano $Ag^0$ [7]. Thus far, antimicrobial geopolymers have been considered mainly as coatings or construction materials.

In this work, geopolymer foam was prepared with bentonite containing nano-$Ag^0$ (ArgiBlock 001.ZnPy, Laboratorios Argenol). The composite foam was used as a filter with the goal of evaluating the potential for drinking water disinfection in terms of chemical and mechanical stability and inactivation of indicator microbes.

## 2. Materials and methods

### 2.1. Preparation of geopolymer–bentonite composite foam

The foam preparation was conducted according to [5], where the physical, chemical, and morphological properties of the foam are reported in detail. Metakaolin, ArgiBlock 001.ZnPy (with 1.93 wt-% of Ag), alkali-activator (87 wt-% of sodium silicate solution [Merck, $SiO_2 \approx$ 27 wt-%, $Na_2O \approx 8$ wt-%] and 13 wt-% NaOH pellets [VWR Chemicals]), and deionized water were mixed in a weight ratio of 1.00/0.16/1.36/0.18, respectively, for 5 min. $H_2O_2$ (Honeywell, 30%) and Triton X-100 (Sigma-Aldrich) were added at 1.75 and 0.12 wt-% of paste, respectively, and mixing was continued for 2 min. The paste was poured into a plastic column (height 99 mm, Ø = 44 mm) and cured at 60 °C for 4 h.

* Corresponding author.
*E-mail address:* tero.luukkonen@oulu.fi (T. Luukkonen).

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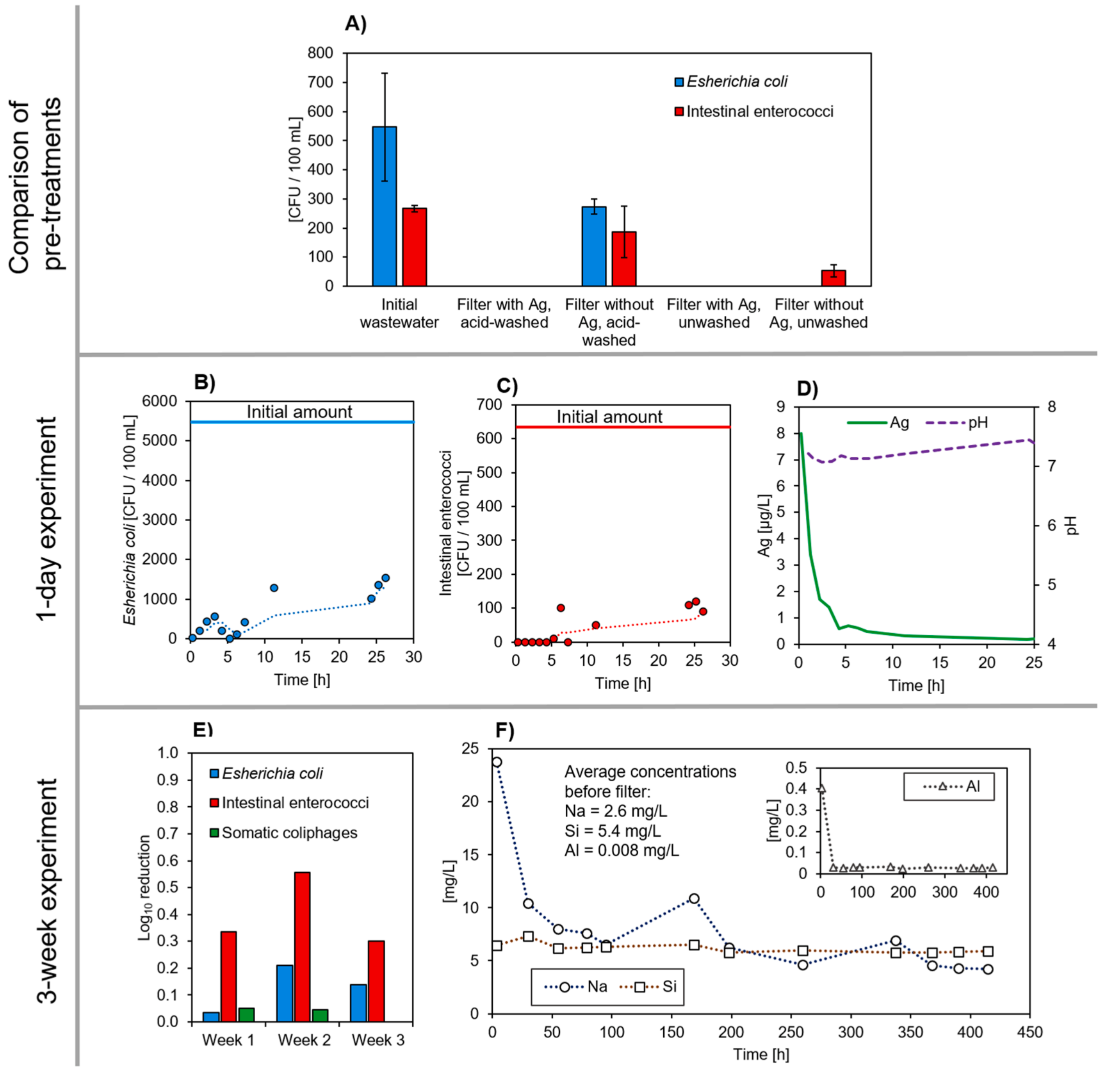


