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CuO nanoparticles as modifiers for membranes for anaerobic membrane digestion

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Abstract Membrane separation technologies offer a promising solution for anaerobic digestate treatment but are limited by membrane fouling and reduced flux. This study investigated the use of CuO nanoparticles (NPs) on ultrafiltration membranes to mitigate fouling and improve separation performance during digestate treatment. CuO NPs were synthesized via a sonochemical process and deposited onto NADIR® UP150 T membranes. The modified and unmodified membranes were evaluated using anaerobic sludge from a pilot-scale anaerobic digester under two operational modes: continuous and intermittent with reverse flow cleaning. Results showed that although modified membranes had slightly lower initial permeate flow rates, they exhibited greater stability over time and reduced fouling rates compared to the unmodified membrane. Under intermittent cleaning, the unmodified membrane displayed the highest cleaning impact, with a 100% increase in permeate flow post-cleaning, versus 66.7–88.9% for coated samples. The findings suggest that CuO-modified membranes can provide a trade-off between fouling resistance and flux performance, particularly in systems with limited cleaning capacity.

Keywords: membranes, anaerobic digestion, digestate treatment, CuO nanoparticles

1. Introduction

Effective treatment of digestate from anaerobic digestion plays a key role in sustainability of the process. Membrane separation technologies are increasingly used for digestate treatment but their performance is often affected by fouling and flux decline. Embedding CuO nanoparticles (NPs) onto membranes offers a promising antifouling strategy, through hydrophilicity alterations and antimicrobial action. For example, ceramic based membrane modified with CuO NPs anaerobic bioreactor reached 93% COD removal and exhibited significantly slower transmembrane pressure rise compared to unmodified membrane (Qiu et al., 2023). Studies on PVDF ultrafiltration membranes blended with CuO and graphene oxide report enhanced flux recovery, reduced irreversible fouling, and broad-spectrum antibacterial activity (Zhao et al., 2023). Furthermore, morphologically tuned CuO nanomaterials integrated in PVDF/PVP membranes achieved flux recovery >90%, improved hydrophilicity, and exhibited negligible Cu^{2+} leaching (Pakan et al., 2023). Based on these insights, this study evaluates CuO NPs modified membranes for digestate treatment, focusing on separation efficiency and fouling mitigation in real anaerobic digestate samples.

2. Materials and Methods

This work has been carried out as part of the Horizon Europe SYMSITES project. The SYMSITES initiative focuses on implementing industrial-urban symbiosis strategies to convert waste and by-products into environmentally sustainable value-added products. The project has tested innovative technologies, methodologies, and stakeholder engagement approaches across four EcoSites located in different European regions, each characterized by distinct socioeconomic and environmental conditions—ranging from northern Europe (Denmark), through central Europe (Austria), to southern regions (Spain and Greece). At the Greek EcoSite, an anaerobic membrane bioreactor (AnMBR) has been employed as the core equipment for the production of methane, water for irrigation and compost.

2.1. Materials

The original membranes used and modified were NADIR® UP150 T Polyethersulfone (PES) ultrafiltration membranes (MANN+HUMMEL GmbH, Germany) with a nominal pore size of 40 nm and a molecular weight cutoff (MWCO) of 150 kDa. Chemicals used for CuO formation and coating were Copper (II) acetate monohydrate, ACS reagent, ≥98%, Ammonium hydroxide solution, ACS reagent, 28.0-30.0% (Sigma –Aldrich). The anaerobic sludge used for the evaluation of the modified membrane performance was sampled from the anaerobic membrane digester of the Greek EcoSite. The anaerobic sludge used during the membrane performance evaluation exhibited a total suspended solids (TSS) concentration of 3.0 g/L, with volatile suspended solids (VSS) measured at 1.6 g/L. This indicates that a substantial portion of the suspended matter was organic and potentially biodegradable. The pH level of the sludge was maintained at 7.2, which is conducive to optimal anaerobic microbial activity and helps ensure stable biological treatment conditions.

2.2. Membrane Modification

Modification of the original membrane was performed through sonochemical synthesis. Copper (II) acetate was dissolved in a sonochemical tank prior to sonotrods activation for 1 hour heating the solution to 60^0C. Ammonium hydroxide was subsequently added in the system and the formation of CuO NPs took place according to the following equations at a pH of 8.5.

$$Cu^{2+}_{(aq)} + 4NH_3 \cdot H_2O \rightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 4H_2O$$

$$[Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)} + 3H_2O \rightarrow CuO_{(s)} + 4NH_3 \cdot H_2O$$

The membrane was rolled through the solution as the formed CuO NPs were deposited on its surface with sonication. Modification was evaluated using sonotrod intensity of 47.5, 90.0 and 95.0%.

2.3. Digestate Treatment

Evaluation of original and modified membrane samples was performed in 4h continuous operation and 4h operation with intermittent reverse flow cleaning every 60 minutes in order to examine the permeate flow rate fluctuations and the impact of reverse flow cleaning for each membrane. Reverse flow cleaning was performed using the same permeate volume in each case. Permeate volume over time was monitored.

3. Results and Discussion

3.1. Continuous Digestate Treatment

During continuous operation, modified membranes exhibited lower initial permeate flux rates compared to non-modified sample as described in Figure 1. However, the non-coated sample displayed a higher drop in the flux already within the first hour of operation. All membrane samples show similar behaviour after 2h of operation without cleaning.

3.2. Intermittent Digestate Treatment

The cumulative permeate volume was monitored and the results are presented in Figure 2. The cleaning efficiency for each specimen was calculated.

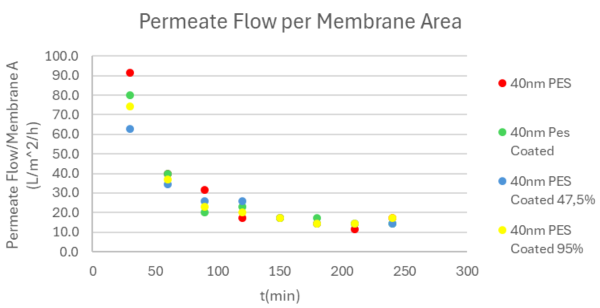

Figure 1. Permeate flux (L/m²/h) over time for 40nm PES membrane and 3 different modifications during 4h continuous operation.

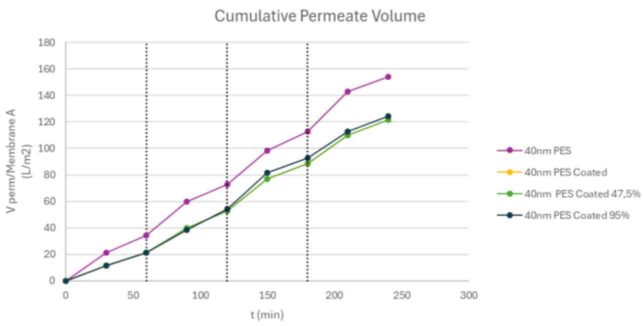

Figure 2. Cumulative permeate volume per membrane surface area (L/m²/h) over time for 40nm PES membrane and 3 different modifications during 4h operation with intermittent cleaning, every 60 minutes (dotted vertical lines).

4. Conclusion

The hypothesis that the coating on the membrane active surface should reduce both the total permeate passing and the clogging effect was confirmed. The non-coated membrane sample did display higher flow rates and increased cleaning requirement to maintain these flows. However, if sufficient reverse flow cleaning of the specific membrane type is used, the non-modified version seems to achieve the highest permeate fluxes.

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