1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title:

Covalently created membranes with adjustable adhesion, hydrophobicity and omniphobicity for robust membrane distillation

1.1. Project goals

Wetting, scaling, and functionality loss of the active layer are critical challenges facing membrane distillation (MD) process that substantially hinder its practical applications. To solve the mentioned problems, an effective strategy to design and generate superomniphobic MD membrane with excellent wetting/scaling resistance and mechanical robustness will be developed. Precisely, a hierarchical re-entrant architecture will be created by immobilizing inorganic particles onto a poly(vinylidene fluoride) (PVDF) membrane surface via covalent bonds, followed by fluorination via thiolene click chemistry. The requirement is to build surfaces with highly hydrophobic features and low sliding angle (tuned adhesion) to ensure superhydrophobicity and slippery characteristics of the modified membranes. The study of wetting resistance toward various liquids with low surface tension will be an important issue. Long-duration MD for the treatment of a highly saline brine (synthetic multi-component hypersaline wastewater), with a surfactant content will be used to study membrane stability and robustness. Overall, the project foreseen to produce and fully characterize a novel and effective separation materials that will be implemented to membrane distillation operated under harsh environments.

1.2. Outline

Membrane distillation (MD) has converted recently to be an emerging technology owing to increasing demand for the treatment of industrial hypersaline effluents [1,2]. MD technology, which is driven by a water vapor pressure gradient, can tolerate ultrahigh-salinity brine, which cannot be treated by other desalination processes, such as reverse osmosis (RO), owing to high osmotic pressure [1]. Therefore, MD has received significant attention for the potential treatment of hypersaline wastewaters.

One of the most critical matters with MD is the insufficient performance of commercial hydrophobic membranes, due to scaling, wetting, and delamination of the active layer of the membranes. Precisely, the membrane wetting phenomenon, related to low-surface-tension substances in the wastewater, e.g. surfactants, undermines the ability of membranes to reject involatile salts [3,4].

In view of this, researchers have made efforts to decrease the risk of membrane wetting and scaling [5], and surface (superhydrophobic or omniphobic) engineering has proven to be an effective approach. The low adhesion of these surfaces to various liquids significantly reduces the contact area and/or duration between the liquids and the membrane surface, which impedes crystal creation and deposition on the membrane surface [4]. Unique hierarchical surfaces inspired by the microscale structures of lotus leaves could be fabricated readily by constructing re-entrant architectures with ultralow surface energy [5-7]. Regardless of the progress [5,6], the current membrane surface modification technologies have some inherent drawbacks. For instance, owing to the negatively charged nature of silica nanoparticles (SiNPs), commercial membranes (e.g., poly(vinylidene fluoride), PVDF membranes) require an initial surface silanization step to introduce protonated amino groups, followed by the physical deposition of nanoparticles (NPs) onto the membrane surface via electrostatic interactions. The NPs and/or perfluoro coating layers on top of these

NPs are likely to delaminate during long-term membrane operation. The leaked NPs and fluorinated compounds can also pose a significant threat to the environment and human health [8] Alternatively, plasma etching, photolithography, electrochemical surface modification have also been explored [9]. However, their extensive application is limited by low fabrication efficiency, low reproducibility, and high costs.

The lack of a robust membrane surface that can sustainably operate in harsh environments prompted us to explore a new membrane chemistry and the corresponding fabrication methodology. Herein, the proposed omniphobic MD membrane entirely composed of covalent bonds can be an interesting alternative. An advantage to the universal method of solution deposition of SiNPs, is to design a series of functionalization steps to form an alkene group-modified outer surface, which enabled the final surface fluorination via a highly efficient thiol-ene click reaction [7,10].

1.3. Work plan

- preparation of the porous polymeric membranes from hydrophobic material, e.g. polyvinylidene fluoride (PVDF),
- covalent modification of the membrane material by changing the chemical composition and/or physical structure (e.g. pattering, roughness tuning) via chemical attachment of inorganic nanoparticles.
- material characterization with the implementation of various analytical methods, e.g. microscopic, spectroscopic techniques,
- membrane tests in the separation processes, e.g. membrane distillation under harsh conditions, e.g. hypersaline wastewater
- description of material features and correlation with the transport and separation efficiency.

1.4. Literature

1. E. Mohammadi Shamlou,R. Vidic, V. Khanna, Optimization-based modeling and economic comparison of membrane distillation configurations for application in shale gas produced water treatment, Desalination 526 (2022) 115513
2. L. Cao, Y. Zhang, L. Ni, X. Feng, A novel loosely structured nanofiltration membrane bioreactor for wastewater treatment: Process performance and membrane fouling, Journal of Membrane Science 644 (2022) 120128
3. G. Zaragoza, J.A. Andrés-Mañas, A. Ruiz-Aguirre, Commercial scale membrane distillation for solar desalination, npj Clean Water 1 (2018) 20
4. T. Horseman, Y. Yiming, C.S.S. Kofi, W. Zhangxin, T. Tiezheng, L. Shihong, Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies ACS EST Engineering 1 (2021) 117–140
5. Z.C. Xiao, H. Guo, H.L. He, Y.J. Liu, X.M. Li, Y.B. Zhang, H.B. Yin, A.V. Volkov, T. He, Unprecedented scaling/fouling resistance of omniphobic polyvinylidene fluoride membrane with silica nanoparticle coated micropillars in direct contact membrane distillation, Journal of Membrane Science 599 (2020) 117819
6. V. Karanikola, C. Boo, J. Rolf, M. Elimelech, Engineered slippery surface to mitigate gypsum scaling in membrane distillation for treatment of hypersaline industrial wastewaters, Environmental Science &Technology, 52 (2018) 14362-14370

7. S. Owusu-Nkwantabisah, M. Robbins, D. Y.Wang Towards superhydrophobic coatings via thiol-ene post-modification of polymeric submicron particles, Applied Surface Science 450 (2018) 164-169
8. W. Wang, X.W. Du, H. Vahabi, S. Zhao, Y.M. Yin, A.K. Kota, T.Z. Tong, Trade-off in membrane distillation with monolithic omniphobic membranes, Nature Communications 10 (2019) 3220
9. W. Zhang, B.Y. Hu, Z. Wang, B.A. Li, Fabrication of omniphobic PVDF composite membrane with dual-scale hierarchical structure via chemical bonding for robust membrane distillation, Journal of Membrane Science, 622 (2021), 119038
10. C Hoyle, C. Bowman, Thiol–Ene Click Chemistry. Angewandte Chemie International Edition, 49 (2010) 1540-1573.

1.5. Required initial knowledge and skills of the PhD candidate

- Basic knowledge in the field of membrane separation techniques, membrane formation and modification
- Basic knowledge in the analytical techniques used for membrane characterization, SEM, AFM, DSC, porosimetry, zeta potential,
- The ability to cooperate in a team, also in international one

1.6. Expected development of the PhD candidate's knowledge and skills

- The ability to analytical thinking
- Keen to learn new techniques and instrumentations
- Eager to work hard and contribute to the success of the project
- Be interested in interdisciplinary science fields from the borderline of material chemistry, membranes, and separation techniques