

Improvement of antifouling resistance of polymer membranes using CuO nanoparticle incorporation-long-term performance evaluation

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Abstract

Long-term biofouling significantly limits continuous membrane filtration operated under constant transmembrane pressure, causing progressive hydraulic resistance and permeate flux instability. This study examined the long-term performance of polypropylene capillary membranes modified with a thin polysulfone layer containing CuO nanoparticles under cross-flow microfiltration with *Escherichia coli*. The focus was on operational stability during extended filtration rather than short-term material properties. Scanning electron microscopy, X-ray fluorescence, and capillary porosimetry confirmed that the modification was confined to the near-surface region without altering intrinsic pore structure or initial hydraulic permeability. Ninety-six-hour continuous filtration tests showed similar initial fluxes for both membranes. However, CuO-modified membranes exhibited a markedly slower flux decline. Consequently, cumulative permeate production was approximately 43% higher compared to unmodified membranes. Hermia model analysis indicated that fouling followed the intermediate pore-blocking mechanism in all cases. To account for time-dependent biofouling dynamics, the model was extended using a Weibull formulation, allowing separation of fouling time scale from intensity. The generalized model revealed a lower initial fouling rate and significantly longer characteristic fouling time for CuO-modified membranes, indicating delayed transition to high-resistance conditions. From a process-engineering standpoint, bacteriostatic surface modification effectively enhances long-term operational stability.

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Article info:

Received: 13 January 2026
Revised: 24 March 2026
Accepted: 27 April 2026

Keywords

membrane biofouling, long-term filtration, Hermia model, Weibull model, bacteriostatic modification

1. INTRODUCTION

Microorganisms such as bacteria, fungi and other microorganisms are ubiquitous and in real industrial operations it is difficult to eliminate the adverse effects resulting from their presence. Biofouling remains one of the most significant problems limiting the effectiveness of long-term membrane processes in water filtration applications (Alnumani et al., 2024; Zhang et al., 2022). Biofilm formation by bacteria, fungi, and other microorganisms leads to the formation of a dense, resistant layer that accelerates material aging and dramatically increases flow resistance of filtration media (fibrous filters or membranes), thus reducing the efficiency and economic viability of the system (Gaylarde and Morton, 1999; Momba et al., 2000; Vishwakarma, 2020). Biofilm is an organized structure stabilized by a matrix of extracellular polymeric substances (EPS) secreted from cells, which facilitate adhesion of bacteria and promote the rapid increase in filtration resistance early in membrane life (Di Martino, 2018; Salama et al., 2016).

More precisely, biofilm can be defined as a structured microbial consortium irreversibly attached to a surface and embedded in a self-produced EPS matrix composed of polysaccharides, proteins, lipids and extracellular DNA. This matrix provides mechanical stability, enhances resistance to hydrodynamic shear, and creates a diffusion barrier that limits mass transfer of nutrients and antimicrobial agents. As a consequence, once

established on a membrane surface, biofilm significantly alters local transport conditions and promotes progressive hydraulic resistance buildup.

In membrane systems operated under constant transmembrane pressure (TMP), biofilm development manifests as a time-dependent decline in permeate flux. The accumulation of cells and EPS within and on the membrane structure leads to pore constriction, partial or complete pore blocking, and eventually formation of a cake-like layer. Unlike purely inorganic or colloidal fouling, biofouling is dynamic and evolves due to microbial growth, EPS secretion, structural rearrangement of the deposited layer, and possible detachment events. Therefore, the rate of resistance increase is rarely constant over time, which complicates predictive modelling of long-term performance.

One of the methods being intensively developed to improve the resistance of separation materials to biofouling is their modification using additives having confirmed antibacterial properties (Desiriani et al., 2023; Geng et al., 2022; Younas et al., 2016). The effectiveness of metals and metal oxides such as Ag, Cu, ZnO and CuO, especially in the form of dispersed nanoparticles, is widely described in the literature, and their effects include both bactericidal and bacteriostatic effects (Asamoah et al., 2020; Dadi et al., 2019; Dehghani et al., 2019; Krasiński et al., 2025; Pandey et al., 2021). The latter mechanism, which slows down the growth of microor-



ganisms and limits the rate of surface colonization, is particularly important for the membrane durability and the stability of process parameters. Our previous studies confirmed that CuO nanoparticles exhibit significant bacteriostatic properties against microorganisms relevant to water-quality assessment, including common indicator species, as demonstrated in dynamic tests conducted according to the ASTM E2149-13a standard (Szwaś et al., 2023).

However, *in vitro* studies, typically conducted on solid substrates or in simple contact systems, do not fully capture the complexity of phenomena occurring under real membrane operating conditions, where variable flow regimes, mass-transfer processes, repeated passage of the medium through the porous structure, and the development of biofilm under hydrodynamic stresses all play a significant role.

From a mechanistic standpoint, the decline in permeate flux during membrane filtration is commonly interpreted using classical pore-blocking models, among which the Hermia model is one of the most frequently applied frameworks. The Hermia approach distinguishes between four principal fouling regimes: complete blocking, standard blocking, intermediate blocking, and cake formation. Each regime reflects a distinct physical mechanism of pore obstruction or surface coverage. Although originally derived for constant-pressure dead-end filtration, the model is widely used for analysing cross-flow microfiltration and ultrafiltration data due to its ability to relate flux decline to dominant fouling mechanisms.

Nevertheless, in long-term biologically active systems, fouling rarely proceeds at a constant rate assumed in the simplest Hermia formulations. The interaction between microbial growth kinetics, EPS (extracellular polymeric substance) accumulation, and hydrodynamic shear may lead to time-dependent changes in fouling intensity. Therefore, a more comprehensive theoretical framework is required to adequately describe resistance development under realistic operating conditions.

Consequently, the natural next step in research on antibiofouling materials is to move from model tests to verifying membrane properties under conditions as close as possible to those in operation (Tian et al., 2023). In the present study, this challenge was addressed by using polypropylene membranes modified with CuO nanoparticles. The aim of the research was to determine the extent to which the previously confirmed antibacterial properties of CuO translate into a real reduction of biofouling on the membrane surface in a flow-through filtration system operated at constant transmembrane pressure, by monitoring the evolution (decrease) of time-dependent permeate flux. In this approach, the decline in permeate flux is considered a direct measure of the increasing flow resistance associated with fouling and biofouling.

In addition to assessing the effectiveness of CuO in a real process, it was also important to determine the additive's effect on the dynamics of resistance buildup (i.e. clogging of pores), its ability to inhibit early stages of colonization, and

any differences in fouling mechanisms compared to unmodified membranes. In particular, we were interested in answering the question of whether the bacteriostatic effect of CuO, previously demonstrated *in vitro*, is a relevant assessment method and could be strong enough to significantly delay the achievement of critical membrane resistance values in conditions very similar to the realistic operation of membrane filtration systems.

The novelty of the present work lies in combining long-term (96 h) uninterrupted cross-flow filtration under constant TMP with time-resolved flux monitoring and mechanistic modelling of fouling dynamics. In contrast to studies focused primarily on short-term antibacterial assays or material characterization, this study evaluates membrane performance from a process-engineering perspective, linking bacteriostatic surface modification with quantitative analysis of resistance development and dominant fouling regimes.

By integrating experimental long-term filtration data with Hermia-based modelling, the study aims not only to identify the prevailing fouling mechanism but also to assess whether bacteriostatic modification alters the temporal characteristics of resistance buildup. Such an approach provides a bridge between material-level antibacterial properties and system-level operational stability.

