Development of nanofiltration membranes for offshore recovery of H2S scavenger chemicals

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19th Nordic Filtration Symposium, June 2023

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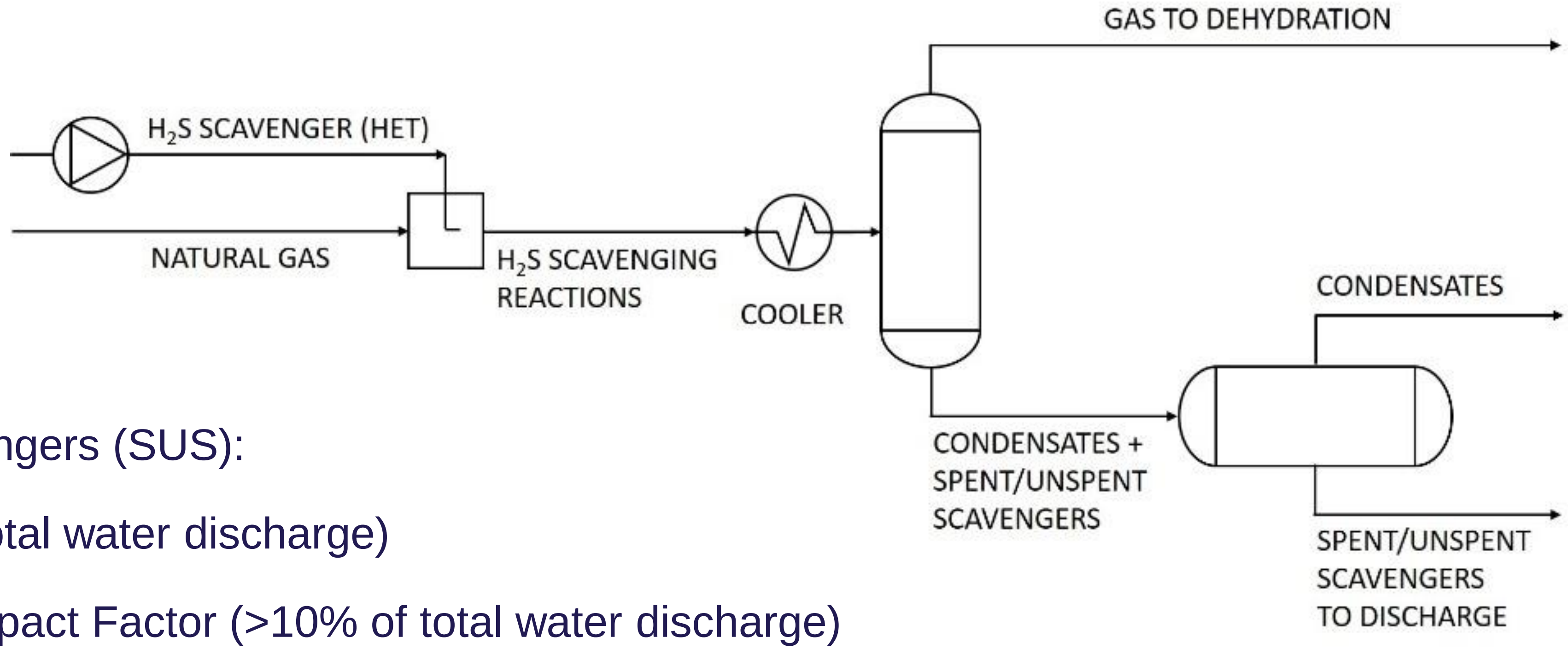
H_2S SCAVENGING OF NATURAL GAS: NECESSARY BUT EXPENSIVE AND PROBLEMATIC FOR THE ENVIRONMENT



THE PROBLEM

- Spent and Unspent Scavengers (SUS):

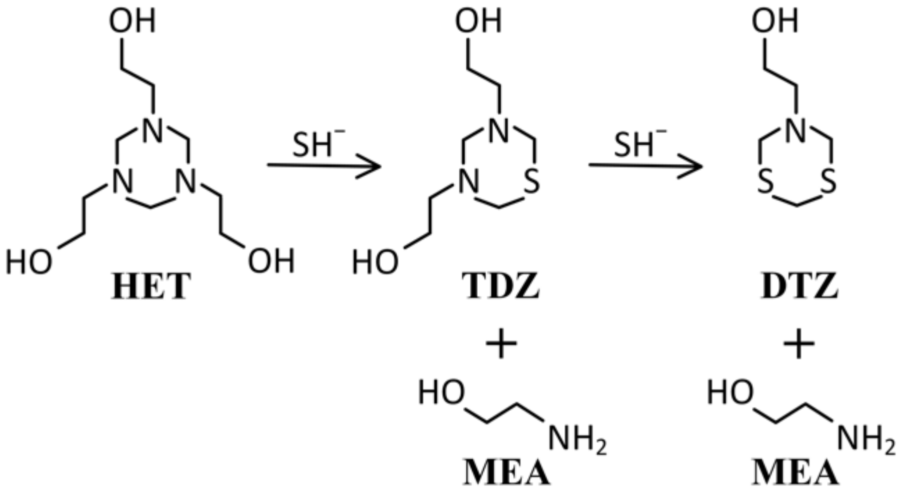
  small quantity (<0.1% of total water discharge)

  but high Environmental Impact Factor (>10% of total water discharge)