**Fig. 1.** Disinfection and leaching results: A) comparison of filters with or without Ag and acid washing, B-D) 1-day experiment, E-F) 3-week experiment.

### 2.2. Leaching evaluation and disinfection experiments

The column was connected to Teflon tubing (Ø = 2 mm) and a peristaltic pump (Gilson MINIPULS 3). The pore solution of the foam was neutralized by pumping 2 L of 0.1 M acetic acid (Merck) through the column (1 L/h) and flushing with deionized water. Effluent pH was monitored (Hach HQ11d/PHC10101) and leached Ag, Si, Al, and Na were analyzed following [8] using XSeries II ICP-MS (Thermo Fisher Scientific).

Tertiary-treated, non-disinfected municipal wastewater (from the Taskila wastewater treatment plant, Oulu, Finland) was pumped through the filter (1.0 L/h, empty bed contact time ~9 min) in two experiments: 1) filters with or without silver and acid flushing were compared and 2) a filter with silver and acid flushing was used for ~1 day. The third experiment lasted for three weeks, with continuous pumping of groundwater (1 L/h) with a weekly wastewater pulse (1 L) and sampling before and after the pulse. All samples were collected as duplicates or triplicates in sterilized bottles and analyzed for *Escherichia coli* and intestinal enterococci [9,10]. Samples from the three-week experiment were also analyzed for viral indicator somatic coliphages [11]. The filters were analyzed with an electron probe microanalyzer (JEOL JXA-8530FPlus) before and after the 3-week experiment to obtain elemental maps.

## 3. Results and discussion

The performance of differently pre-treated filters was evaluated after 2 h of wastewater pumping (Fig. 1A). The non-acid-washed filters decreased bacteria amounts likely due to the increased pH (up to 12.1). Filter without Ag and acid washing did not affect water pH, and thus the observed *E. coli* removal was possibly due to physical separation. The filter with Ag addition and acid washing resulted in a complete inactivation of *E. coli* and intestinal enterococci and, as it had no impact on the water pH, it was likely related to the presence of Ag.

The 1-day experiment (Fig. 1B-C) revealed an effective inactivation of *E. coli* and intestinal enterococci, especially during the first ~7 h (up to 2.4 and 1.4 $\log_{10}$ reductions, respectively). The leaching of Ag decreased sharply after ~4 h (cumulative leaching was ~4.6% of the added Ag up to this point) and then remained < 1 µg/L (Fig. 1D; ≤ 100 µg/L is acceptable for drinking water [12]). The pH of the water remained at 7.0–7.5.

