Chemical and Process Engineering: New Frontiers, 2025, 46(3), e103
DOI: 10.24425/cpe.2025.155541

Reduction of biofouling rate of water filters exposed to *Escherichia coli* by incorporating aluminosilicate-Ag composite particles into melt-blown media

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Article info:
Received: 03 May 2025
Revised: 22 July 2025
Accepted: 08 August 2025

Abstract
In this work, a preparation method of composite particles having bacteriostatic properties, which were subsequently incorporated into polymer filter media, is presented. The novel reliable method of antibacterial filter testing is proposed. The procedure of depositing silver nanoparticles on a support made of aluminosilicates was developed. The antibacterial properties, both bactericidal and bacteriostatic, against *Escherichia Coli*, commonly encountered in water, were verified in experiments. Maintaining thermal stability of additives and their antibacterial characteristics at high temperatures, relevant for the melt-blown processing, was also confirmed. The practical outcome of the research was incorporating composite particles into polymer fibers to reduce the rate of pressure drop (dP) increase after a long time of operation, which is often observed for water filters exposed to microorganisms. When compared to unmodified polypropylene structures, the time of reaching the terminal dP value in test conditions was increased by up to 80% and 185% for the filter media with an addition of raw mineral and composite particles, respectively. The results of water analysis confirmed the reduction of bacteria concentration and the stability of additive – neither particles incorporated into the fibers nor silver ions were detected downstream of the filter.

Keywords
modified melt-blown filters, water filtration, biofouling resistance, bacteriostatic additives, Ag-halloysite composite

1. INTRODUCTION

Water pollution is one of the greatest problems of civilization. The cleaning technologies, especially for emerging contaminants, often constitute a significant technical challenges that must be economically viable and consistent with an appropriate global water resources management strategy. The effects of various contaminants can be serious and long-lasting for both the environment and human health. In the face of industrial development and the emergence of new groups of pollutants, there is a constant need to search for new ways of purifying water that do not require expensive equipment and to keep the operating costs on a reasonable level. One of the threats is the presence of microorganisms, which in water environment have favorable conditions for existence and reproduction. Microorganisms, chemicals, heavy metals and other toxic compounds can lead to diseases and negatively affect aquatic ecosystems, disturbing their biological balance and reducing biodiversity. According to the World Water Development Report from 2024 (UNESCO, 2024), it is estimated that one quarter of humanity does not have permanent access to clean water, and 46 percent to basic sanitation facilities. One of the assumed goals is the so-called Sustainable Development Goal 6: "Ensure access to water and sanitation for all", which is to be achieved by 2030. Pollution also affects industry, generating several challenges for companies. In industrial processes, water is one of the most used media, and has a wide range of applications, being an energy carrier (heating, cooling), a solvent for many substances, a raw material or a product of chemical transformations. The source of water is most often surface water (e.g. rivers and lakes), which are exposed to various natural and industrial factors causing their pollution. Among the numerous components, aquatic environments and natural waters contain various bacteria and other microorganisms, which not only affect their viability for direct consumption, but can also result in serious operational issues in various industrial processes. The most common problems result from the intensive development of microorganisms in favorable conditions due to the formation of so-called biofilm, which often leads to covering devices and affects their operation (e.g. blocking filters, sorption beds, catalysts, heat exchange surfaces). Another common problem is microbiological corrosion, which is caused by the destructive effect of metabolites released by microorganisms into the environment. Bacterial growth can be prevented in various ways, e.g. by using chemical additives having antibacterial activity, UV sterilization, mechanical or ultrasonic cleaning of surfaces or creating low-adhesive coatings ensuring low adhesion to the surfaces covered with them, sometimes additionally with metal nanoparticles, e.g. silver, gold or copper, with confirmed and documented antibacterial effect against various microorganisms (Bergemann et al., 2017; Franci et al., 2015; Gu et al., 2021; Inkinen et al., 2017; Valdez-Salas et al., 2021; Zhan et al., 2022).

Bacteria have the ability to adhere to the surface of various materials, including filter media, and form a biofilm on them (Fig. 1). Microorganisms develop in it as colonies, creating a highly organized multicellular grouping (Desai et al., 2014; Łyszcz, 2020). They can be microorganisms of one or many species and types. Cells living in biofilm perform different functions and have different characteristics than those living freely. Its structure is stabilized by the extracellular matrix of polymeric substances (EPS) (Kołwzan, 2011). These substances create an impermeable layer and isolate the three-dimensional macrocolony of bacteria from the environment (Furowicz et al., 2010). Prokaryotes in the biofilm have higher resistance to disinfectants and antibiotics (Łyszcz, 2020). Biofilm formation is also the main reason for significant reduction of filter permeability as a result of EPS secretion, which often leads to formation of "sail-like" structures between the fibers, preferentially at their intersections (as presented in Fig. 1b).

Various bacteriostatic and bactericidal agents are used to limit the number and inhibit the growth of bacteria. Bacteriostatic compounds are substances that inhibit the growth and development of microorganisms by slowing down metabolic processes. As a result, bacterial proliferation is prevented, but this does not necessarily lead to cell death. Examples of such substances include antiseptics, detergents or preservatives, e.g. hydrogen peroxide, ethyl or isopropyl alcohols, chlorine or iodine. Bactericidal compounds, on the other hand, are substances that cause the death of microorganisms. They can cause damage to the cell membrane, which disrupts the integrity of the cell, and then inhibit the synthesis of bacterial proteins that are necessary for cell growth and division, or disrupt the synthesis of nucleic acids, which prevents DNA replication and RNA transcription. They can also deactivate enzymes or disrupt metabolism, which leads to the formation of toxic substances inside the cell (Walsh, 2003). These can be antibiotics, e.g. penicillin or metal particles, including silver nanoparticles (AgNPs). This noble metal has been used in medicine for many years as an antiseptic and antibacterial agent against Gram-positive and Gram-negative bacteria. Silver particles can physically interact with the cell surface and destroy the cell wall, as well as cause the disintegration of DNA chains, deactivate enzymes, denature proteins, disrupt ribosomes or generate reactive oxygen species (ROS) (Xu et al., 2020). Reactive oxygen species are an important element in the biological processes of organisms. They are produced as intermediate products in basic biochemical processes and should be reduced in subsequent transformations, but this is not always the case. In homeostasis conditions, they have many positive functions for the body, generally acting as mediators and regulators of metabolism. However, reactive oxygen species can also have a toxic effect on the body in a state of "oxidative stress". This is a phenomenon when ROS are produced in excessive amounts and antioxidant reserves are depleted. This leads to the oxidation of proteins and the triggering of chain reactions that intensify cell damage. Integral parts of the cell are destroyed, e.g. the cell membrane, enzymes, DNA strands, chromosomes, mitochondria, and cytoskeleton. This can cause damage inside the cell that is very difficult to restore (Łuszczewski et al., 2007).