- HET: >50% of total expenditure of production chemicals

CHARACTERISTICS OF THE SUS

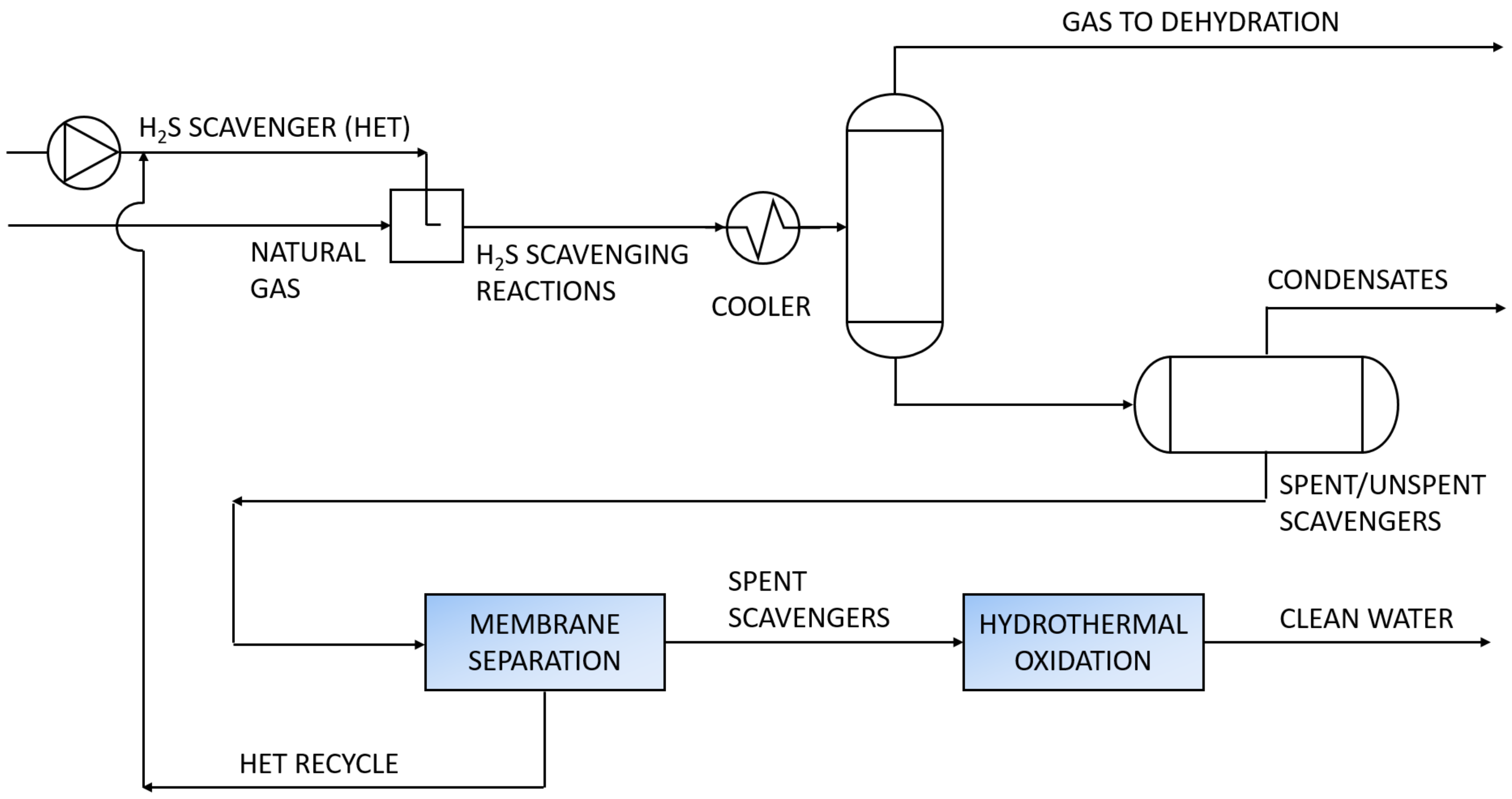
- High concentration of organics of moderate toxicity
- Large amount of unreacted triazine (HET)
- Problematic to re-inject due to fouling/scaling propensity



COD	(120 – 320) g/L
pH	8.9 – 9.6
Triazine (HET)	(8 – 15) wt%
Monoethanolamine (MEA)	(2 – 5) wt%
Dithiazine (DTZ)	(1 – 4) wt%
Formaldehyde (FA)	(1 – 2) wt%

THE CHALLENGE

- Can HET be separated before discharge for recycling?
- Can the spent scavengers be treated in a compact unit for clean discharge?



ZEROH2S PROJECT: WORK DONE during 2020-2021

- Experimental tests on commercial membranes for removal of SUS organics and separation of HET

Separation and Purification Technology 277 (2021) 119641

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Separation and Purification Technology

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Performance evaluation of membrane filtration for treatment of H_2S scavenging wastewater from offshore oil and gas production

Mahdi Nikbakht Fini, Nikolaos Montesantos, Marco Maschietti, Jens Muff *

- Experimental tests on hydrothermal oxidation of SUS

Chemical Engineering Journal 427 (2022) 131020

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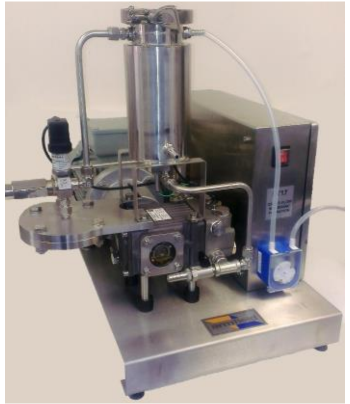
Proof of concept of hydrothermal oxidation for treatment of triazine-based spent and unspent H_2S scavengers from offshore oil and gas production

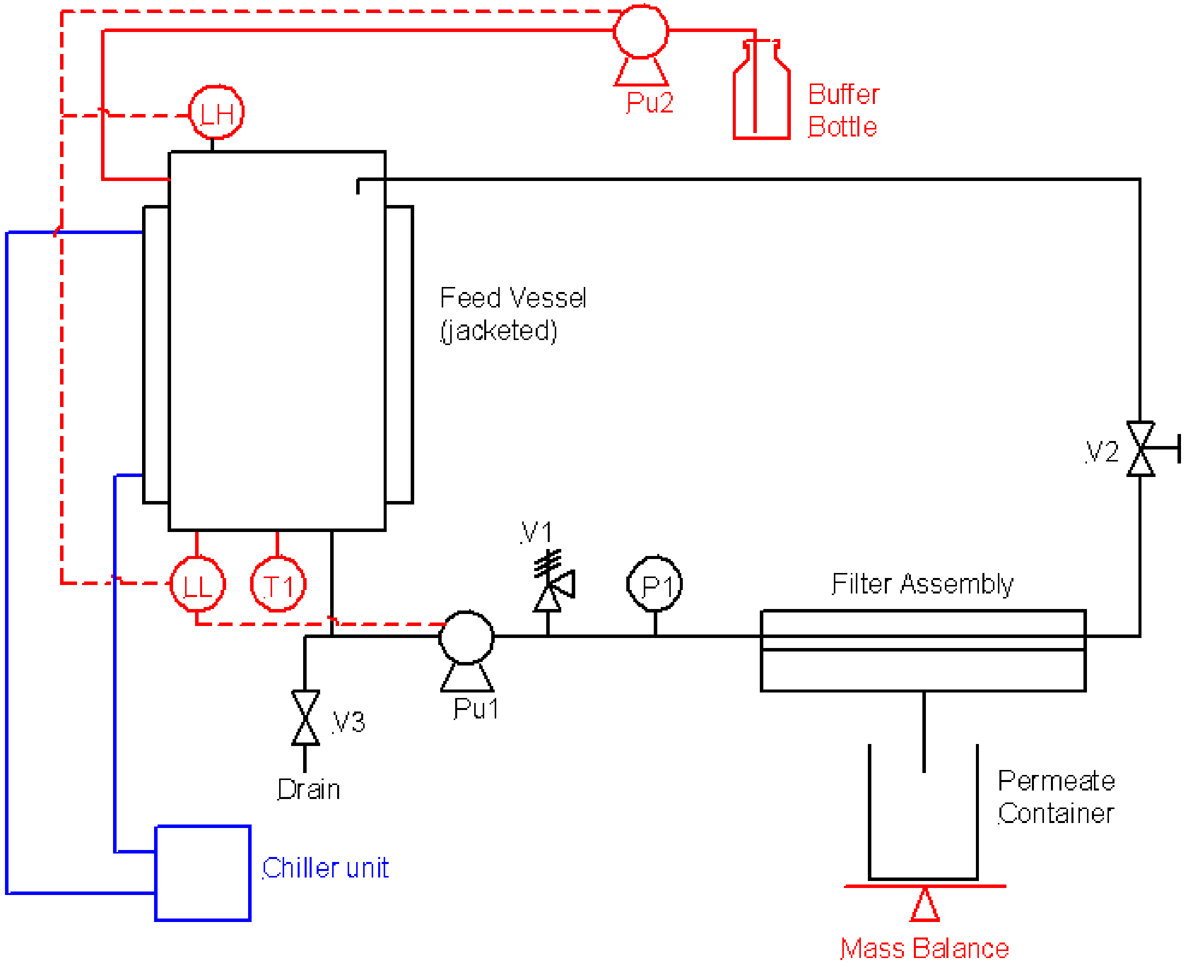
Nikolaos Montesantos, Mahdi Nikbakht Fini, Jens Muff, Marco Maschietti *