Therefore, the present study addresses a key process-engineering problem related to the long-term stability of membrane filtration systems operated under constant transmembrane pressure in biologically active environments. By combining long-term cross-flow filtration experiments with time-resolved analysis of permeate flux decline, this work aims to quantify how bacteriostatic membrane modification influences the dynamics of hydraulic resistance buildup under realistic operating conditions. Such an approach enables direct assessment of membrane performance from the perspective of process continuity, operational stability, and effective operating time, which are critical parameters in the design and operation of membrane-based separation systems.

2. MATERIALS AND METHODS

In the present study, capillary polypropylene membranes with an average pore size of 0.2 μm (3M, model MF-PP S6/2) were employed. Polysulfone (PSf, Sigma-Aldrich) and nanometric copper(II) oxide nanopowder (according to specification the particle size $< 50\text{ nm}$ based on TEM; surface area $\approx 29\text{ m}^2/\text{g}$; CuO nanoparticles, Sigma-Aldrich, product no. 544868) was used as the inorganic modifier. N-methyl-2-pyrrolidone (NMP, Pol-Aura) served as the primary solvent, filtered tap water was used as the secondary (nonsolvent) phase, whereas filtered water treated with activated carbon was employed as the process medium in microfiltration experiments to isolate the effects of other compounds, including chlorine or ozone.

2.1. Membrane preparation

In presented research the commercially available polypropylene membranes (used as reference) and in-house modified membranes with enhanced antibacterial properties were utilized. The functional coating was deposited onto the outer surface of the polypropylene membranes using the dip-coating technique. In this procedure, the membrane was immersed in the modifying solution and subsequently withdrawn at a precisely controlled speed of 20 mm/min to achieve uniform layer formation. Dip-coating was performed using the NIMA Dip Coater (KSV NIMA Dip Coaters). The withdrawal speed was low enough to enable formation of an ultrathin and integral coating layer.

To generate a functional porous layer on the membrane surface, the coated membranes were subsequently subjected to a wet phase inversion process. For this purpose, the membranes covered with the film-forming solution were immersed in a water bath, where water, acting as a non-solvent, replaced the primary solvent (NMP) in the polymer solution. This exchange induced a liquid–solid phase transition, resulting in the development of a porous structure within the deposited layer.

The modifying formulation consisted of 11% (w/w) polysulfone (PSf) solution in NMP supplemented with 2% (w/w) CuO nanoparticles, calculated in relation to the mass of PSf. The fabrication procedure and properties of this type of composite material have been discussed in detail in the authors' previous work (Szwast et al., 2023).

2.2. Membrane characterization

A set of instrumental methods was used to characterize the obtained heterogeneous membranes, enabling the assessment of morphological parameters and filtration properties. The effectiveness of coating the supporting membrane with the modifying layer was determined by scanning electron microscopy (SEM) using a PhenomPro G2 microscope (PhenomWorld, Eindhoven, The Netherlands) equipped with a holder that did not require sample sputtering. The membranes were also subjected to X-ray fluorescence (XRF) analysis to confirm the presence of copper on their surface, which is crucial for the bacteriostatic properties associated with CuO nanoparticles. The bacteriostatic properties of these nanoparticles and the heterogeneous membranes containing CuO produced by our team have been demonstrated in previous studies conducted on agar media (Szwast et al., 2023). XRF analyses were performed using an X-ray Fluorescence Spectrometer (Epsilon 3XLE, Malvern PANalytical Ltd, Malvern, Worcestershire, UK).

The effect of modification on material structure was also assessed by capillary porosimetry, comparing unmodified and modified membranes using a PMI Capillary iPore-1200A apparatus (Porous Materials, Inc., Ithaca, NY, USA).

2.3. Filtration tests

Long-term studies of the membrane filtration process were conducted on a large-scale research setup supplied by Polymemtech (Warsaw, Poland). This setup included a replaceable membrane module (Mem), a 10-liter feed tank (Tk), and product tanks (permeate and retentate), which were not used in this experiment, as both streams were recirculated to the feed tank. The setup was equipped with a centrifugal pump (PM), pressure transducers (P) located upstream (in the feed stream) and downstream (in the retentate stream) of the membrane module, and flow transducers (F) installed in the permeate and retentate lines. The setup was also equipped with a heat exchanger (HE), which enabled temperature control of the liquid circulating in the system. The valve configuration allowed for continuous recirculation of both flows to the feed tank, allowing the process to run for several days without the need for feed replenishment or product removal. The configuration of the experimental setup used in this study is presented in Fig. 1. In current research the system was equipped with a three-port module, developed in-house, containing a bundle of 40 tubular (capillary) membranes with the length of 1 m and the inner diameter of 1.8 mm, which results in 0.27 m² of total filtration area. The module operated in a cross-flow configuration. The applied configuration allows for continuous operation of the membrane module over several days under controlled hydraulic conditions, enabling direct observation of time-dependent resistance development. From a process-engineering perspective, this setup represents a simplified model of industrial cross-flow microfiltration units operated without intermediate cleaning, making it suitable for evaluating long-term process stability rather than short-term material performance.

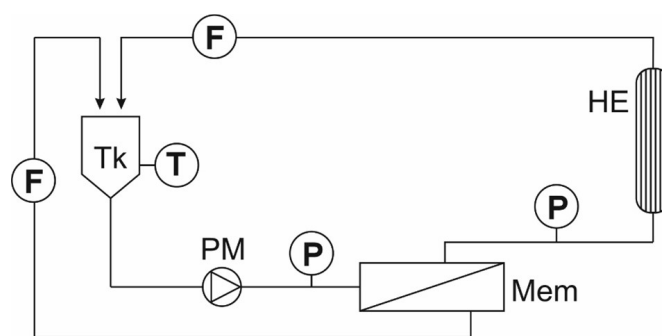


Figure 1. Experimental setup; F – flow transducer, HE – heat exchanger, Mem – membrane module, P – pressure transducer, PM – pump, T – temperature transducer, Tk – tank.

The control and monitoring system was equipped with a recorder enabling storage of process data at one-minute intervals. The control system guaranteed also a stable temperature of the feed water.

The measurements were conducted continuously for 96 hours, maintaining constant system operating parameters, in particular the feed pressure at 0.5 bar and the feed temperature

at 294 K. Once daily, a portion of the bacterial suspension was introduced into the system and a diluted nutrient was continuously supplied to the feed tank to maintain bacteria life functions (the procedure is described in more detail Section 2.4). Other process variables, such as the permeate flow rate – whose variability served as a measure of bacterial growth leading to membrane fouling – were derived quantities taking values dependent on the current operating conditions.

Following the completion of the modified membrane testing, water samples were analysed to assess the stability of copper additive on the membranes' surface. This study aimed to determine whether Cu^{2+} ions or fine fractions of CuO particles were released into the permeate and retentate streams during long-term filtration. Visocolor ECO Copper cuvette tests (Macherey–Nagel) were used to determine Cu^{2+} ion concentration. The concentration range of this method was 0.1–1.5 mg/L, where the lower limit corresponds to the detection threshold.