The paper presents research on the developed method of synthesis of a bioactive additive and its introduction into fibrous material. The bacteriostatic effect of filters produced by the melt-blow technique was confirmed in experiments. Even in such "difficult" operating conditions as the test methodology used in comparative studies, a significant extension of the working time of modified elements was obtained when compared to unmodified filters (i.e. made of pure polypropylene). The use of such filters in filtration systems, especially closed water systems, in which the medium circulates multiple times through the filter as used in presented study, not only slows down the biofouling process, but also allows for a reduction in the number of living bacteria in the circulating water, which increases the safety of its use in downstream processes.

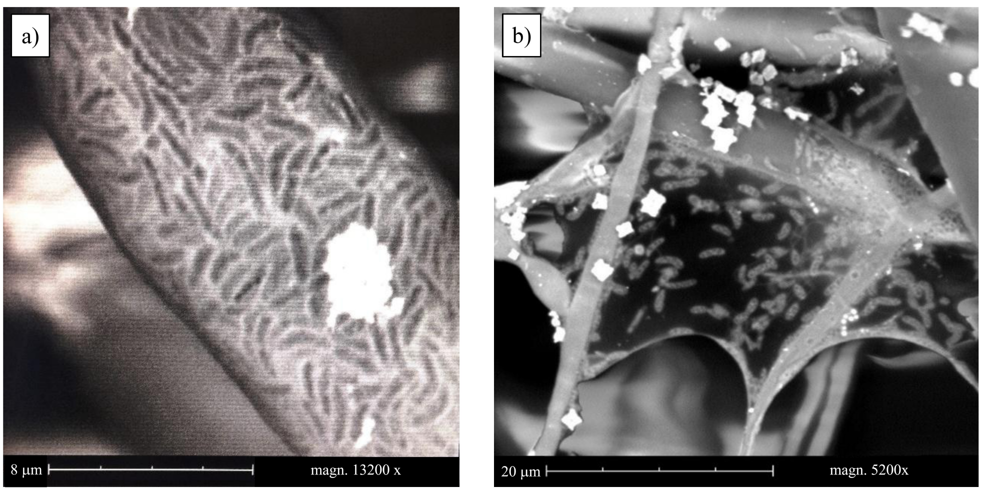

Figure 1. Biofilm formed by *Escherichia Coli* inside a fibrous filter media: a) on fiber surface, b) "sails" in the vicinity of fiber interception. Copyright © 2023 A. Krasiński.

2. MATERIALS AND METHODS

Various natural materials, including raw minerals or plant-derived media, serve as compounds used in water treatment processes. Some of them possess reasonable inherent functionality, for example as sorbents. The inorganic silica-based media are a wide range of materials that can be utilized for a variety of potential water applications. To this group belong kaolinites that comprise various structural forms of silica-aluminates. In recent years, special interest has been focused on halloysite – it offers unique features that can be utilized as a sorbent or the platform for deposition of various functional particles (such as photocatalytic or bioactive etc.). Halloysite is characterized by good mechanical strength, excellent chemical inertness and a well-developed surface (Filice et al., 2021). The general formula is: $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ (in hydrated form). The crystal structure of halloysite is defined as a structure formed by two layers: a corner-sharing tetrahedral SiO_4 and an edge-sharing octahedral AlO_6 (Atyaksheva and Kasyanov, 2021; Gray-Wannell et al., 2023; Papoulis, 2019). However, in the presented research the halloysite, which in form of nanotubes and nanoplates was present in the bulk, was not isolated from the raw fossil material – the crushed solids were used in its original form (selected size fraction as described below).

2.1. Synthesis of bioactive composite particles

The methodology of synthesis of a bioactive composite containing silver nanoparticles as described in (Zhang et al., 2013) was followed, although with some minor modifications introduced. The aluminosilicate granules from the Dunino mine (Poland), containing halloysite, were used in this work. A few variants of the synthesis of silver nanoparticles were carried out, differing in concentrations in the procedure. The results presented in the work concern the selected conditions described below, for which the obtained composites were characterized by good structural parameters of the dispersion of active particles while maintaining good bacteriostatic features and small amounts of substrates used for the synthesis. From the crushed base material (a platform for the deposition of active particles) a fraction of particles below 40 microns was separated on sieves. Next, they were purified in a 50% sulfuric acid solution at 100 °C for 2 hours, then rinsed with distilled water until a neutral pH was achieved and dried for 24 hours at 60 °C. From this material a suspension was prepared at a concentration of 1 g of particles per 98 mL of toluene (pure, from POL-AURA, Zabrze, Poland), to which 1 mL of [3-(2-aminoethyl) aminopropyl] trimethoxysilane (KH-792 from Sigma–Aldrich, Saint Louis, USA) was added. The suspension was placed in a beaker and agitated for 24 hours using a magnetic stirrer. Then the particles were separated using a filtration set on a 0.45 micron PES membrane filter and washed several times with the isopropyl alcohol (IPA, from POL-AURA, Zabrze, Poland) to remove the remaining silane, and then the obtained particles were dried at 60 °C for approx. 1 day. In the next step of the synthesis procedure, 0.5 g of particles was introduced into a silver nitrate solution (1 g of $AgNO_3$ per 100 ml of methanol) and placed on a laboratory cradle for 24 hours. The process was carried out in a tightly closed polyethylene container isolated from the ambient light. After stopping the agitation, the particles settled down, and the remaining silver nitrate supernatant was decanted. A reducing agent, which was a 0.2 mM sodium borohydride ($NaBH_4$) solution, was introduced into the container and agitated using a magnetic stirrer for 5 minutes. The particles were then separated using a laboratory centrifuge, washed three times with the IPA, centrifuged after each wash, and dried (60 °C, 1 day).

2.2. Analysis of synthesized particles

The prepared composites were analyzed with SEM imaging using two microscopes: Phenom G2 and Helios 5, both from Thermo Fisher Scientific, Waltham, USA. The presence of silver was confirmed based on the energy dispersive X-ray (EDX) microanalysis system (X-MAX from Oxford Instruments, Abingdon, UK).