CROSS-FLOW FILTRATION SETUP

Operating conditions:

- 30 bar and 40°C
- Recovery of 250 mL of permeate out of 500 mL of feed or recycle of permeate for 24 h fouling tests
- Flow rate: 100 L/h
- Cross-flow velocity: 24.5 cm/s
- Duration: (2 – 10) hours

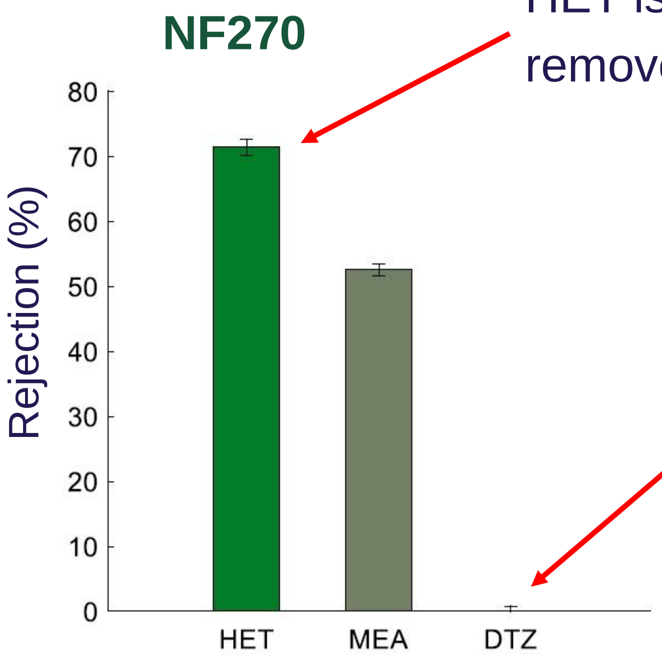




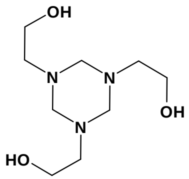
Nikbakht Fini, M., Montesantos, N., Maschietti, M., & Muff, J. (2021). Separation and Purification Technology, 277, [119641].

KEY RESULTS FROM THE MEMBRANE TESTS

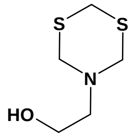
- NF270: best compromise between recovery and permeability
- No evidence of fouling up to 24 hours of operation

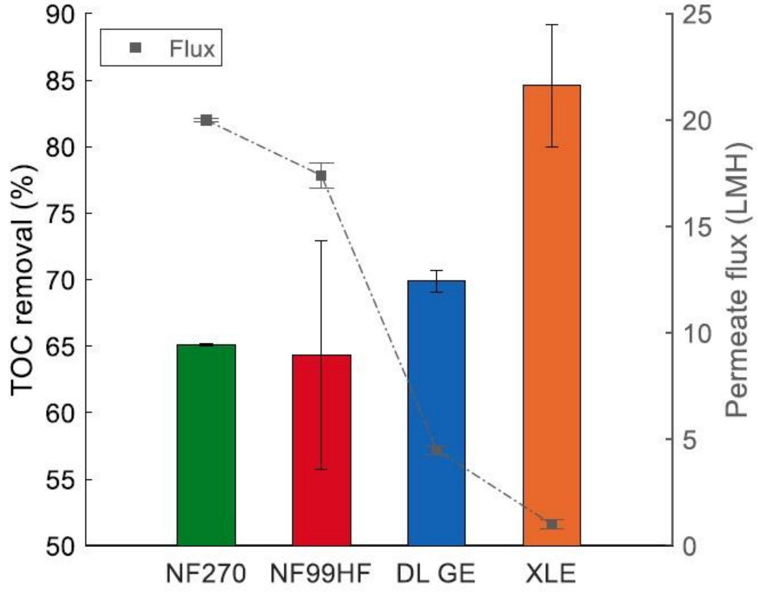


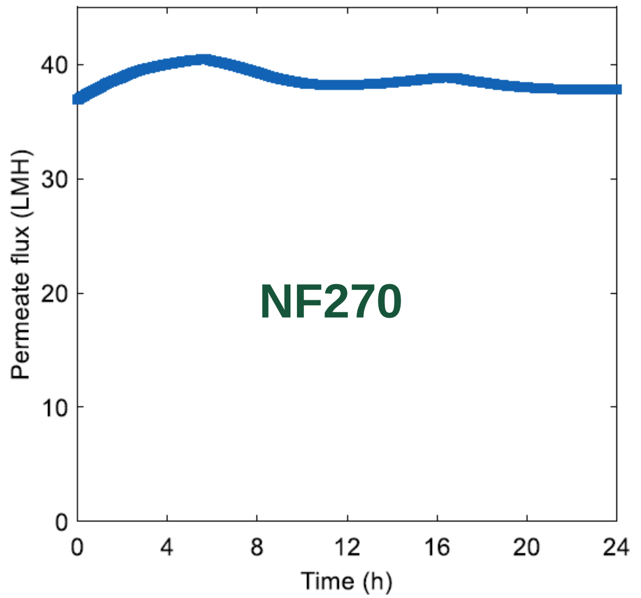
HET is removed



DTZ permeates through the membrane







- The separation HET/DTZ is possible!
- Membrane separation cannot be explained on the basis of molecular size only
- The permeation of DTZ can be explained by its high polarity and hydrophobicity