2.4. Determination of bacterial content in the water

In this study, bacterial cultures of *Escherichia coli* Castellani & Chalmers (ATCC 8739) were used. The water was inoculated with *E. coli* by the injection of 1 mL of bacterial suspension ($3\text{--}5 \cdot 10^8$ CFU/mL) once per day to obtain the initial concentration of cells in the feed tank in the range of $10^3\text{--}10^4$ CFU/mL. The nutrient was supplied directly to the tank with the flow rate of 10 mL/day (concentration of the Luria-Bertani broth was 2.5 g/L). The same procedure was used for reference and modified membranes (a comparative study) to enable verifying the impact of modifications on the membrane biofouling rate. Throughout the process, *E. coli* bacterial content in the feed water and permeate were monitored. Samples of the feed water were taken from the feed tank immediately after the bacteria were added (bacteria were injected once per day) to verify their initial concentration, which was expected to be in the afore-mentioned desired range (i.e., $10^3\text{--}10^4$ CFU/mL). Petri dishes with a solidified culture medium consisting of bacteriological agar and LB broth (Miller) were used for this purpose. A water sample in the amount of 0.1 mL was spread on the surface of the culture medium, and after 24 hours of incubation, the CFU count was determined and then converted to concentration (per 1 mL of water).

In the present study, the feed solution was prepared from filtered tap water and inoculated with a controlled culture of *E. coli*, which served as a model microorganism representing biofouling-forming bacteria. Due to the use of filtered tap water and the closed recirculation configuration of the experimental setup, the development of other microbial populations during the experiment was considered unlikely. The applied experimental design was therefore intended to provide controlled conditions enabling the analysis of biofouling dynamics associated with a well-defined bacterial species.

For the permeate samples, a similar estimation of the concentration of viable bacteria after passing the membrane was carried out based on water inoculations in Petri dishes. The bacterial concentration was determined immediately after feeding a fresh portion of bacteria into the system and after 1, 2 and 4 hours. No growth in colonies in the Petri dishes was observed in any case. However, it is reported in the literature that in certain situations bacteria can go into so-called VBNC state, which stands for viable but nonculturable (Liu et al., 2023). It refers to a situation where bacteria are alive but cannot grow on standard lab media. They often enter VBNC state in response to environmental stress, e.g., a shortage of nutrients or interaction with compounds having a detrimental effect on their living functions. They do not proliferate (divide), so they often do not form colonies, but to some extent are metabolically active and can contribute to biofilm formation. Therefore, MicroSnap Total tests from Hygiene Diagnostics GmbH were also used for measuring the total viable bacterial count, which is a method certified by Association of Official Analytical Chemists (AOAC). It includes incubating a sample to allow bacterial growth and produce biomarkers, which are then measured using a luminometer. The test is a two-step procedure involving enrichment and a detection phase. First, the sample is incubated with a special growth medium that also contains enzymes to reduce background ATP. During the 7-hour incubation, bacteria multiply and produce more biomarkers. An aliquot of the enriched sample is transferred to a detection device, which is then activated. This releases bioluminescent reagents that react with the biomarkers produced by the bacteria. The resulting light emission was measured using EasyTouch luminometer from Hygiene Diagnostics GmbH, providing a quantitative result in RLU units, which is correlated with a bacterial count.

Additionally, membrane fragments collected after the filtration experiments were placed onto standard culture media to assess the potential presence and viability of bacteria adhering to the membrane surface. This procedure allowed verification of whether microorganisms remained associated with the membrane material after the filtration process.

3. RESULTS AND DISCUSSION

3.1. Membrane characterization

The composite membranes produced by dip-coating were subjected to morphological evaluation. SEM images were taken without sputtering, allowing direct observation of the modified membrane surface and comparison to unmodified membranes (Fig. 2). The SEM image of the unmodified membrane (Fig. 2A) shows a characteristic microporous structure of moderate regularity; some pores are partially obscured, likely due to local polymer melting during the fabrication process. The pore structure is characterized by a distinct orientation parallel to the capillary axis, which is typical for capillary polymer membrane formation technologies.

The image of the modified membrane (Fig. 2B) shows the presence of CuO nanoparticles deposited on the surface. The visible bright clusters are several micrometres in size (approx. 4–6 μm), indicating the tendency of CuO nanoparticles to agglomerate, a phenomenon commonly observed and reported in the literature (Dumitriu et al., 2016; Sotto et al., 2011). In this case, agglomeration is not necessarily undesirable; effective attachment of CuO nanoparticles to the surface of the microporous membrane and their presence on this surface are crucial. The surface of the original membrane is transparent through the applied layer, which suggests that the transport and separation properties of the modified membrane will not change significantly compared to the unmodified membrane.

Cross-sectional images of the capillaries were also captured, but the thickness of the layer formed during the dip-coating process proved too small to be clearly captured in SEM observations. This is beneficial from the perspective of membrane functionality: with confirmed surface modification, no additional, thick layer was observed, which could increase flow resistance and impair transport properties.

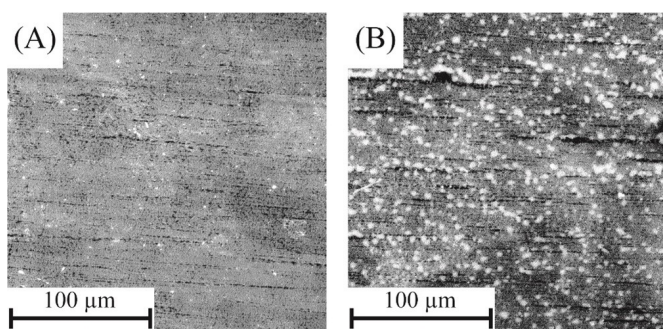


Figure 2. SEM images (1000 $\times$ magnification): (A) outer surface of the unmodified membrane; (B) outer surface of the modified membrane with visible agglomerates of CuO nanoparticles.

The SEM images indicate that CuO nanoparticles embedded in a polysulfone matrix were successfully introduced into the surface region of the microporous capillary membrane. A similar material system was previously used to create a membrane exhibiting bacteriostatic properties (Szwast et al., 2023). In this context, it was important to ensure that Cu-containing species remained accessible at or near the membrane surface, as achieving the bacteriostatic effect, and thus antibiofouling properties, requires the availability of copper to enable interaction with bacterial cells (Banerjee et al., 2011; Khan and Shakoar, 2023).

X-ray fluorescence (XRF) was used to map the elements present in the near-surface region of the modified membrane and compare them with the unmodified membrane. The results of this analysis are summarized in Table 1.

The XRF measurement results are consistent with the conclusions drawn from the SEM analysis. A very high sulphur content was detected in the modified membrane, originating

Table 1. XRF analysis results.

Compound	Unit	Unmodified membrane	Modified membrane
Mg	%	0.006	0.000
Al	%	0.025	0.002
Si	%	0.169	0.006
P	%	0.255	0.008
S	%	0.000	0.889
Cl	%	0.146	0.065
Ca	%	0.312	0.016
Fe	%	0.021	0.001
Cu	%	0.000	0.011
Ag	%	0.071	0.003

from the polysulfone, indicating the presence of a thin PSf layer in the near-surface region of the membrane. At the same time, the copper signal appeared only in the modified membrane, confirming the effective introduction of Cu-containing species into this region.