The 3-week experiment (Fig. 1E-F) showed that the inactivation efficiency for *E. coli* and intestinal enterococci (0.03–0.2 and 0.3–0.6 $\log_{10}$ reductions, respectively) was lower in comparison to the 1-day experiment. This indicates that the short-term inactivation could have been partly due to initial silver leaching (Fig. 1D); in contrast, long-term Ag leaching was low during the 3-week experiment (constantly < 0.2 µg/L). The inactivation of somatic coliphage viruses was also evaluated but it

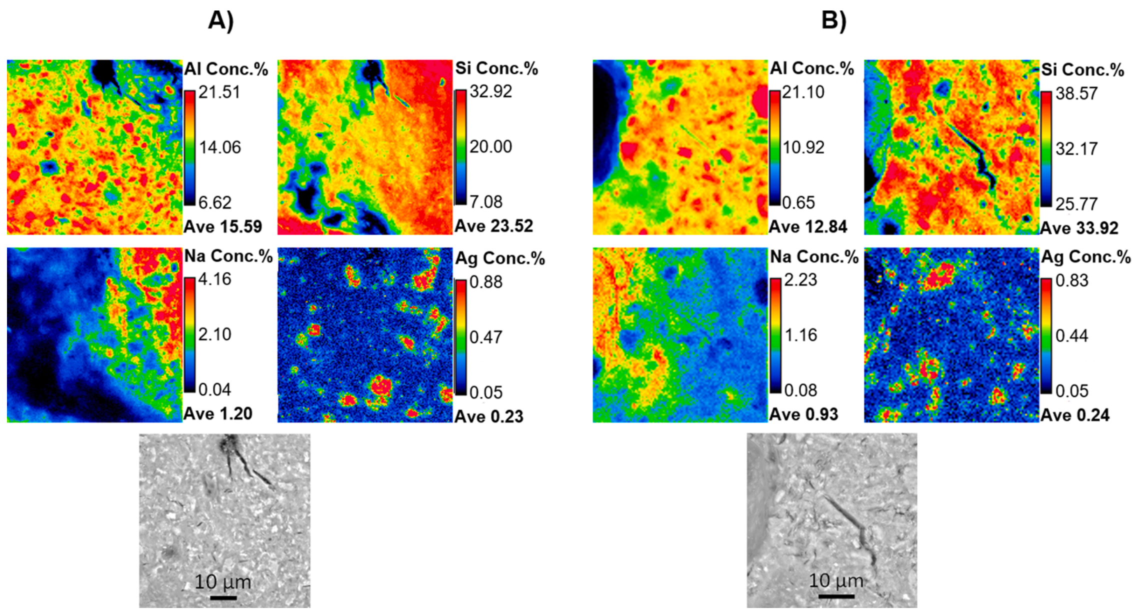


**Fig. 2.** Elemental maps of geopolymer foams after A) acid-flushing and B) the 3-week experiment.

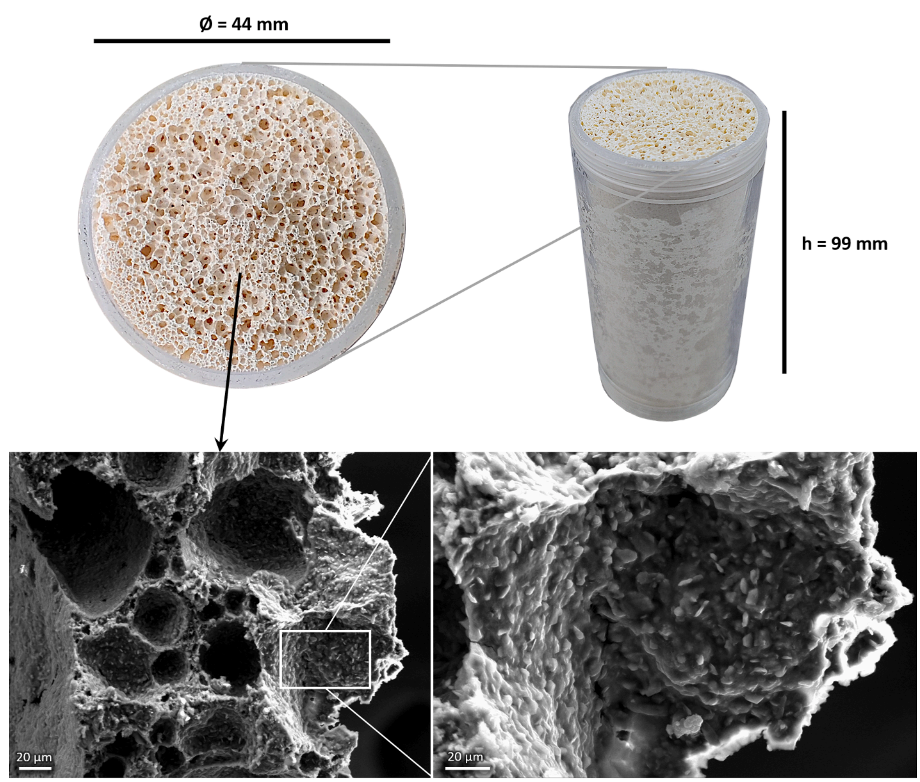


**Fig. 3.** Photographs and micrographs of geopolymer–bentonite composite foam.

was found to be poor (< 0.05 $\log_{10}$). The studied filter had a higher constant-head water permeability coefficient (0.009 cm/s) than typical ceramic filters (0.0014–0.0042 cm/s), as reported earlier [5]. Since physical separation also contributes to bacteria and virus removal and lower permeability provides more contact time with Ag, filter performance could be improved by decreasing porosity. Interestingly, intestinal enterococci inactivation was more efficient than *E. coli,* even though the former is smaller in size. This could be due to the differential persistence of these bacteria against metal ions [13], the motility of *E. coli* cells, and/or the active gene correction mechanisms present in *E. coli* that are missing from *Enterococcus* spp. [14,15]. The leaching of Al and Na remained in acceptable ranges for drinking water (for Si, no guideline value exists) (Fig. 1F) [12].

High-temperature ceramic point-of-use filters with Ag have been reported to result in an initial 3–4.5 $\log_{10}$ reduction for *E. coli* [16] with comparable Ag leaching to this work. However, similar to the present study, the inactivation rate decreased upon extended use, going down to 0.2 $\log_{10}$ but being revived by reapplying colloidal Ag to the surface [16]. Bacteriophage removal by ceramic filters has been reported to be over ten-fold higher than the results of the current study (0.6–0.9 $\log_{10}$