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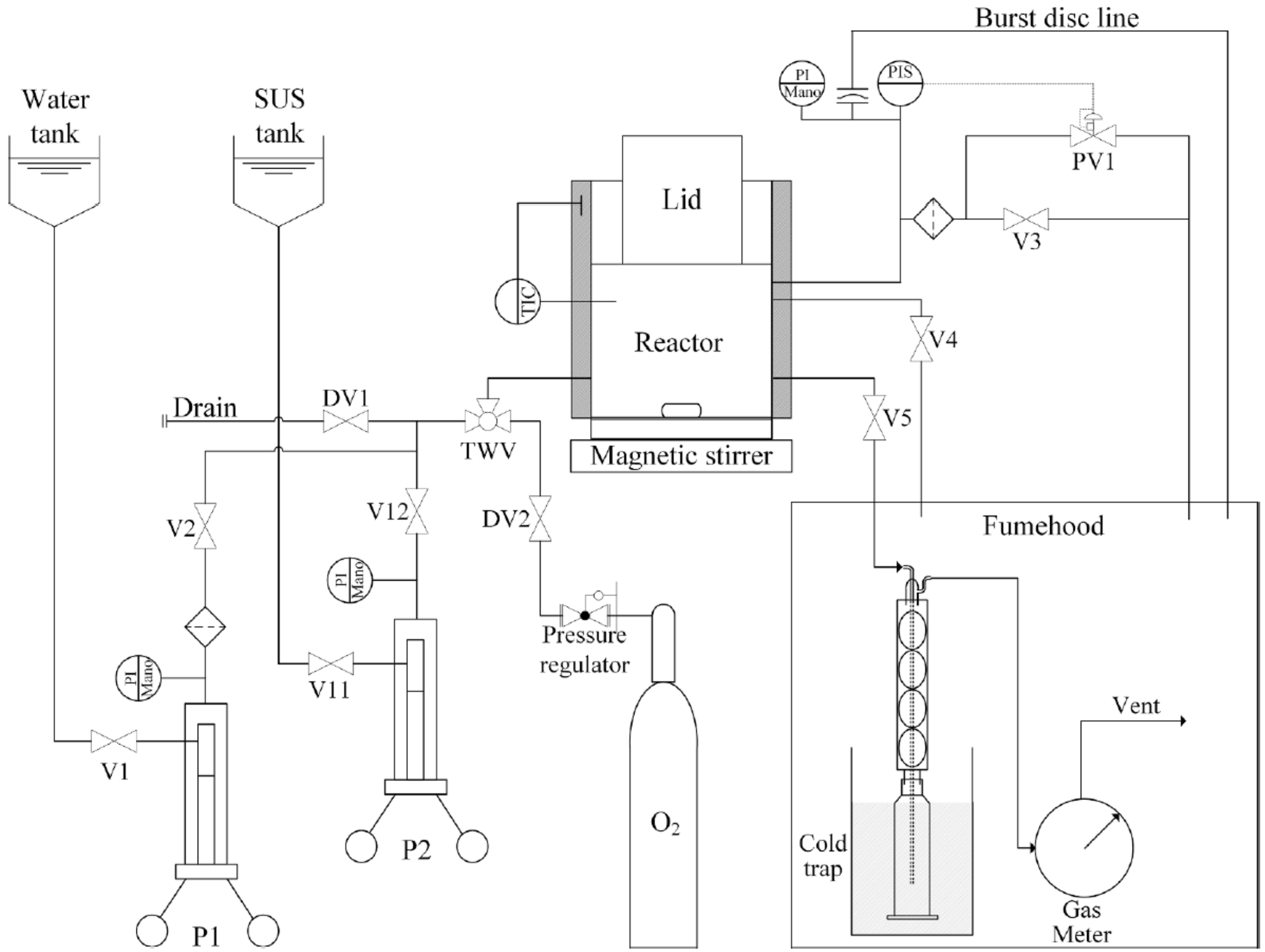
HYDROTHERMAL OXIDATION SETUP



Customized HPHT injection reactor:

- Quick heating and product quenching
- Accurate P, T control
- Accurate results supporting the scale-up to continuous-flow reactors

Operating conditions:

- Low temperature experiments: 200°C and 70-90 bar
- High temperature experiments: 350°C and 210-250 bar
- Excess of oxygen
- Reaction time: from 1 to 360 min

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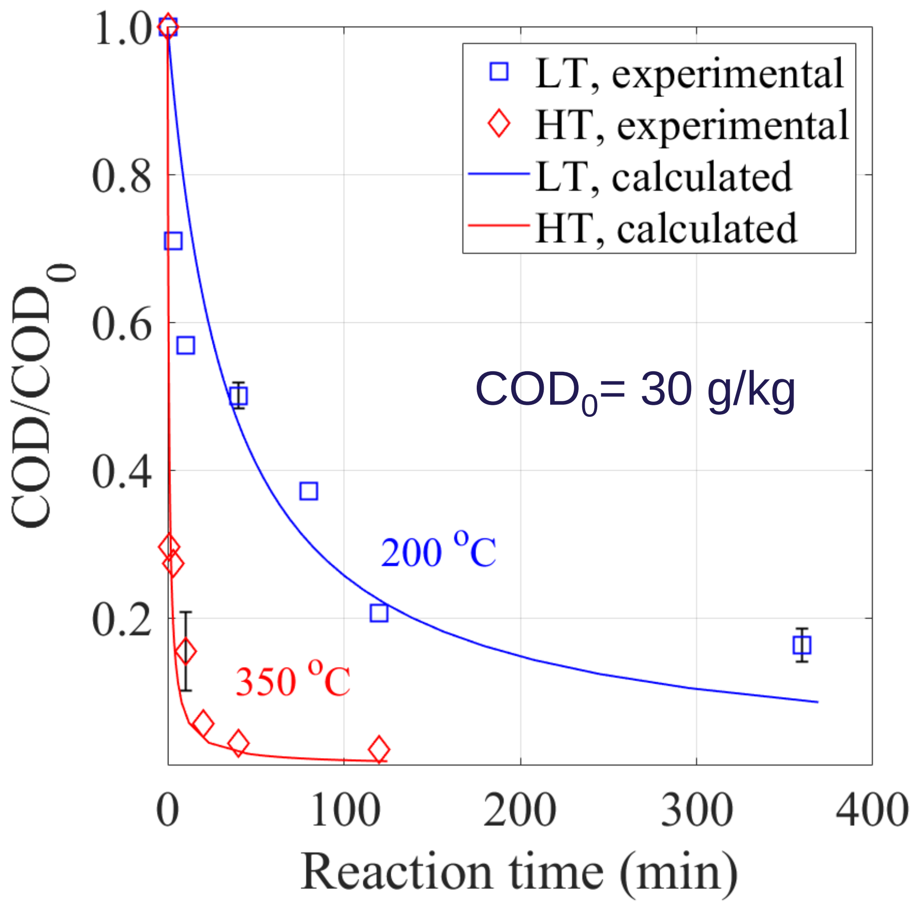
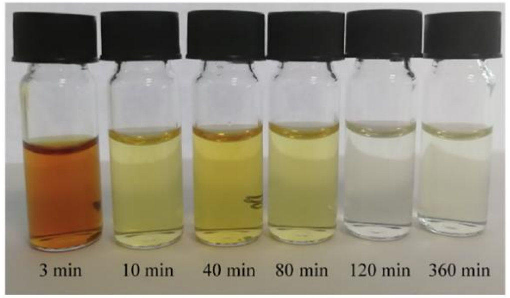
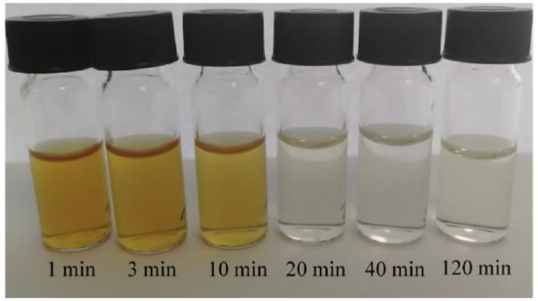
COD REDUCTION AND REMOVAL OF KEY POLLUTANTS