2.3. Verification of antibacterial properties of synthesized materials

The antibacterial properties were assessed for both unprocessed particles and finished structures containing 2% of polymer additive by weight. Since they were subjected to high temperatures in the melt-blow process, the preservation of these properties was confirmed under corresponding conditions, e.g. temperature 290 °C, time 1 hour, which were even more demanding than those during the melt-blow process. Bacteriostatic properties were determined based on a qualitative test of the formation of the halo effect around the material placed on a culture medium on a Petri dish inoculated with *E. coli* bacteria (incubation for 24 hours at 37 °C). The second study allowing for the determination of a quantitative measure of the bactericidal effect was a test of the contact of the material with bacteria in their aqueous suspension, which reflected the environment of filter use. The procedure was based on ASTM E2149-13a "Standard Test Method for Determining the Antimicrobial Agents Under Dynamic Contact Conditions" and consisted of shaking a specified mass of material (0.1 g or 1 g of particles or fibrous, respectively) for 1 hour in 50 mL of a suspension of a bacterial strain at a concentration of $1.5\text{–}3.0 \cdot 10^5$ CFU/mL in a physiological saline solution of 0.9% NaCl. A sample without the addition of the active agent was used as a reference. A specified volume of the suspension of microorganisms after contact with the test sample for 1 hour was seeded in accordance with microbiological standards on Petri dishes with solidified TSA medium. Then the plates were incubated for 24 hours at 37 °C and the number of colony-forming units (CFU) was counted. The antibacterial effect of the samples containing the biocidal agent was presented as a percentage reduction in the survival of microorganisms.

2.4. Melt-blown technique of filter manufacturing

One of the widely applied methods of fabrication of fibrous polymer structures is the melt-blow process, which was used in this research. The polypropylene media were manufactured in-house using an automated full-scale system, which guarantees good reproducibility of produced fibers. 2% of particles was blended and extruded into filter media – higher concentrations were tested, but in the existing system setup (the design of the dye), 2% by mass appeared to be the limiting concentration for the maximum antibacterial effect, and for an undisturbed and repeatable processing.

2.5. Structural analysis of filtration materials

The tested filters were in the form of cylindrical elements. Three different types of filter material were used in the melt-blown process to fabricate filters: PP made of pure polypropylene, HAL made of polymer blended with raw halloysite granules (fraction below 40 microns), and HAL–Ag with the addition of composite of halloysite and silver nanoparticles. Although the addition of particles in the polymer melt substantially changed the rheology, the effort was made to fabricate similar structures of all filters. The details of cartridges, including dimensions and flow direction, are presented in Fig. 2. The 5-micron rated filters with an out-to-in flow arrangement consist of two layers characterized by different structural parameters. The fiber size distributions in each layer were determined based on SEM image analysis, while porosity was estimated knowing the mass and dimensions of each layer (Table 1).

Although the structural parameters of the fibrous media differ slightly between the layers (Tab. 1), the repeatability of the production process can be considered as good. The satisfactory structural similarity was also confirmed by the initial flow resistance, which was on a very similar level for all filters (as shown in Fig. 8).

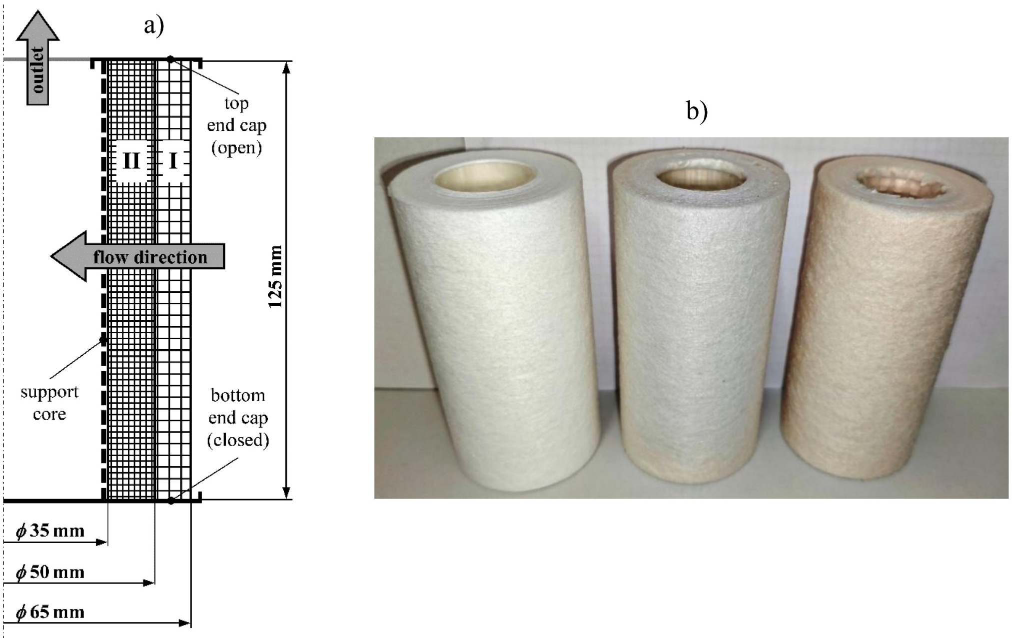

Figure 2. a) Details of filter cartridge, b) Photographs of elements without end caps: PP, HAL, HAL–Ag (from left to right).

Table 1. Statistical analysis of fiber diameters and porosity of individual layers.

Filter element		Fiber diameter Mean ± stddev [µm]	Min [µm]	Max [µm]	Porosity [%]
PP	Layer I	15.6 ± 7.24	3.78	36.8	71.9
	Layer II	6.63 ± 2.82	1.43	32.7	78.3
HAL	Layer I	19.7 ± 14.3	6.89	68.3	73.2
	Layer II	8.54 ± 5.10	3.45	38.1	77.2
HAL–Ag	Layer I	18.2 ± 12.5	7.14	71.7	73.0
	Layer II	7.64 ± 4.88	3.01	42.8	77.7

2.6. Test rig for water filters and experimental methodology

The experimental system for a multipass mode of filter operation is schematically shown in Fig. 3. Water was inoculated with *Escherichia coli* (Castellani & Chalmers ATCC 8739 strain) by the injection of 1 mL of bacteria suspension (3–5 CFU/mL) once per day to obtain the initial concentration of cells upstream the filter (in the water tank 2, volume 20 L) in the range of 10^3–10^4 CFU/mL. The filtered water circulated at a flow rate of 300 L/h through the 5-inch long filter in a closed loop, until a terminal value of the pressure drop 0.75 bar was reached. The temperature was controlled and kept at 20 °C. The total test time and the time-dependent dP profiles were compared.

The nutrient was continuously fed directly to the water tank with the flow rate of 20 mL/day (10% of the nominal Luria-Bertani concentration, i.e. 2.5 g/L). The water samples for analysis of bacteria concentration were collected before and after the feeding of bacteria.