It is worth emphasizing that, due to the finite penetration depth of XRF, this technique does not exclusively probe the outermost surface. Nevertheless, the combined SEM and XRF results indicate that the polysulfone layer formed during dip-coating is thin and likely discontinuous, and does not constitute a thick, continuous barrier fully isolating CuO nanoparticles from the external environment. This is crucial for the assumed bacteriostatic effect, as either direct contact between bacteria and exposed CuO nanoparticles or the diffusion of copper ions through a thin polymer layer may contribute to antibacterial activity. Partial encapsulation of CuO nanoparticles may therefore be beneficial, as it can moderate copper release and enhance the long-term stability of the antibiofouling effect.

In addition to the elements characteristic of the modifying layer (S and Cu), a number of other elements were also detected in both membranes, such as Al, Si, P, Ca, Fe, and Ag. Their presence is typical for capillary polypropylene membranes and results primarily from the use of inorganic fillers, stabilizers, and technological additives used in the polymer production process. However, such information is not provided by manufacturers. The slight differences in their concentrations between the unmodified and modified membranes can be attributed to the partial obscuration of the PP surface by a thin polysulfone layer, which naturally affects the intensity of the XRF signal from deeper layers of the material. This is particularly noticeable in the case of elements with relatively low content, whose signal may be subject to local fluctuations dependent on the microscopic heterogeneity of the surface. It is also worth noting that the presence of chlorine in the modified membrane at a higher level than in the unmodified membrane may result from residual salts or reagents used in the preparation of the dip-coating solution. This is not a disturbing artifact but only indicates the introduction of additional ingredients as a result of modification.

From the perspective of the filtration and separation properties of modified membranes, the potential change in pore size and distribution introduced by the modification process is crucial. Ideally, modified membranes would be identical in this respect to unmodified membranes, but complete preservation of identical porosity parameters is impossible due to the application of an additional polymer layer to their surface. The results of pore size distribution analyses for the unmodified and modified membranes are presented in Fig. 3 and Table 2.

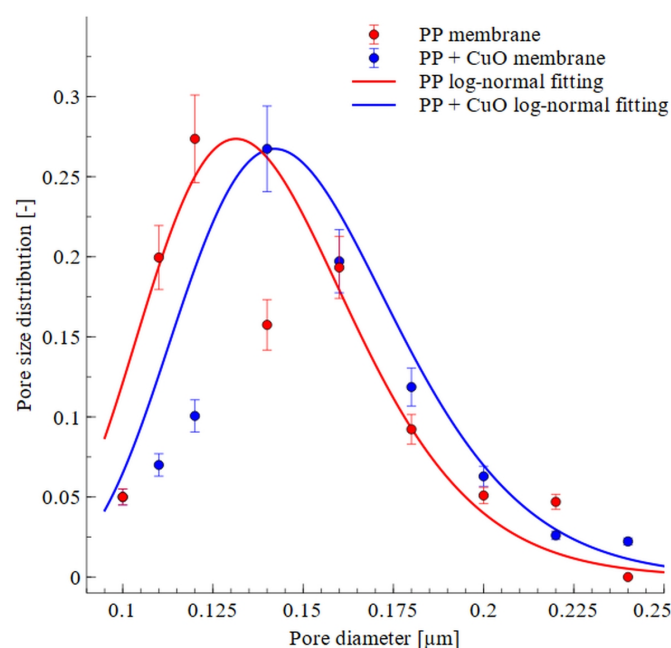


Figure 3. Pore size distribution in unmodified and modified membranes.

Table 2. Statistical parameters of pore size distribution.

Parameter	Unmodified membrane	Modified membrane
Arithmetic mean pore diameter [μm]	0.141	0.152
Standard deviation, SD [μm]	0.032	0.032
Mode (maximum at diameter, [μm])	0.12	0.14
Log-normal $\mu_{\ln}$	-1.984	-1.908
Log-normal $\sigma_{\ln}$	0.214	0.209
Geometric mean pore diameter [μm]	0.139	0.150
Median (log-normal) pore diameter [μm]	0.139	0.150
R^2 (log-normal fit)	0.690	0.748

Analysis of the pore size distributions shown in Fig. 3 indicates that modification of polypropylene membranes with a polysulfone layer containing CuO nanoparticles does not lead to significant changes in their porosity in terms of filtration and sep-

aration properties. The pore distribution curves for the unmodified membrane (red line) and the modified membrane (blue line) are similar in shape and width, confirming the preservation of the essential microporous structure after the modification process. However, a slight shift in the main distribution peak for the modified membrane toward larger pore diameters is noticeable. This may be due to partial occlusion of the smallest pores by the thin polysulfone layer, which is consistent with SEM observations indicating the presence of a discontinuous, very thin polymer coating on the capillary surface. At the same time, the lack of a significant decrease in the proportion of larger pores and the similar profile of both curves suggest that the modifying layer does not create any significant additional resistance to mass transport. The statistical analysis summarized in Table 2 confirms the qualitative observations from Fig. 3. The arithmetic mean pore diameter increases only slightly from 0.141 μm for the unmodified membrane to 0.152 μm after modification, while the standard deviation remains essentially unchanged (0.032 μm for both samples). Similarly, the parameters of the log-normal distribution indicate only a minor shift of the distribution toward larger pore diameters without a noticeable change in dispersion. Although the coefficients of determination obtained for the log-normal fitting are moderate ($R^2 \approx 0.69$ – 0.75), the overall statistical analysis supports the conclusion that the modification does not significantly alter the pore structure of the membrane.

The obtained results allow us to conclude that the modification process does not significantly affect the filtration properties of the membranes, which is beneficial from the point of view of maintaining their functionality while potentially giving them anti-biofouling properties.

3.2. Filtration performance

The studies were conducted in a cross-flow filtration system using three separate membrane modules. In the first series of experiments, a module containing unmodified membranes was used and pure water was filtered (red line in Fig. 4). In the second series, a new, identical membrane module was used and pure water containing a bacterial suspension was filtered (blue line in Fig. 4). In the third series of studies, a module equipped with membranes modified with CuO nanoparticles was used and filtered tap water with the addition of a bacterial suspension was filtered (green line in Fig. 4). The time course of changes in permeate flux is shown in Fig. 4a.

Figure 4a shows the actual permeate flux values obtained in three test series. It should be noted that the initial flux values are very similar, which is particularly important when comparing the properties of unmodified and modified membranes. This result was expected given the similar porosity parameters obtained in the porosimetric analysis (Fig. 3). The curves presented in Fig. 4a show local deviations from the trend, resulting primarily from momentary pump disturbances and small fluctuations in feed pressure, as recorded by the

monitoring system. Therefore, it was decided to normalize the measured data to the operating pressure and to the initial permeate flux value. Based on this processed data, the graph shown in Fig. 4b was prepared. It is crucial that the similar initial permeate flux values in all three measurements ensure that the normalization performed does not introduce interpretation errors and allows for a reliable comparative analysis of changes occurring during filtration.

A slight decline in permeate flux during pure water filtration (red line in Fig. 4a) is typically attributed to membrane compaction and surface relaxation phenomena. Even in the absence of foulants, polymer chains may rearrange upon long-term contact with water, leading to increased hydraulic resistance (Persson et al., 1995). In addition, trace organic impurities and dissolved gases can adsorb or accumulate within the pores, contributing to a gradual permeability loss (van der Bruggen et al., 2002).

In studies involving bacteria, the decreases in permeate flux are clearly more pronounced. In the long term, flux values for both membranes tend to similarly low levels, but the rate of flux degradation for the unmodified membrane (slope of blue line in Fig. 4a) is significantly greater than for the membrane modified with CuO nanoparticles (green line in Fig. 4a).