- HET, MEA, and DTZ rapidly decompose
- FA: >98% reduction in 10 min at 350°C or 30 min at 200°C
- COD reduction ca. 70 times faster at 350°C
- C, N, S converted into CO_2, ammonium, nitrate, and sulfate





Feed 200°C 350°C

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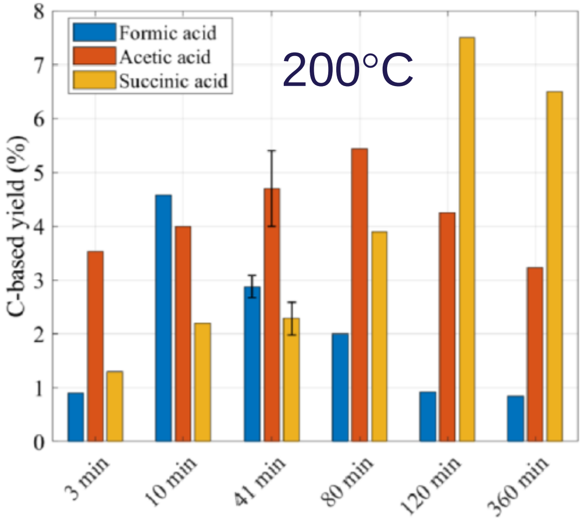
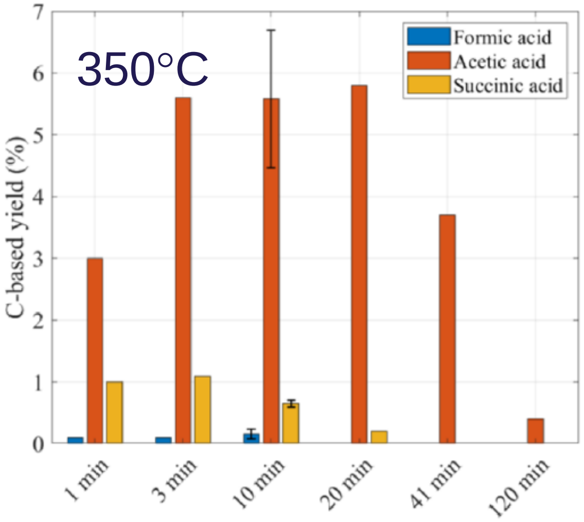
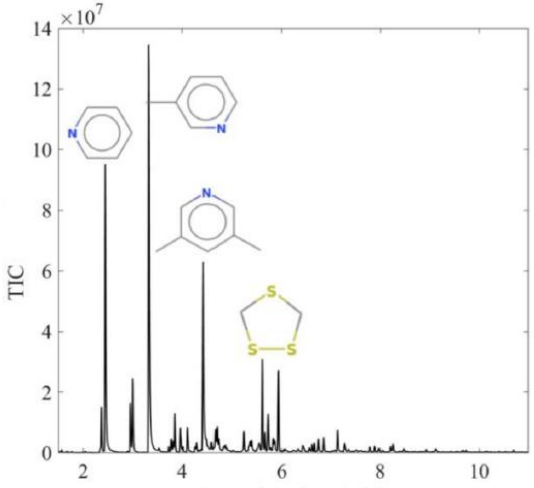
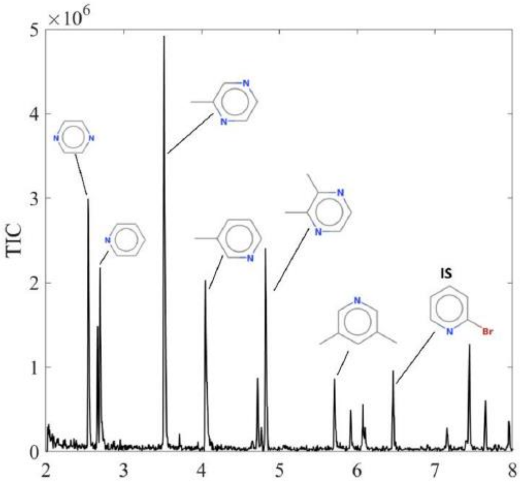
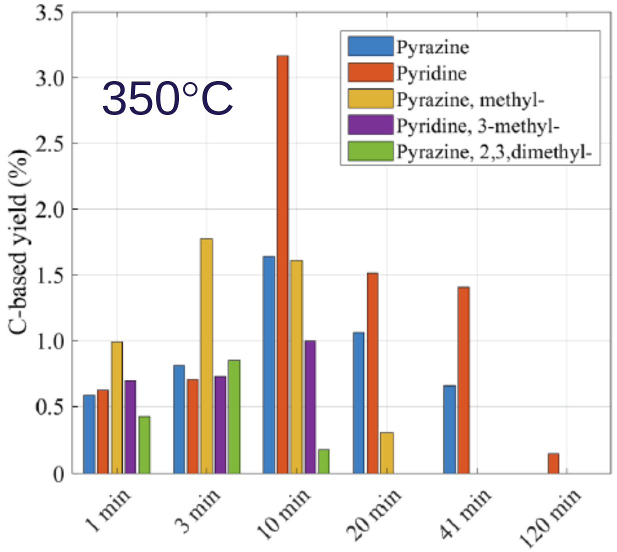
INTERMEDIATE OXIDATION PRODUCTS







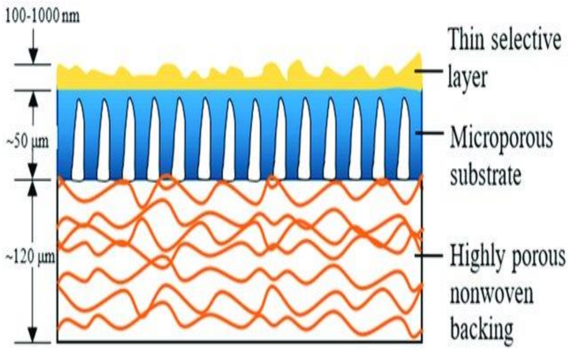




- C1-C4 acids show a maximum and then decreases over time
- Same happens for pyridines and pyrazines, with pyridine being slowly degraded
- Toxicity substantially reduced anyway (e.g., 74% reduction with 20 min at 350°C)