The devised procedure allowed carrying out comparative testing of reference and modified filters to benchmark them under the conditions of filtering the water contaminated with bacteria. A good repeatability of results was obtained in a relatively short time, i.e. significantly faster than the average operation time of filters in real applications.

Before the presented experiments were carried out, it was confirmed that the selected lobe pump characterized by a low local shear rate did not significantly affect the concentration of living bacteria cells circulating in the system. The reduction of living bacteria concentration in the circulated water was compared to similar conditions in a gently agitated 5-liter bioreactor (Biostat® B from Sartorius, Germany). The bacteria amount was reduced by approximately 20% after 3 days of operation in the filter test rig, while in the bioreactor the decrease of living bacteria concentration was around 13%.

2.7. Analysis of deposited particle release (stability of additive)

The key challenge when creating coatings on the surface of various materials is always their stability and durability in real conditions. In the case of filters studied in the presented work, the issue concerns the durability of the connection of particles immobilized in polymer fibers in an aqueous environment, which are additionally affected by forces from the flow. The lack of their release is not only a need of maintaining the functional durability of the additive to the filter material for a long time, but also avoiding the contamination of the purified water with these particles or dissolved components released into the water, e.g. metallic ions. Therefore, tests were carried out on water circulating for 3 days in a closed filter chamber and the silver content was analyzed using a F-AAS iCE 3500 spectrometer from Thermo Fisher Scientific.

In addition, filter samples were mineralized – it was done for a new unused element and for filter used in the process for several days. The presence of silver on the fibers was determined for both elements and compared (tests of mineralization products using the same instrument).

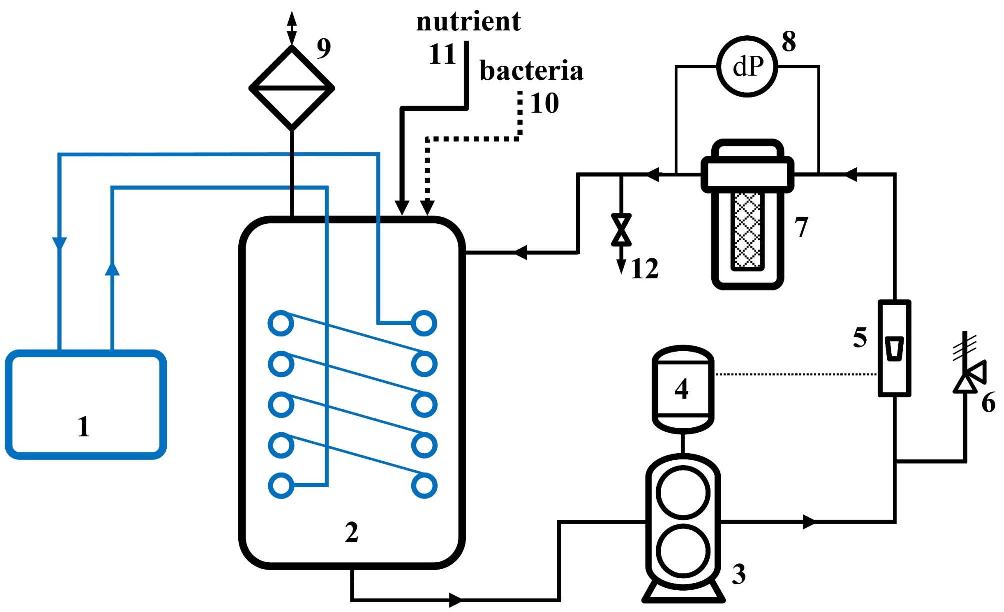

Figure 3. The experimental setup for testing antibacterial water filters: 1–thermostat (connected to a coil), 2–water tank, 3–circulating pump (lobe type), 4–electric motor with inverter, 5–rotameter, 6–pressure safety valve, 7–test filter housing, 8–dP sensor, 9–HEPA vent filter, 10–bacteria feed, 11–nurtient feed, 12–sample point.

3. RESULTS AND DISCUSSION

3.1. Morphology of composite particles

In Fig. 4, a composite of silver nanoparticles synthesized on the surface of mineral granules is presented. SEM observation (Fig. 4) confirm that active Ag particles are well dispersed on the surface of the base material, and they are not aggregated (which is often a problem for nanoparticle suspensions).

As the Ag nanoparticles were deposited on base mineral material, it was impossible to use any particle sizing instrument to determine their distributions. Based on SEM images, the majority of silver particles were estimated to be in the size range of 20–50 nm. Based on EDS analysis their amount was roughly estimated as approximately $2\%_{mas}$ in the granulate.

In Fig. 5 the melt-blown fibrous media containing antibacterial particles are presented. SEM imaging confirms that although the particles were blended in the melt, many of them were exposed at the surface of fibers, which is necessary to maintain their activity against deposited bacteria. During testing no material damage (rupture of filter media) or structure deformation was observed, hence the mechanical strength of filter was not affected in any noticeable way by adding of composite particles to polymer for the considered application.

3.2. Antibacterial properties of HAL–AgNP composites

For further processing using the melt-blown technique, stability and thermal resistance had to be confirmed. But first, the bacteriostatic and bactericidal properties were determined.

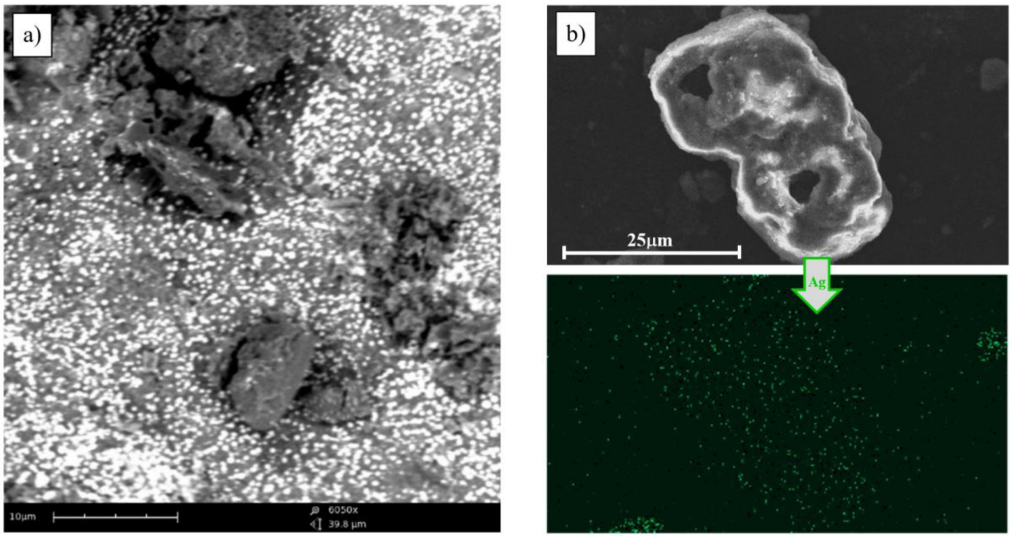

Figure 4. SEM image of kaolinite granule with Ag nanoparticles deposited on the surface.