Integration of the permeate flux curves indicates that the modified membranes produced nearly 43% more permeate over 96 hours of operation. From an operational standpoint, this result corresponds to a substantially slower increase in hydraulic resistance and an extended effective operating time of the membrane module under constant transmembrane pressure, which is directly relevant for maintaining stable throughput and reducing process interruptions in continuous filtration systems.

A significant result of the measurements is that samples taken from the permeate streams in all three filtration variants always showed a complete absence of bacteria. This means that the membranes used maintained full selectivity towards the bacterial culture and effectively retained microbial cells regardless of the membrane type and process conditions.

A preliminary analysis of the permeate flux curves for filtration using modified and unmodified membranes already provides a clearly positive answer regarding the membranes antibiofouling properties, which was the main goal of this research. However, to deepen the analysis and consider potential fouling mechanisms, the remainder of this manuscript will attempt to mathematically describe the observed phenomena.

Figure 5 shows the growth of bacterial cultures around membrane fragments placed in Petri dishes: (a) initial state and (b) image after 24 hours of incubation. Figure 5b clearly shows the appearance of bacterial colonies on solid support adjacent to the membrane fragments. The observed growth indicates the migration of live bacterial cells from the membrane surface to the agar medium, where they could multiply under favourable conditions. The arrangement of colonies around the samples

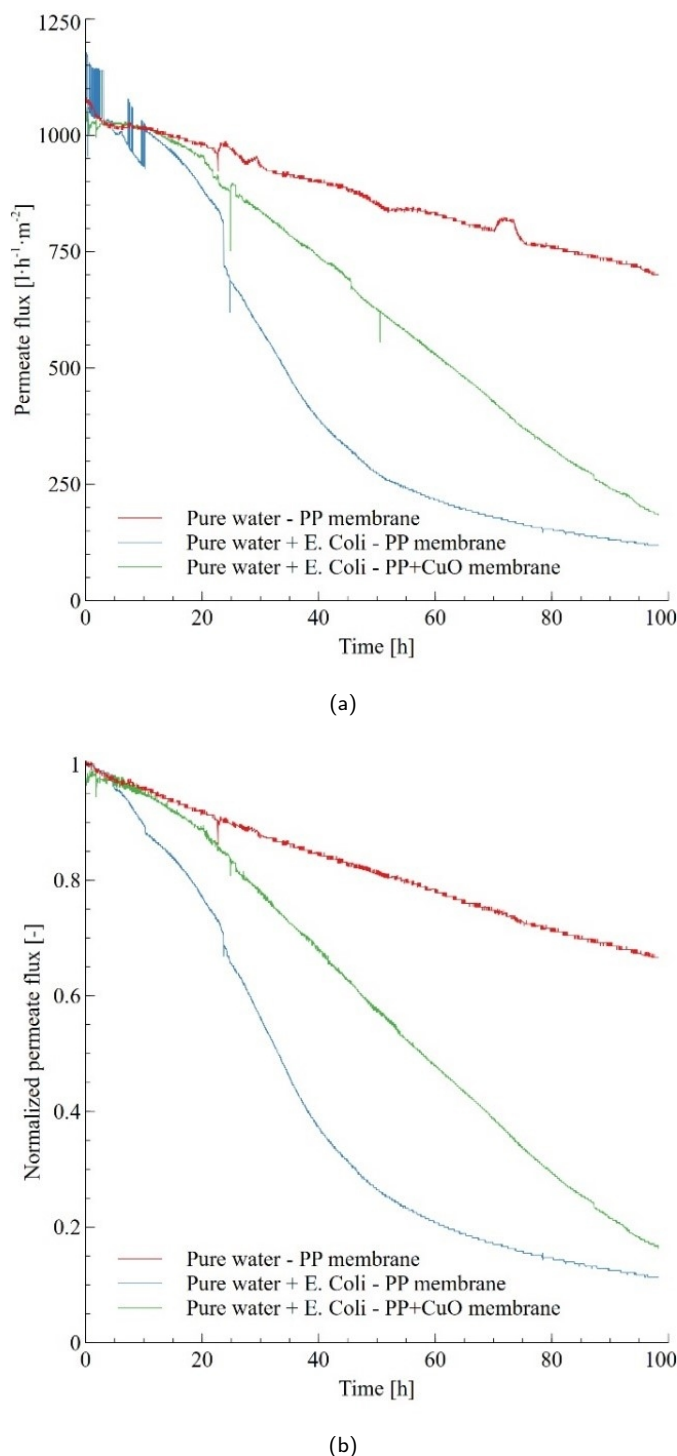
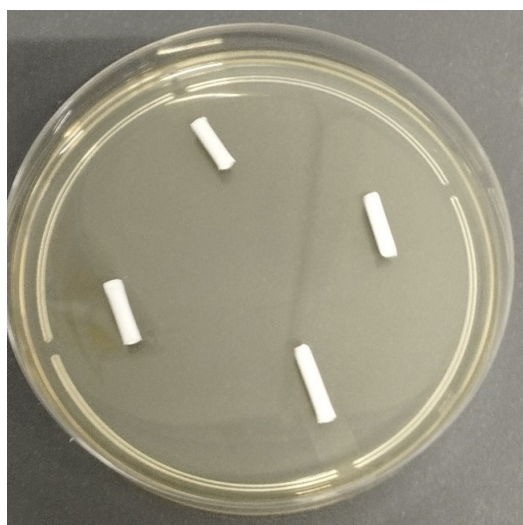


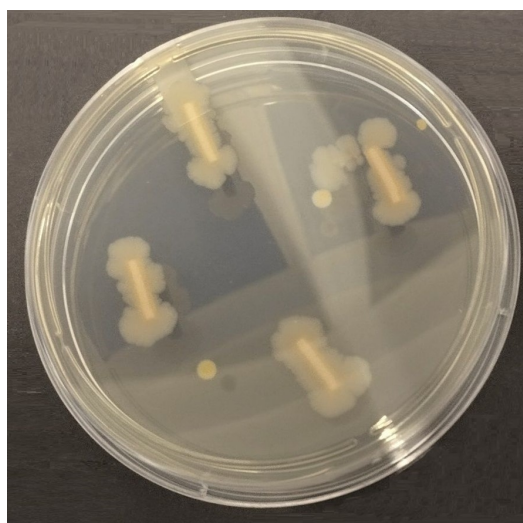
Figure 4. Permeate flux values for three filtration variants; (a) Actual measured values, (b) Normalized values.

suggests that viable bacteria were present on the membrane surface after the filtration process and then demonstrated the ability to colonize the surrounding medium, indicating a lack of bactericidal effect. These observations confirm that any interactions between the membrane and microorganisms were bacteriostatic, not lethal, limiting local surface colonization but not eliminating live cells at test conditions, which to some extent seems to be contrary to previous results (Szwast et al.,

2023). However, it should be emphasized that experimental conditions in the present work and in the ASTM test differ significantly in contact time and composition of the surrounding medium (e.g., the presence of nutrient).



(a)



(b)

Figure 5. The growth of bacterial cultures around the membrane fragments on the Petri dishes: (a) initial, (b) after 24h of incubation.

After completing the tests involving CuO-modified membranes, copper was analysed in the retentate and permeate streams after 96 hours of continuous operation of the membrane module. Within the detection limits of the analytical method used, no Cu was detected in either the permeate or retentate. This result, of course, does not definitively confirm the absence of CuO nanoparticle released from the membrane surface, but it does indicate that the degradation of active layer (if any) is negligible and should not affect the quality of the purified stream or the durability of the membrane's functional properties.