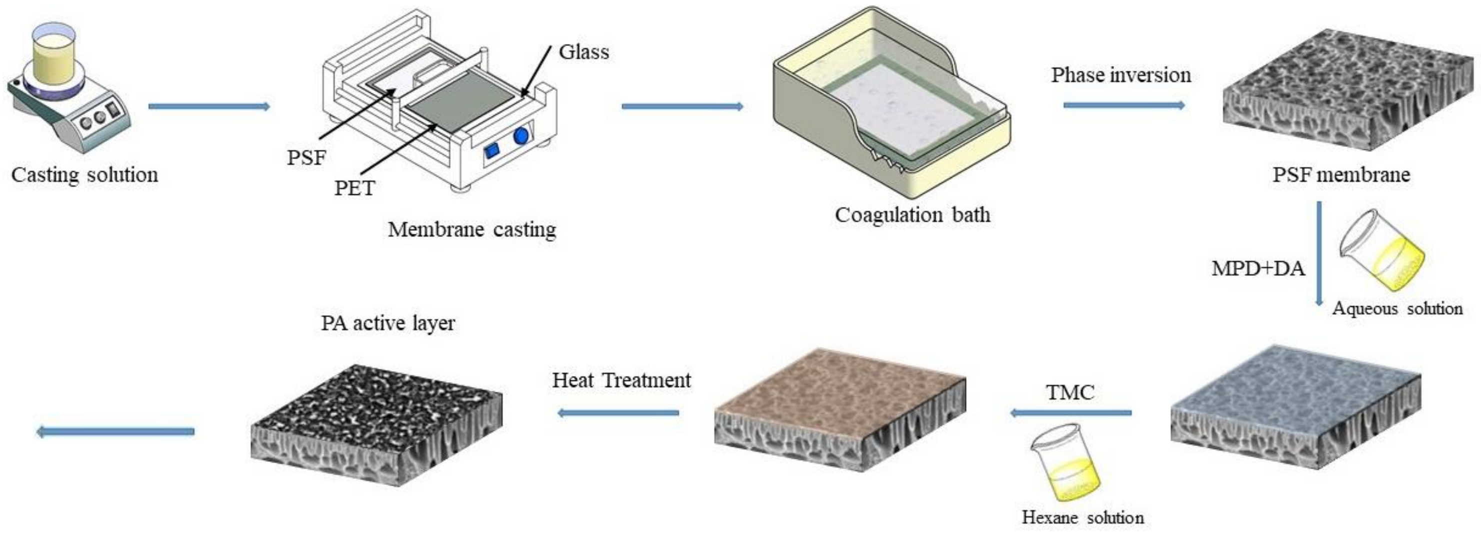
Montesantos, N., Skjolding, L. M., Baun, A., Muff, J., & Maschietti, M. (2023). Water Research, 230, [119507]
Montesantos, N., Nikbakht Fini, M., Muff, J., & Maschietti, M. (2022). Chemical Engineering Journal, 427, [131020]

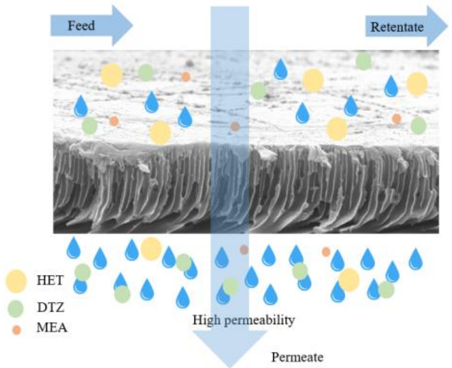
Next challenge: Tailor make a TFC membrane that improves separation of HET and DTZ



Research aim

Evaluate the effect of the polysulfone layer thickness on the membrane performance.



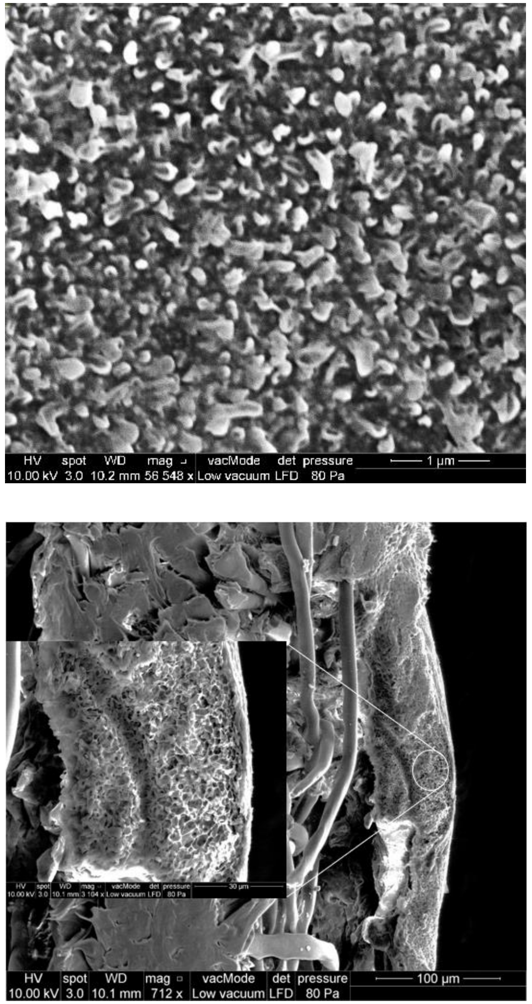


Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Journal of Environmental Chemical Engineering, 10(6), [108735].

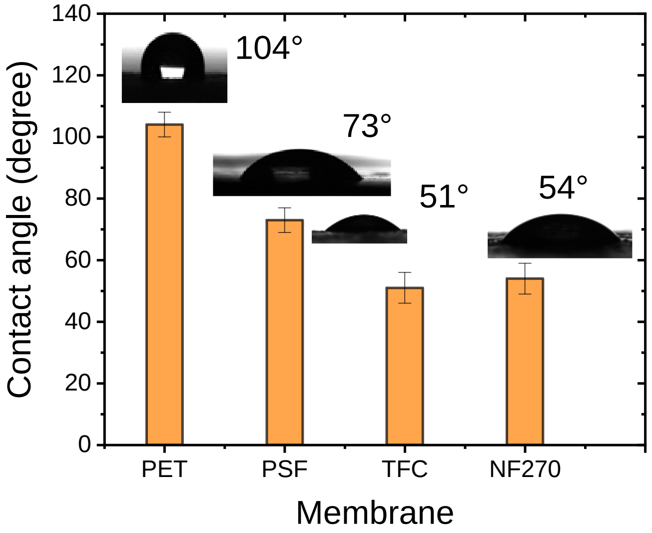
Characterization of synthesized TFC membranes

- The synthesized TFC membrane has granular-like structures on the top surface without distinct cavities.

- The cross-sectional SEM images of the synthesized TFC membrane show a sponge-like pore structure that initiates just below the top surface of the porous PSF support, which is uniformly coated with a thin layer of polyamide (100–250 nm).