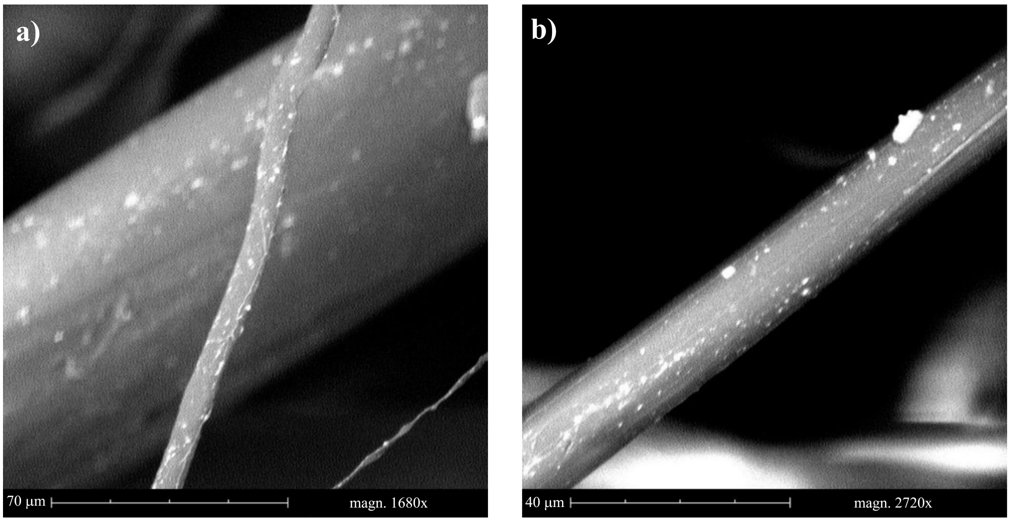

Figure 5. SEM images of filter material with HAL–Ag particles incorporated on the fibers in: a) layer I (magnification 1680×), b) layer II (magnification 2720×).

The tests on the Petri dishes showed that in this procedure only the HAL–AgNP composites exhibited a pronounced bacteriostatic effect (see Fig. 6) for both particle types with and without thermal treatment after the synthesis, i.e. heating to 290 °C for 1 hour, which corresponds to the maximum temperature of polypropylene processing using the melt-blow technique. However, the bacteria growth inhibition in this procedure is related to the diffusion of active compounds into culture medium, which creates different conditions than their interactions in the water.

In Fig. 7 the results of the reduction of bacteria concentration after 1 hour of dynamic contact with the materials are presented. The strongest antibacterial properties are demonstrated by HAL–Ag particles, which in either the unprocessed state or incorporated into the filter structure cause the greatest decrease in the number of live bacteria. A mild bactericidal effect is also demonstrated by particles of unpurified fossil mineral (pHAL and HAL in Fig. 7), which can be attributed to the presence of various metallic impurities of natural origin present in the ground particles. Their presence was confirmed by earlier work conducted in our research group, in which the composition was analyzed and the presence of various metallic compounds, which can potentially deliver the observed antibacterial effect, was confirmed (Stor et al., 2023).

3.3. Experiments of water filtration contaminated with bacteria

The experimental curves of the pressure drop increase during experiments with bacteria contaminated water are presented in Fig. 8. In a closed loop (multipass) operation mode the test time directly reflects the number of passes, which is related to a contact time. For a constant flow rate of 300 L/h used in experiments and 20 L system volume, the number of passes was equal to 15 per 1 hour, while the contact time of water with filter media was around 3.2 s per 1 pass. A good repeatability was observed for each filter type – the deviation of the test time, after which the terminal value of the differential

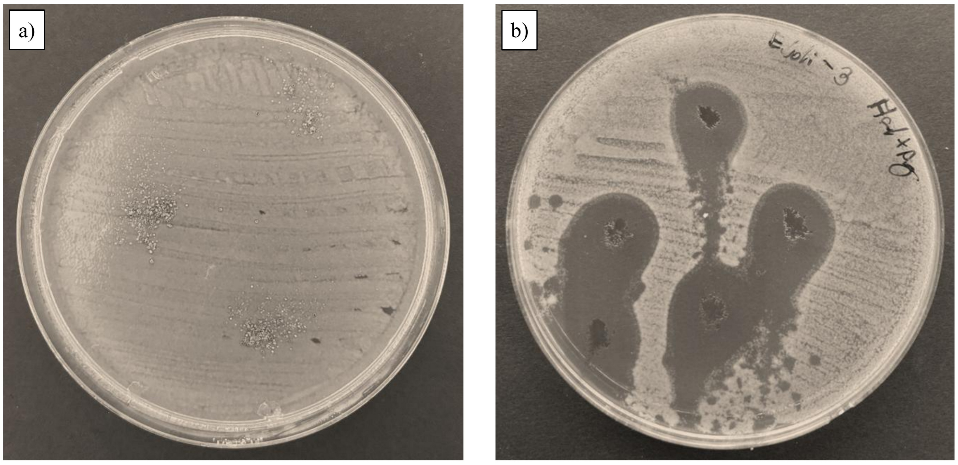

Figure 6. Photo of Petri dish after 24 hours of *E. Coli* incubation: a) no bacteria inhibition around HAL particles, b) halos around thermally treated HAL–AgNP composites.

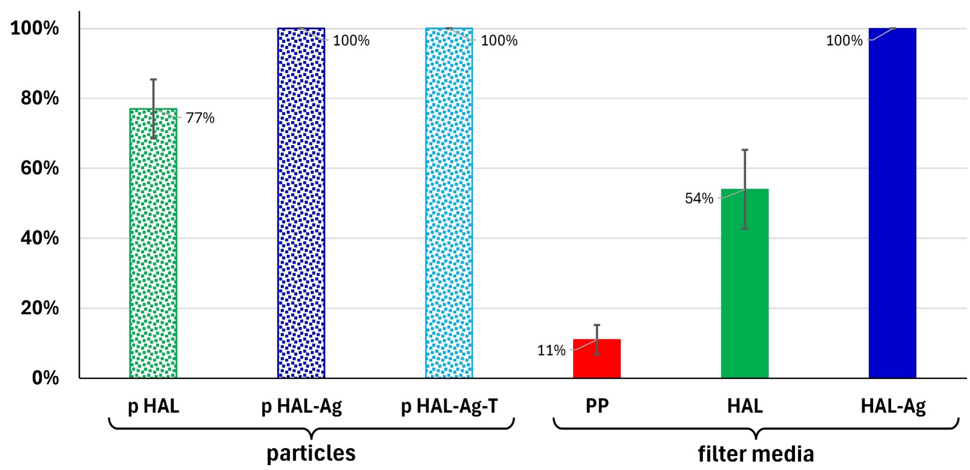

Figure 7. Reduction of bacteria concentration after 1 hour of contact with synthesized materials (p HAL–Ag-T denotes particles exposed to elevated temperature before the test).

pressure equal to 0.75 bar was achieved, was less than 10%. Moreover, the time-dependent dP profiles are quite similar in each group of curves. In particular, the steepness which reflects the biofouling rate, also provides consistent results (only a slightly slower increase of the dP value was obtained for the PP2 filter – marked with the red dots in Fig. 8).