for MS2 after 5-week use) and, interestingly, this increased over time (1.1–1.8 $\log_{10}$ after 13-week use) [17].

The elemental maps taken before and after the 3-week experiment (Fig. 2) indicate no observable decrease in the Ag content. The variations in Al, Na, and Si could be related to surface heterogeneity. The bentonite particles were clearly visible in the pore walls of the composite foam, and they appeared to be uniformly distributed (Fig. 3).

## 4. Conclusions

Geopolymer-bentonite composite foam can potentially be used in a similar manner as high-temperature ceramics in point-of-use drinking water treatment. The geopolymer matrix containing a commercial bentonite with nano-$Ag^0$ appears to be chemically stable (in terms of Al, Ag, Na, Si, and $OH^-$ leaching) after an initial flushing with 0.1 M acetic acid. The disinfection performance of the foam was promising for the first day (0.6–2.4 and 0.3–1.4 log reductions for *E. coli* and intestinal enterococci, respectively) but diminished over three weeks of continuous use (0.03–0.2 and 0.3–0.6 log reductions of *E. coli* and intestinal enterococci, respectively). This could potentially be improved by selecting a different Ag-impregnation method, reapplying Ag to the surface of the filter, or decreasing the porosity (i.e., water permeability) to a level similar to that used in conventional ceramic point-of-use filters.

### *CRediT authorship contribution statement*

**Tero Luukkonen:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing – original draft, Visualization. **Mohammad Bhuyan:** Investigation, Writing – review & editing. **Anna-Maria Hokajärvi:** Investigation, Writing – review & editing. **Tarja Pitkänen:** Methodology, Writing – review & editing, Supervision. **Ilkka T. Miettinen:** Methodology, Writing – review & editing, Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### *Data availability*

The raw and processed data required to reproduce these findings are available for download from https://doi.org/10.23729/9b15aadf-bfc3-4199-9fca-679dfbf88516.

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