SEM image of surface morphology and cross section of TFC membranes



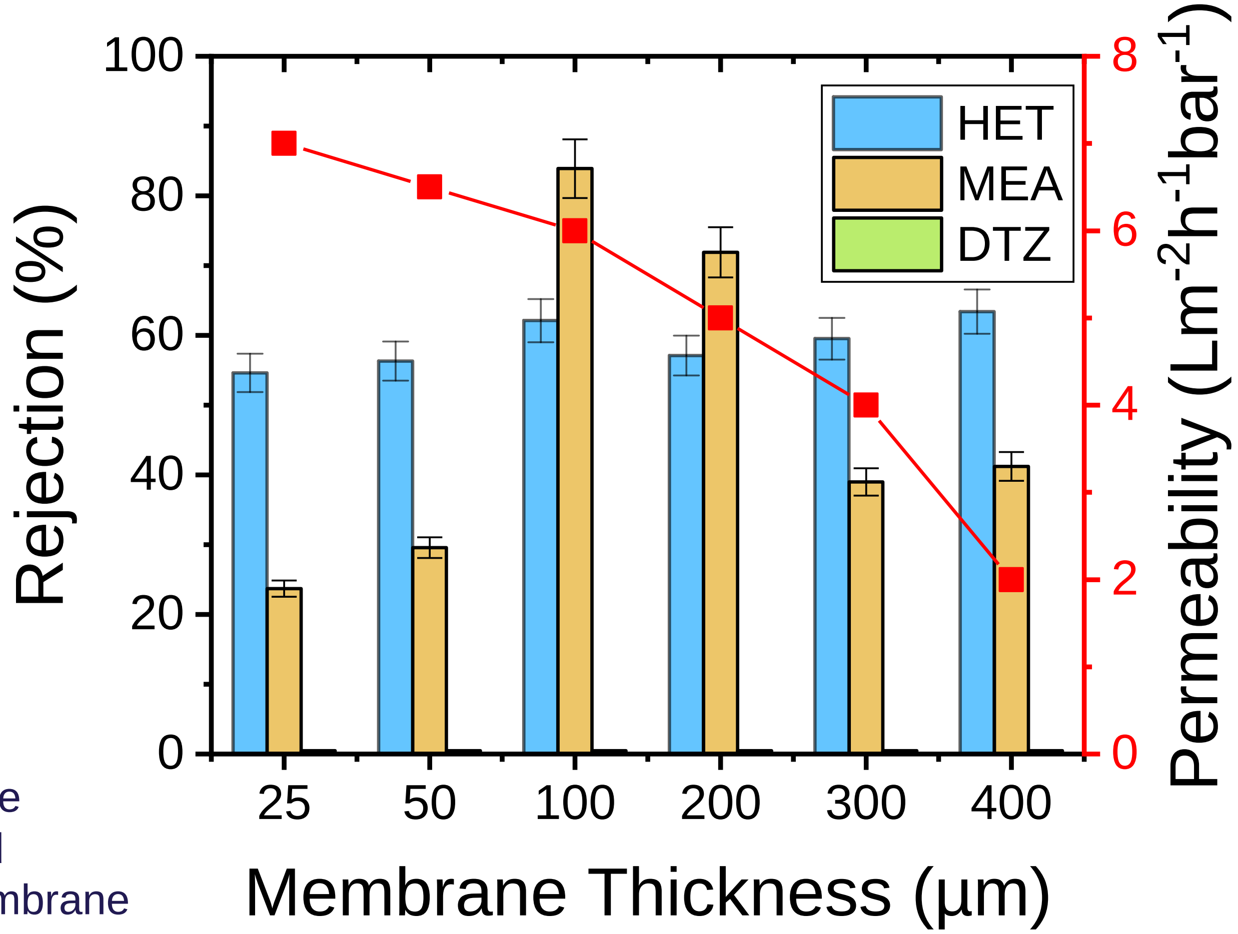
Contact angle of the PET, PSF, TFC and NF270 membrane

The hydrophilicity of the synthesized TFC membrane was improved during the interfacial polymerization.

Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Journal of Environmental Chemical Engineering, 10(6), [108735].

Performance of synthesized membranes

- The synthesized TFC membrane at 100 µm exhibited high rejection of unspent HET and MEA by 62 % and 82 %, respectively.
- The permeability of the synthesized TFC membrane decreased with increases membrane thickness.

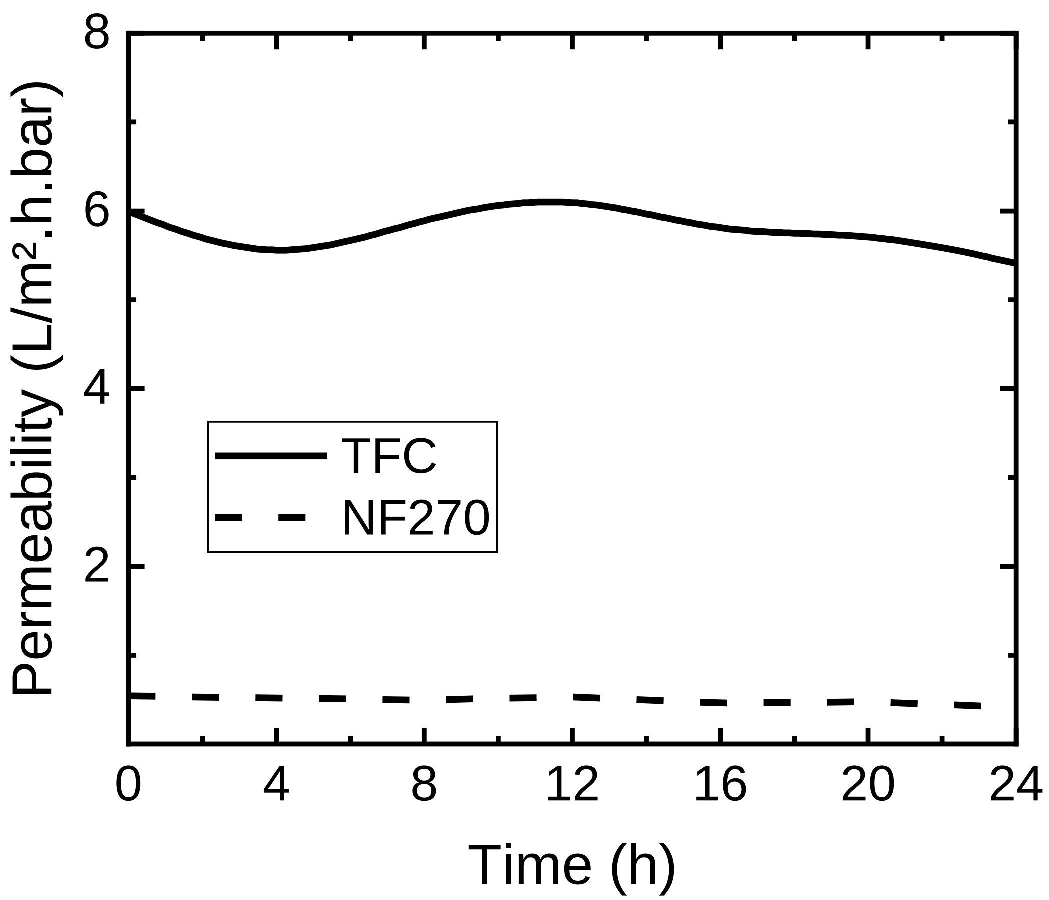


Effect of membrane thickness on the rejection of HET, MEA and DTZ and permeability of the synthesized membrane

Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Journal of Environmental Chemical Engineering, 10(6), [108735].