3.3. Model analysis of biofouling mechanisms

In long-term membrane operation, fouling rarely develops at a constant rate, as assumed in classical pore-blocking models. From a process-engineering perspective, the intensity of resistance buildup often changes over time due to evolving surface coverage, restructuring of deposited material, and biological activity. Therefore, while the Hermia model provides a useful first-order description of dominant fouling mechanisms, an extended formulation capable of capturing time-dependent fouling dynamics is required to better reflect real operating conditions.

In the literature on the mathematical description of fouling and biofouling, models based on the Hermia approach are commonly used (Niu et al., 2022; Shams et al., 2022). It allows for the description of permeate flux changes as a function of time by relating them to the dominant fouling mechanism. The general form of the Hermia model equation is presented in Eq. (1) (Pereira et al., 2023).

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (1)$$

where t is the filtration time [s], V is the permeate volume [m^3], k is the fouling rate [unit depends on n value] and n is the exponent defining the fouling mechanism [–]. The fouling constant k has units dependent on the value of exponent n and can be expressed as $\text{s}^{1-n}\text{m}^{3n-6}$. For the mechanisms considered in this study the corresponding units are: $\text{s}\cdot\text{m}^{-6}$ for $n = 0$, m^{-3} for $n = 1$, $\text{s}^{-0.5}\text{m}^{-1.5}$ for $n = 1.5$, and s^{-1} for $n = 2$.

Different fouling mechanisms can be described using the Hermia model by selecting an appropriate value of the exponent n , which determines the dominant pore-blocking regime. When $n = 2$, the model represents complete blocking, whereas $n = 1.5$ corresponds to standard blocking. A value of $n = 1$ describes intermediate blocking, while $n = 0$ is associated with cake formation. The choice of the exponent thus allows the observed decline in permeate flux to be linked directly to the physical nature of the fouling phenomena occurring on and within the membrane structure. A graphical interpretation of the described fouling phenomena is presented in Figure 6.

To determine the mechanism responsible for fouling and biofouling in the studies presented in this paper, the Hermia model was fitted to the results presented in Fig. 4b, covering the three analysed filtration variants. For each variant and for all four values of the exponent n , the model coefficient was estimated by selecting the parameter k using the least squares method. The Bayesian Information Criterion (BIC) was then calculated to assess the quality of the model fit (Lee et al., 2014). The best model was the one for which the BIC value reached its minimum (Zhang et al., 2023), indicating the most adequate description of the observed changes in permeate flux density. The calculated k , BIC, R^2 , and RMSE values are collected in Table 3.

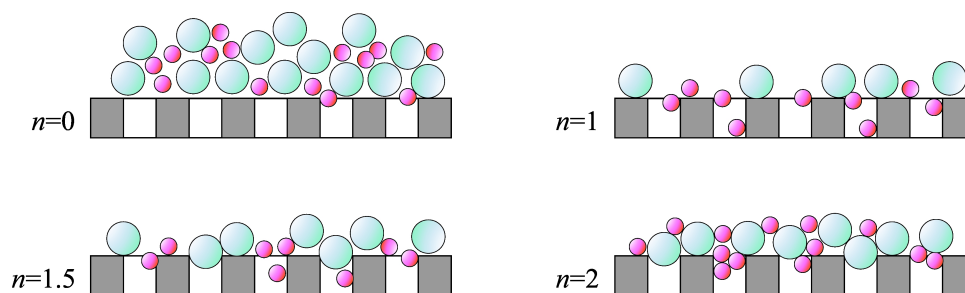


Figure 6. Graphical interpretation of the fouling phenomena described by Hermia equation: $n = 0$ is associated with cake formation, $n = 1$ describes intermediate blocking, $n = 1.5$ corresponds to standard blocking, $n = 2$ represents complete blocking.

Table 3. Calculated values of the k coefficient and the BIC criterion, R^2 and RMSE for Hermia model fits.

		Pure water– PP membrane	Pure water + <i>E. coli</i> – PP membrane	Pure water + <i>E. coli</i> – PP+CuO membrane
$n = 2$	k	0.0042	0.0224	0.0126
	BIC	–66917	–32647	–30691
	R^2	0.998	0.979	0.976
	RMSE	0.003	0.063	0.074
$n = 1.5$	k	0.0045	0.0293	0.0149
	BIC	–64075	–28415	–27989
	R^2	0.998	0.969	0.945
	RMSE	0.004	0.089	0.093
$n = 1$	k	0.0048	0.0378	0.0176
	BIC	–58465	–25504	–26129
	R^2	0.998	0.949	0.921
	RMSE	0.007	0.115	0.109
$n = 0$	k	0.0056	0.0633	0.0245
	BIC	–51376	–22052	–23692
	R^2	0.991	0.903	0.875
	RMSE	0.012	0.154	0.134

Analysis of the data presented in Table 3 indicates that for all filtration variants, the best model fit (lowest BIC value) was obtained for $n = 2$. The analysis of both R^2 and RMSE values also indicates that the best fit is obtained for $n = 2$. This means that the fouling process is best described by the complete blocking regime. In this case, the increase in filtration resistance occurs in a mixed mode, meaning it is not solely determined by membrane surface blocking or pore blocking. This mechanism is commonly observed in ultrafiltration and microfiltration processes of biological and colloidal solutions, where partial particle deposition on the surface and their penetration into the porous structure simultaneously occur (AlSawaf et al., 2022; Yang et al., 2022). Figure 6 presents the measurement data obtained for three filtration variants, along with the corresponding model curve determined using the Hermia equation for $n = 2$.

Analysis of the graphs presented in Fig. 7 reveals significant differences in the quality of the Hermia model fit for $n = 2$ depending on the filtration variant. In variant Fig. 7a, the model curve matches the experimental data very well, confirming that the intermediate blocking mechanism adequately describes the observed mild fouling behaviour. However, a different situation occurs in variants in Fig. 7b and Fig. 7c. Although for both cases the value of $n = 2$ provided the best fit among the four Hermia model regimes considered, the graphs clearly show that the model's agreement with the experimental data is far from satisfactory. These differences indicate that fouling in the presence of a bacterial suspension is more complex and requires the use of extended or hybrid models that allow for a more accurate description of the process dynamics in these two filtration variants.

The literature on modelling degradation, aging, and the growth of cumulative phenomena increasingly utilizes approaches based on reliability theory, where the description of event intensity variation over time is crucial. One of the most commonly used distributions in such analysis is the Weibull distribution, traditionally used in statistics and survival analysis to model time to failure or time between events (Weibull, 1951). The model equation has the following form:

$$S(t) = e^{-\left(\frac{t}{\tau}\right)^m} \quad (2)$$

where $S(t)$ is the probability that the system survives until time t [s], τ is the time scale parameter, m is the shape parameter, which describes how the rate of events changes over time: when $m < 1$, the rate decreases and early failures dominate; $m = 1$ it remains constant, corresponding to the exponential case; and when $m > 1$, the rate increases, reflecting ageing or the accumulation of damage.