As observed in Fig. 8, when the biofilm builds up inside the filter structure, the process of filter clogging accelerates. Although this tendency is observed for all tested filters, the instantaneous values of biofouling rate differ much between elements. In addition, the dP increase begins and is intensified after different time of experiments. This phenomenon is explicitly shown in Fig. 9, where the transient values of the differential pressure increase during the tests are plotted (for example, for selected single element of each type). They were calculated as the average increase of the dP over 1 hour:

$$(\Delta \mathrm{d}P/\Delta t)_{1h} = \frac{\mathrm{d}P_{t+1h} - \mathrm{d}P_t}{1h} \tag{1}$$

Although Fig. 9 clearly shows immense differences between native and modified filters in terms of their clogging rate and operation time, it does not provide information about the dP increase rate at a similar state of filter loading, which is straightforwardly reflected by similar flow resistance. These data are presented in Tab. 2, where the rate of biofouling is compared for the same ranges of differential pressure across the filters (which refer to completely different times of experiment).

The data illustrating the rate of flow resistance increase due to bacteria development and colonization of the interior of the filter structure are presented in Tab. 2. The most important indicator is the time to reach the final pressure drop of 0.75 bar, as shown in Fig. 8. The shortest time (i.e. the fastest progressing biofouling) is observed for the polypropylene structure (PPi, $i = 1..3$) without any additives. The addition of crushed particles of fossil material containing aluminosilicates and various metallic impurities such as Fe, Ti, Mg, etc. (Stor et al., 2023) was most likely responsible for a noticeable improvement in the resistance to biological fouling. For the HALi filters and the used bacterial strain an increase of approx. 50-80% in filter operating time was

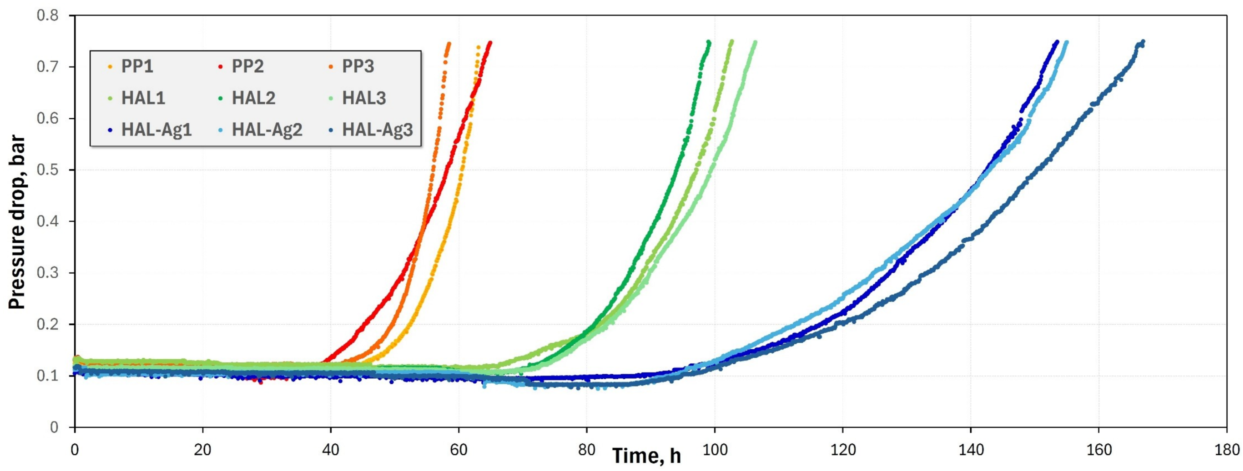

Figure 8. The experimental results of the differential pressure increase versus time.

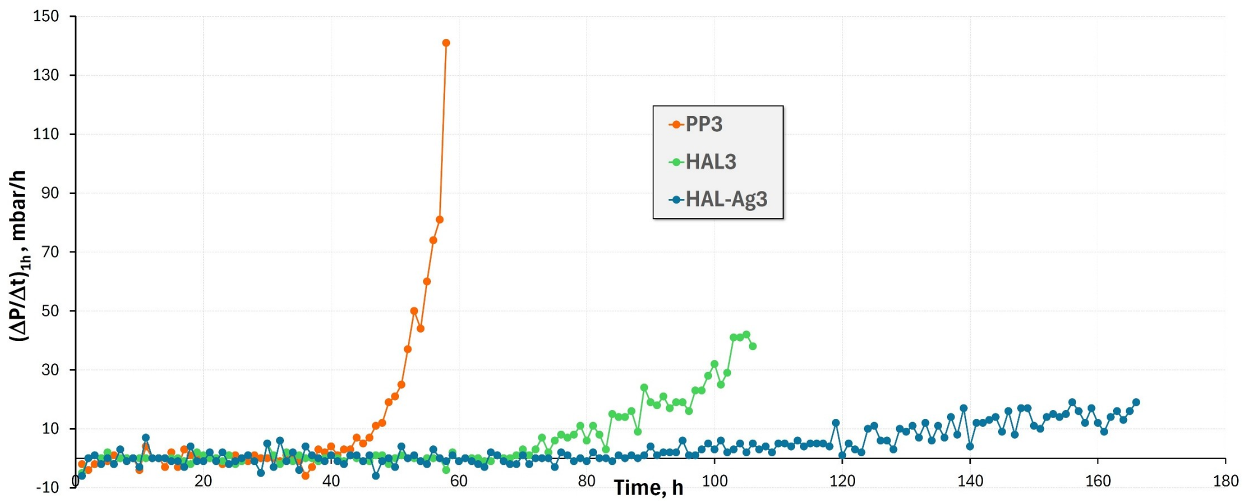

Figure 9. Comparison of transient values of biofouling rate variation during experiment.