Performance of synthesized membranes (24h tests)

- No evidence of fouling up to 24 hours of operation
- The TFC membrane has permeability of 6 ± 0.3 L/(m^2·h·bar), while the NF270 has permeability of 0.45 ± 0.05 L/(m^2·h·bar).
- The developed TFC membrane demonstrated 13 times higher permeability than commercial NF270 membrane.

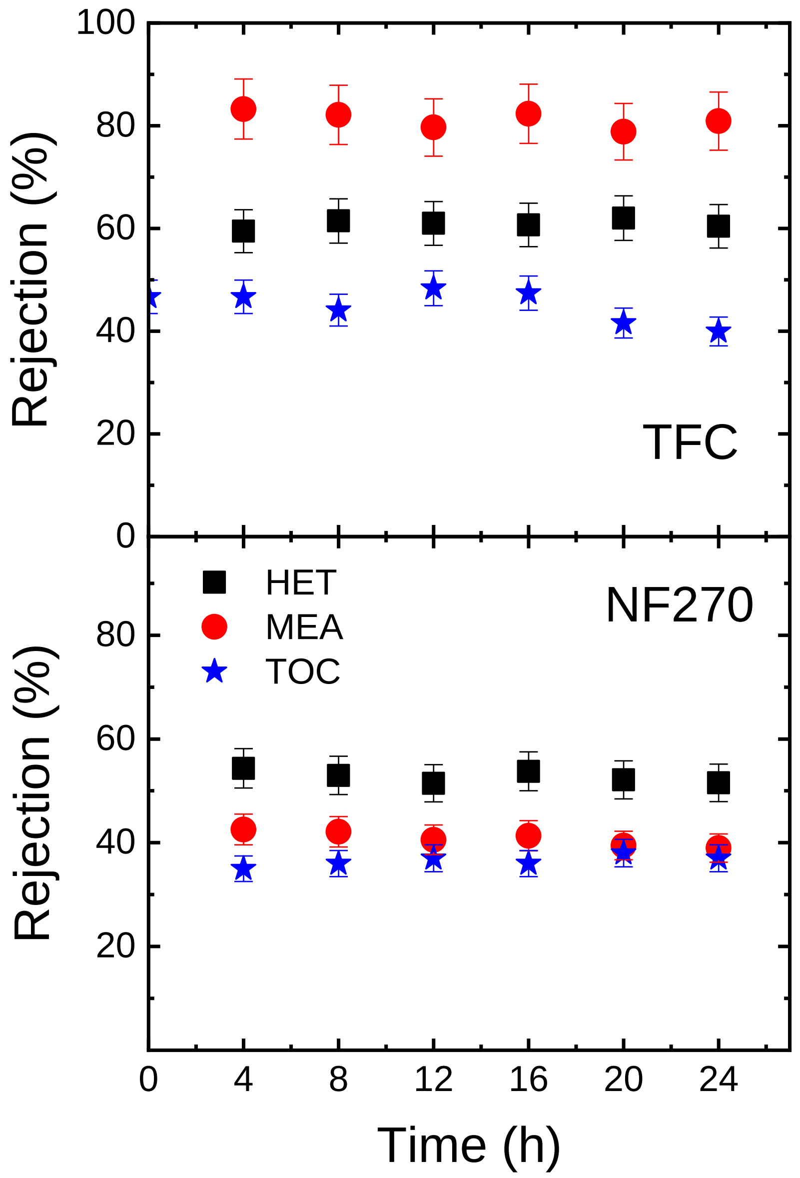


Long term filtration permeability test

Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Journal of Environmental Chemical Engineering, 10(6), [108735].

Performance of synthesized membranes (24h tests)

- The synthesized TFC membrane had good stability and higher TOC rejection (47 %) compared to the NF270 (37 %).
- The rejection of HET and MEA for both the membranes was almost constant during the long period of the filtration process.



HET, MEA, and TOC rejection using NF270 and synthesized TFC membrane at 40 °C, 100 µm membrane thickness, and 50% recovery.

Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Journal of Environmental Chemical Engineering, 10(6), [108735].

LESSON LEARNED SO FAR (2020-2023)

- Unreacted HET can be recovered through nanofiltration.
- The COD of SUS samples can be drastically reduced via hydrothermal oxidation.
- Substantial toxicity reduction of the treated effluent is achieved.
- Tailor made TFC membranes can maintain separation between HET and DTZ and improve permeability compared to commercial NF270
- Results indicate that graphene oxide nanoparticles in the filtration layer can furter improve permeability... – but also rejects DTZ (submitted)
- The project is continuing with a scale up and continuous flow pilot-scale demonstration (ZeroH_2S-DEMO) in collaboration with the company Aquarden, funded by the DTU Offshore.

PROJECT TEAM

Marco Maschietti
Project Leader

Jens Muff
Project Leader

Nikos Montesantos
Postdoc, HTO

Alaa Khalil
Postdoc, membranes

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Collaboration with DTU Environment (Lars Michael Skjolding, Anders Baun) on determination of toxicity of SUS derived water samples

DTU

Publications of the project so far...

Montesantos, N., Skjolding, L. M., Baun, A., Muff, J., & Maschietti, M. (2023). Reducing the environmental impact of offshore H2S scavenging wastewater via hydrothermal oxidation. Water Research, 230, [119507]. https://doi.org/10.1016/j.watres.2022.119507

Khalil, A., Montesantos, N., Maschietti, M., & Muff, J. (2022). Facile fabrication of high performance nanofiltration membranes for recovery of triazine-based chemicals used for H2S scavenging. Journal of Environmental Chemical Engineering, 10(6), [108735]. https://doi.org/10.1016/j.jece.2022.108735

Montesantos, N., Nikbakht Fini, M., Muff, J., & Maschietti, M. (2022). Proof of concept of hydrothermal oxidation for treatment of triazine-based spent and unspent H2S scavengers from offshore oil and gas production. Chemical Engineering Journal, 427, [131020]. https://doi.org/10.1016/j.cej.2021.131020

Nikbakht Fini, M., Montesantos, N., Maschietti, M., & Muff, J. (2021). Performance evaluation of membrane filtration for treatment of H2S scavenging wastewater from offshore oil and gas production. Separation and Purification Technology, 277, [119641]. https://doi.org/10.1016/j.seppur.2021.119641