The classical Hermia model for $n = 2$ (see Appendix), which provided the best description for all three filtration variants considered, describes the exponential decay of flux, assuming a constant blocking intensity (a constant hazard):

$$J = J_0 e^{-kt} \quad (3)$$

where J is the permeate flux [$\text{m}^3\text{h}^{-1}\text{m}^{-2}$], J_0 is the initial permeate flux [$\text{m}^3\text{h}^{-1}\text{m}^{-2}$] and k is the fouling rate (defined earlier).

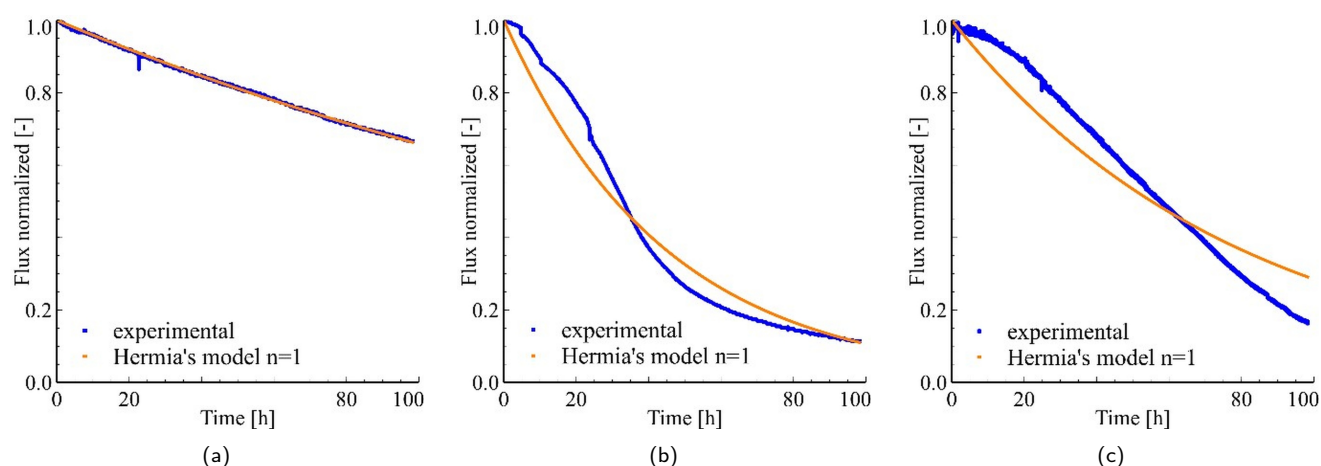


Figure 7. Normalized permeate flux: experimental (blue line) and Hermia model curve (orange line); (a) pure water filtration with PP membrane, (b) pure water with bacterial suspension filtration with PP membrane, (C) pure water with bacterial suspension filtration with PP+CuO membrane.

However, real fouling, especially biofouling, rarely occurs at a constant rate. Therefore, the Hermia model (Eq. 3) was generalized to the Weibull form:

$$J = J_0 e^{(-kt)^m} \quad (4)$$

where the shape parameter m allows the process to be described with variable intensity, i.e., with a fouling rate that changes over time rather than remains constant. In this formulation, $m < 1$ corresponds to a decreasing fouling rate, $m = 1$ represents a constant-rate process equivalent to the classical exponential model, whereas $m > 1$ indicates an increasing fouling rate during filtration. The Weibull formulation thus provides a natural extension of the Hermia's $n = 2$ model, preserving its structure while enabling a more realistic representation of fouling dynamics.

Table 4 presents the least-squares-fitted values of the parameters k and m for the three filtration variants.

Table 4. Calculated k and m coefficients and BIC values for the Weibull-generalized Hermia model fits.

	Pure water–PP membrane	Pure water + <i>E. coli</i> –PP membrane	Pure water + <i>E. coli</i> –PP+CuO membrane
k	0.0041	0.0224	0.0141
m	0.98	1.35	1.65
BIC	−67509	−38967	−54681
R^2	0.999	0.985	0.999
RMSE	0.003	0.037	0.009

When analysing the BIC (Bayesian Information Criterion) values, it should be noted that for all examined cases the data are better described by the model extended with the Weibull formulation than by the standard Hermia model (see

Table 3). Similar conclusions can be drawn from the analysis of the remaining statistical parameters. Moreover, for pure-water filtration on the PP membrane, the parameter m differs only slightly from 1, meaning it deviates only marginally from the classical Hermia model for $n = 1$. In contrast, for both the filtration of water containing *E. coli* using the PP membrane and the filtration of water containing *E. coli* using the PP+CuO membrane, the exponent m takes values noticeably higher than 1. Furthermore, for the PP membrane it is lower ($m = 1.35$) than for the PP+CuO membrane, which exhibits bacteriostatic properties ($m = 1.65$).

The Weibull model makes it possible to separate the time scale of fouling development (parameter k) from the nature of the flux-decline evolution (parameter m). The lower k value obtained for the PP+CuO membrane (bacteriostatic) indicates a slower initial rate of flux reduction and an extended period of effective membrane operation. In contrast, the higher m value reflects a more strongly accelerating fouling behaviour in the later stages of filtration, likely associated with the progressive accumulation and restructuring of biological material at the membrane surface, which, after reaching a certain critical level, forms a rapidly densifying layer.

Figure 8 presents the measurement data obtained for the two filtration variants in which a bacterial suspension was used, along with the corresponding model curve determined using the Hermia model generalized to Weibull form. Since the results obtained for the generalized model in the case of filtration of pure water and a PP membrane do not differ significantly from the results obtained from the classical Hermia model, Fig. 8 only presents the model fits for those filtration variants in which pure water containing a bacterial suspension was used.

Moreover, in both the Hermia model and its extension to the Weibull model, the parameter k defines the time scale of fouling, and thus the rate of flux decay (Pereira et al., 2023).

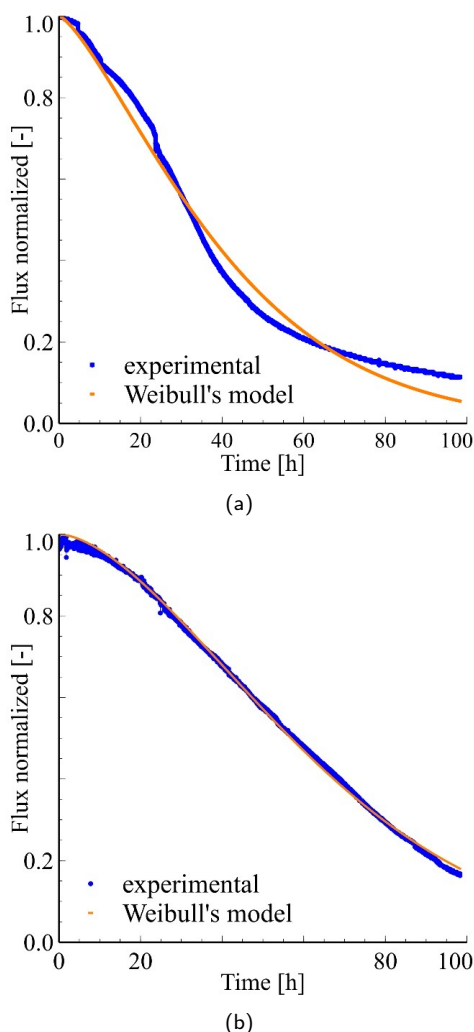


Figure 8. Normalized permeate flux: experimental (blue line) and Weibull model curve (orange line); (a) pure water with bacterial suspension filtration with PP membrane, (b) pure water with bacterial suspension filtration with PP+CuO membrane.