Table 2. Average values of d*P* increase due to biofouling of tested filters at various stages of fibrous media blocking corresponding to selected d*P* ranges.

Element name	Time to reach terminal value of d*P* 0.75 bar [min]	Average rate of biofouling in selected d*P* ranges [mbar/h]		
		0.2 → 0.3 bar	0.3 → 0.4 bar	0.4 → 0.5 bar
PP1	3785	25.4	39.4	47.0
PP2	3895	17.1	25.5	32.3
PP3	3510	25.5	47.0	52.0
HAL1	6160	14.0	22.2	29.0
HAL2	5950	16.5	24.0	29.8
HAL3	6380	14.3	20.3	25.1
HAL–Ag1	9210	8.93	11.9	14.4
HAL–Ag2	9300	7.92	10.6	12.4
HAL–Ag3	10015	7.14	10.5	12.8

obtained. The use of granulate, which was a composite of mineral granules with silver nanoparticles on their surface, allowed for a further, significant extension of the operating time of HAL–Agi filters – in the test conditions by 135–185% compared to the operating time of a pure polypropylene filter. A reliable parameter allowing for comparison and assessment of the ability of the filter structure to slow down the biofouling process is the rate of flow resistance increase in specific ranges of the d*P* value. For different filters, these values correspond to completely different times from the start of the filtration experiment, but they possibly refer to a similar state of loading the filter structure with biological material. Tab. 2 presents the values of the averaged biofouling rate in considered d*P* ranges. In each range, the highest values are achieved for filters without modification and the lowest for elements with the addition of aluminosilicate composite with AgNPs. For all three types of filters, the trend showing the acceleration of the biofouling effect during the test, i.e. for the subsequent d*P* ranges considered, is similar. However, these rates differ significantly between filters. For example, for HAL–Agi filters, values of rate of the d*P* increase in the range of 0.4–0.5 bar, when the fouling process is already in its final phase and much faster than at the beginning, are still at a significantly lower level than for PPi filters even in the first considered range of 0.2-0.3 bar (when the rate of filter clogging is in its initial phase, i.e. relatively slow). Fig. 9 corresponds to the above conclusions from the data presented in Tab. 2.

The results of changes in the concentration of living bacteria in water during the test are shown in Fig. 10. These studies focus on the reduction of the number of *E. coli* during the first 4 hours after the addition of a fresh portion of bacteria on subsequent days of the test (whereas the description "before" and "after" refers to the time just before and just after their injection into the system). In a closed loop of circulating water, bacteria are removed both because of their retention in the filter structure or through the interaction with the biologically active component incorporated into the filter fibers. The reduction in the concentration of live bacteria over time is the smallest for the pure polypropylene filters (PP). Both filters with the addition of raw halloysite particles and containing silver nanoparticle composites reduce the number of bacteria better, and this effect is clearly stronger for composites. For example, in histogram noted "Day 2" of Fig. 10 (the second day of the experiment), the concentration of bacteria after 4 hours from their dosing is almost 2-fold less for the HAL filter and about 10-fold less for Hal-Ag in comparison to the unmodified filter (PP). The differences are greater the longer the filter operation time. Despite the well-reproduced filtration structure for particles with additives, the effect of particle elimination may result from better adhesion of bacteria to the surface of fibers with particles, which are characterized by their greater roughness. As a result, a better adhesion to fibers can translate into better impact of active particles on biological objects. Although the efficiency of bacteria reduction is clearly higher, the bacteriostatic effect resulting from the presence of active silver ions plays significant role in preventing the clogging of filter due to the colonization by retained bacteria. The available analysis methodology used in the studies did not allow for the assessment of the presence of dead bacteria dispersed in the water – hence, it is difficult to clearly determine the dominant mechanism of elimination of living bacteria. However, it can be concluded that this is not solely the effect of the ions being released into the water, as the presence of Ag in the water was not confirmed (or was below the detection threshold), as described below.

In Fig. 11 the results of the reduction of the bacteria concentration on the 5^{th} day of the HAL–Ag filter operation are presented. This was the only filter capable of operating for such a long time under the test conditions. Although it was confirmed that filters of this type have good antibacterial properties, after this time its effectiveness in eliminating *E. coli* was also attenuated. On the other hand, after 4 hours

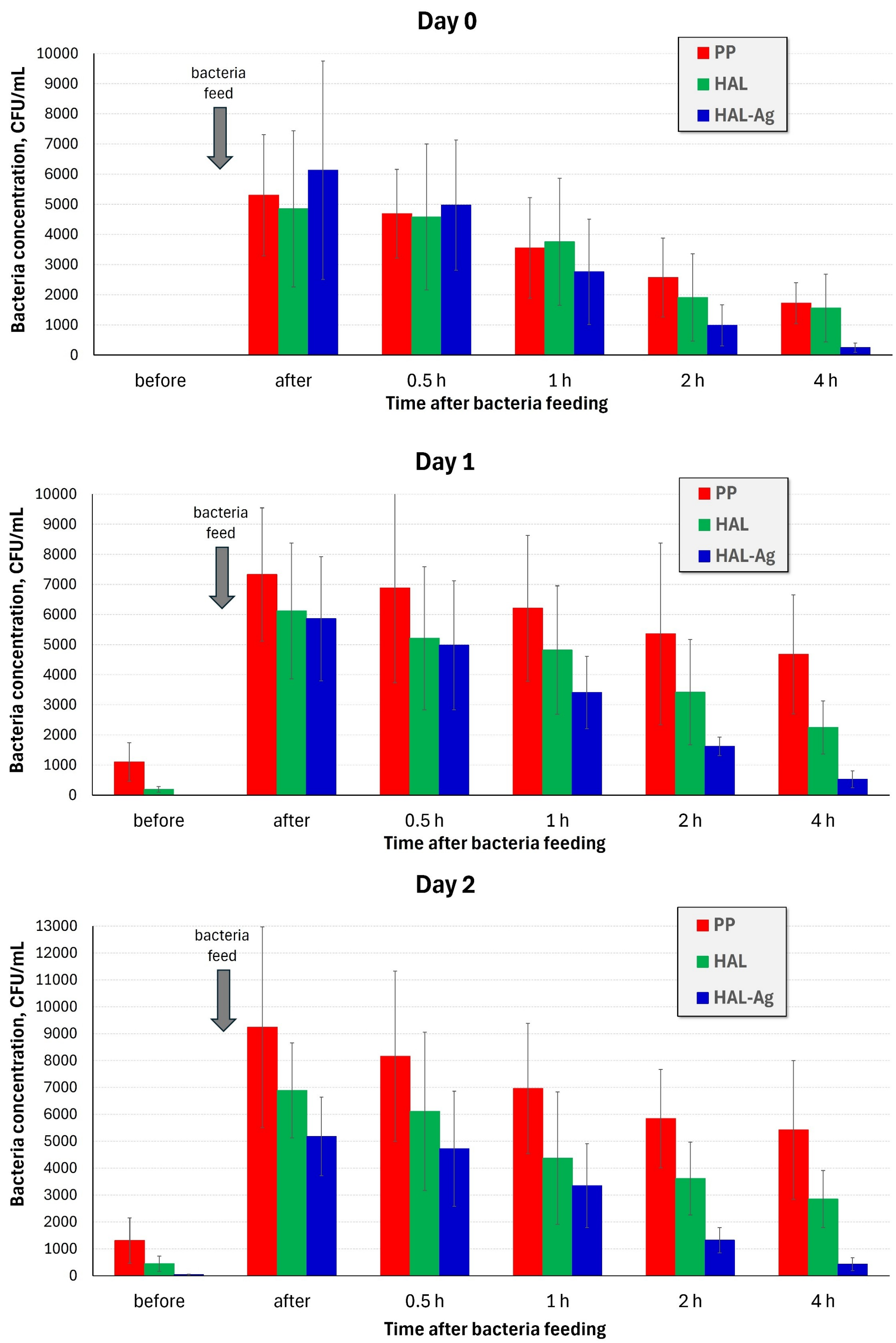

Figure 10. Concentration of living bacteria before and after feeding of fresh dose of inoculum over 3 days of experiment for all studied structures.

after bacteria feeding, the reduction of the amount of living microorganisms was still at the level of approximately 40% of the initial concentration.

In Tab. 3 the results of Ag content in the circulated water and in filter media (determined after material mineralization) are presented. This analysis clearly confirms that particle addition stabilizes the composite filter structure and does not negatively affect the filtered water due to the release of any added compounds. The decrease in Ag content in the filter structure was not very significant even after more than six days of continuous operation.

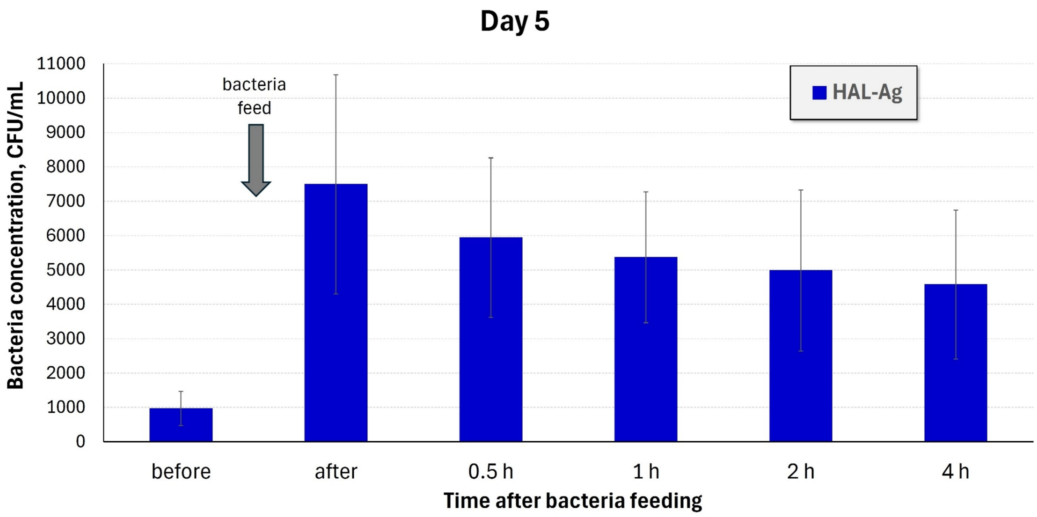

Figure 11. Concentration of living bacteria before and after feeding of fresh portion of inoculum on 5^{th} day of experiment for the material with an addition of HAL–Ag composites.

Table 3. Concentration of Ag in the circulated water and in the HAL–Ag filter media.

Ag in water [μg/L]*		Ag in filter media [mg/kg]**	
initial (clean tap water)	final (after the test)	initial (unused filter)	final (after the test)
0.0 ± 0.0	0.0 ± 0.0	36.7 ± 6.12	34.0 ± 9.77

Detection limits are: * 0.1 [mg/L] and ** 0.02 [mg/kg], respectively

4. SUMMARY AND CONCLUSIONS

The paper presents a method of obtaining composite granulates based on natural aluminosilicate containing halloysite, whose antibacterial properties have been confirmed. The developed material was used to produce water filters designed to operate efficiently in conditions of the presence of bacteria (exposure to various bacteria occurs in most water installations, technical and domestic). The *Escherichia coli*, which is commonly encountered bacteria strain in water and is therefore often used as an indicator of its purity, was used in the presented research. A new test procedure has been proposed and its repeatability was confirmed. Experimental studies have shown a significant improvement in the performance of filters in terms of operating time and elimination of bacteria in the circulated water. When compared to unmodified polypropylene structures, the time of filter clogging (i.e. reaching the terminal value of the pressure drop) was increased by up to 80% and 185% for the filter media with an addition of raw mineral and composite particles, respectively. It is worth emphasizing that test conditions, although they are supposed to correspond to the actual operating conditions of the filters (e.g. in terms of bacterial content), are artificially created to enable conducting reliable comparative tests in a reasonable time. On the one hand, continuous exposure to bacteria means that the applied filter testing conditions are more demanding, and the filters become blocked more quickly – in reality, it may translate into significantly greater extensions of the modified filter's time of operation. However, it should be kept in mind that the diversity of bacteria may mean that the developed active bacteriostatic additive will not have the same efficiency against other species. Another uncertainty is the fact that not all bacterial strains form a biofilm at the same rate as observed in the studies for *E. Coli*. An example can be the *Streptococcus* bacteria (ubiquitous in the surrounding environment) observed during similar studies in the installation, which, despite noticeable growth, did not affect the flow resistance of the filter for up to 4 weeks of operation of unmodified material. Moreover, in real conditions various bacteria strains may interact with each other, but these phenomena can be very complex and a detailed analysis would require more sophisticated microbiological studies.

ACKNOWLEDGEMENTS

This work was supported by the Polish National Centre for Research and Development, grant no. TECHMATSTRATEG-III/0005/2019-00.

We would like to express our gratitude to Mr. Paweł Kmuk from Amazon Filters Sp. z o.o. (Poland) for making the filters for this research, and to Dr. Piotr Wieciński for the support in SEM imaging.

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