The characteristic time of the process can be determined from the condition

$$(kt^*)^m = 1 \quad (5)$$

which leads to (for every m value)

$$t^* = \frac{1}{k} \quad (6)$$

i.e., the moment at which the flux decreases to

$$J = \frac{J_0}{e} \quad (7)$$

For PP membrane, the characteristic time is 45 hours and for PP+CuO membrane it is 71 hours. This means that the bactericidal membrane maintains a high flux level for a much longer period and demonstrates significantly greater temporal resistance to fouling than the reference membrane.

4. CONCLUSIONS

The results of this study demonstrate that surface modification of capillary polypropylene membranes with a thin, porous polysulfone layer containing CuO nanoparticles significantly improves the long-term operational stability of membrane filtration processes conducted under constant transmembrane pressure in biologically active environments. Morphological and structural analyses (SEM, XRF, porosimetry) confirmed that the modification was successfully introduced into the near-surface region of the membrane without causing detrimental changes to its intrinsic porous structure or initial hydraulic performance.

Long-term cross-flow filtration experiments revealed that, despite similar initial permeate fluxes, membranes modified with CuO nanoparticles exhibited a substantially slower rate of hydraulic resistance buildup in the presence of *E. coli*. As a result, the cumulative permeate volume obtained over 96 hours of continuous operation was nearly 43% higher than that of the unmodified polypropylene membranes. From a process-engineering perspective, this improvement corresponds to a prolonged effective operating period of the membrane module and a reduced intensity of biofouling-driven flux decline under steady operating conditions.

Analysis of permeate flux decline using the Hermia model indicated that, for all filtration variants, the dominant fouling mechanism was best described by the complete blocking regime ($n = 2$). However, the limited ability of the classical Hermia model to capture the evolving dynamics of biofouling under long-term operation motivated the application of a generalized Weibull formulation. This extended approach enabled separation of the fouling time scale from the temporal evolution of fouling intensity, providing a more realistic description of resistance development in biologically active systems.

The Weibull-based analysis showed that membranes modified with CuO nanoparticles were characterized by a lower initial fouling rate and a significantly longer characteristic fouling time compared to the reference membranes. The characteristic time increased from approximately 45 hours for unmodified polypropylene membranes to 71 hours for CuO-modified membranes, indicating a delayed transition to high-resistance operating conditions. In practical terms, this behaviour suggests extended filtration cycles, delayed cleaning requirements, and improved reliability of membrane operation in continuous processes.

Overall, the presented results confirm that incorporating bacteriostatic CuO nanoparticles into the membrane surface represents an effective strategy for mitigating biofouling-induced performance deterioration without compromising membrane selectivity or hydraulic functionality. The combination of long-term experimental evaluation with time-resolved process modelling provides a framework that is directly applicable to the design, optimization, and assessment of membrane filtration systems operated under realistic process conditions.

From an application perspective, the obtained results indicate that bacteriostatic surface modification with CuO nanoparticles may represent a promising strategy for improving the long-term stability of membrane systems used in water treatment and other biologically active filtration processes. The demonstrated extension of effective operating time under constant transmembrane pressure suggests potential benefits in terms of reduced cleaning frequency, improved process continuity, and lower operational costs. Future studies should focus on verification of the observed effects under pilot- and industrial-scale operating conditions, as well as on long-term durability of the modifying layer and its performance in the presence of more complex natural microbial consortia and feed compositions.

SYMBOLS

A	membrane area, m^2
J	permeate flux, $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$
J_0	initial permeate flux, $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$
k	fouling rate constant (Hermia model), units depend on exponent n
m	Weibull shape parameter, –
n	Hermia model exponent describing fouling mechanism, –
R^2	coefficient of determination, –
SD	standard deviation, μm
S	survival probability function (Weibull model), –
t	time, s
V	permeate volume, m^3

Greek symbols

μ_{In}	mean of log-normal pore size distribution, –
ρ_{In}	standard deviation of log-normal pore size distribution, –
τ	characteristic time scale parameter (Weibull model), s

Abbreviations

BIC	Bayesian Information Criterion
CFU	colony forming units
CuO	copper(II) oxide
EPS	extracellular polymeric substances
LB	Luria–Bertani broth
NMP	N-methyl-2-pyrrolidone
PSf	polysulfone
RMSE	root mean square error
RLU	relative light units
SEM	scanning electron microscopy
TMP	transmembrane pressure
VBNC	viable but nonculturable
XRF	X-ray fluorescence

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APPENDIX

Derivation of the Hermia model expressed in terms of permeate flux

The general form of the Hermia fouling model is given by

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (\text{A1})$$

where t is the filtration time, V is the permeate volume, k is the fouling constant, and n is an exponent defining the fouling mechanism.

The permeate flux is defined as

$$J = \frac{dV}{dt} \quad (\text{A2})$$

Therefore

$$\frac{dt}{dV} = \frac{1}{J} \quad (\text{A3})$$

Taking the derivative with respect to V

$$\frac{d^2t}{dV^2} = \frac{d}{dV} \left(\frac{1}{J} \right) \quad (\text{A4})$$

Using the chain rule and the relation between derivatives with respect to V and t

$$\frac{d}{dV} = \frac{d}{dt} \frac{dt}{dV} \quad (\text{A5})$$

one obtains

$$\frac{d^2t}{dV^2} = -\frac{1}{J^3} \frac{dJ}{dt} \quad (\text{A6})$$

Substituting this expression into the Hermia equation (Eq. A1) yields

$$-\frac{1}{J^3} \frac{dJ}{dt} = k \left(\frac{1}{J} \right)^n \quad (\text{A7})$$

After rearrangement, the differential equation in terms of permeate flux is obtained

$$\frac{dJ}{dt} = -kJ^{3-n} \quad (\text{A8})$$

For the particular case $n = 0$, Equation (A8) reduces to the form

$$\frac{dJ}{dt} = -kJ^3 \quad (\text{A9})$$

Integration of this equation leads to

$$\frac{1}{J^2} = 2kt + \frac{1}{J_0^2} \quad (\text{A10})$$

and finally

$$J = \frac{J_0}{\sqrt{1 + 2kJ_0^2t}} \quad (\text{A11})$$

For the particular case $n = 1$, Equation (A8) reduces to the form

$$\frac{dJ}{dt} = -kJ^2 \quad (\text{A12})$$

Integration of this equation leads to

$$\frac{1}{J} = kt + \frac{1}{J_0} \quad (\text{A13})$$

and finally

$$J = \frac{J_0}{1 + kJ_0t} \quad (\text{A14})$$

For the particular case $n = 1.5$, Equation (A8) reduces to the form

$$\frac{dJ}{dt} = -kJ^{1.5} \quad (\text{A15})$$

Integration of this equation leads to

$$\frac{1}{\sqrt{J}} = 0.5kt + \frac{1}{\sqrt{J_0}} \quad (\text{A16})$$

and finally

$$J = \frac{J_0}{(1 + 0.5k\sqrt{J_0t})^2} \quad (\text{A17})$$

For the particular case $n = 2$, Equation (A8) reduces to the form

$$\frac{dJ}{dt} = -kJ \quad (\text{A18})$$

Integration of this equation leads to

$$\ln\left(\frac{J}{J_0}\right) = -kt \quad (\text{A19})$$

and finally

$$J = J_0 e^{-kt} \quad (\text{A20})$$