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MABMEM – a material toolbox for the modification of ultrafiltration membranes

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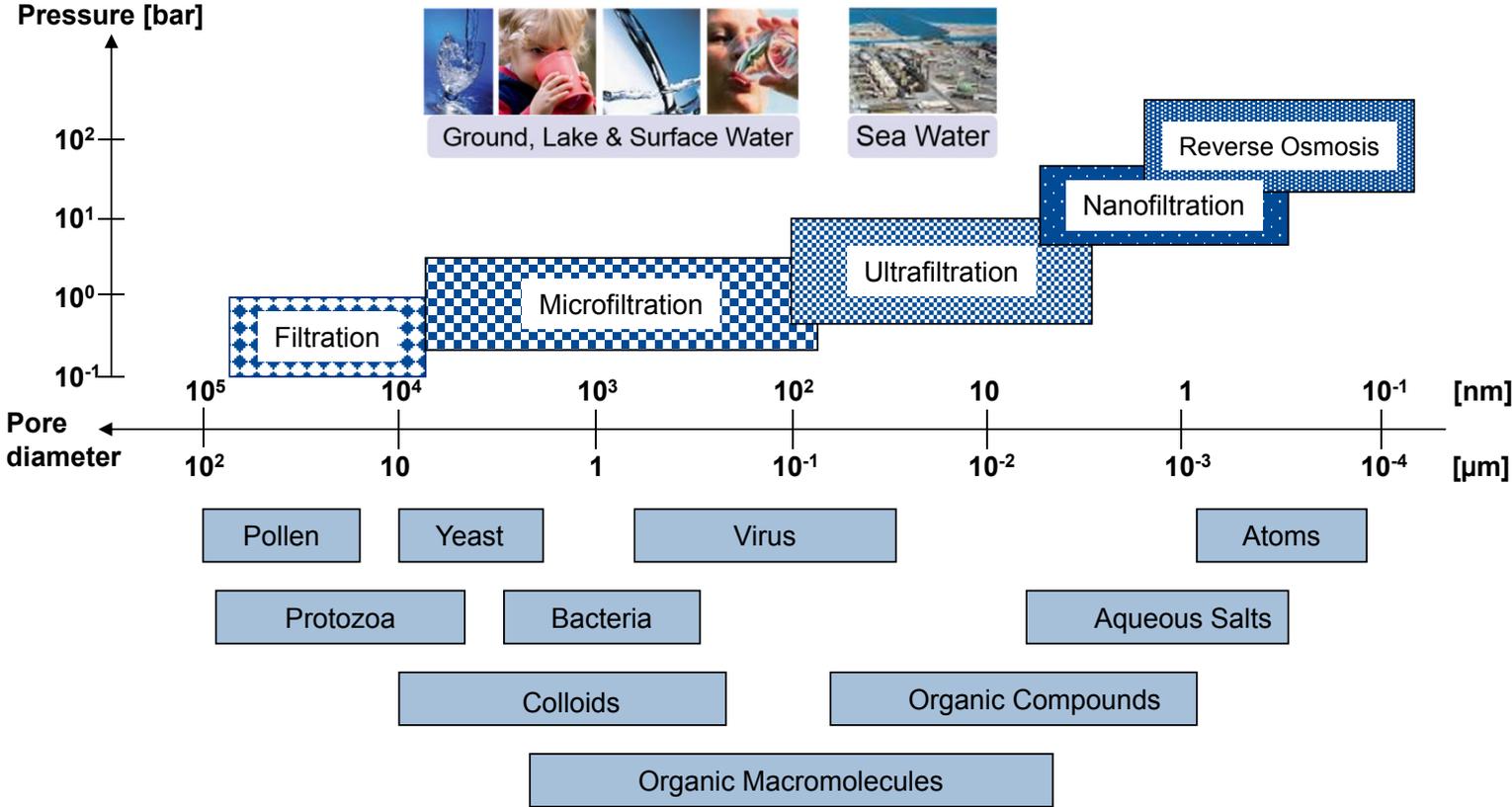
Aachen, 15.11.2018

Outline

- Introduction (filtration technologies, membrane materials)
- Objectives MABMEM project
- Results MABMEM project (properties of FS and SB ultrafiltration membranes)
- Results on testing of dizzer modules
- Conclusion

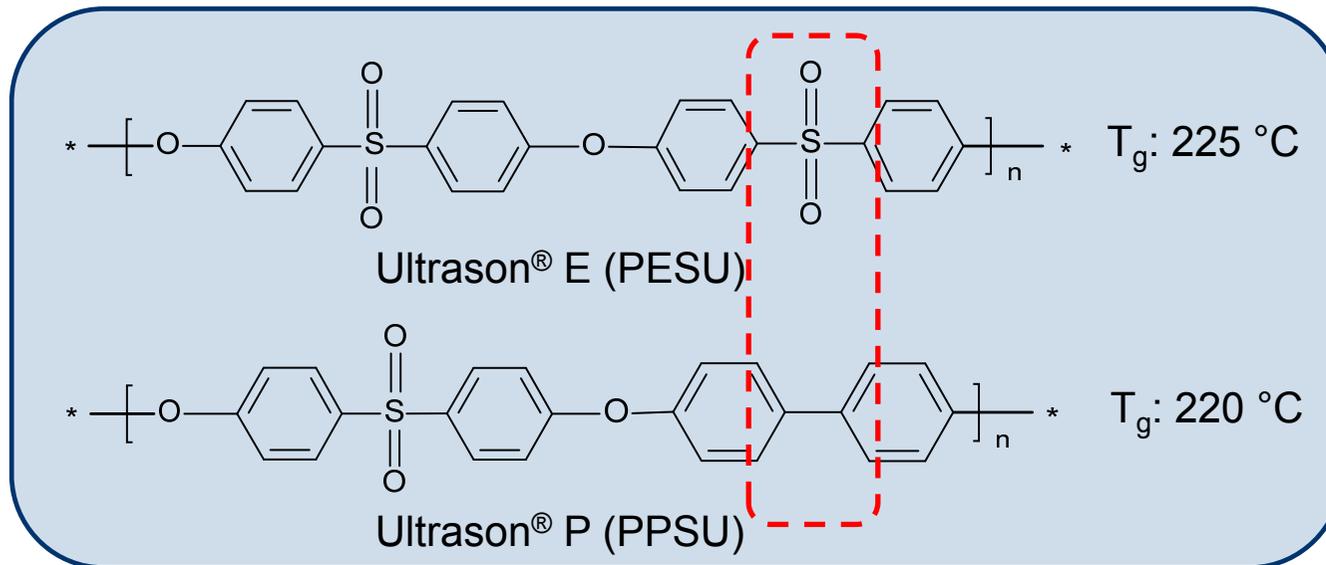
Introduction

Overview on filtration technologies



MABMEM project: Objectives

New membrane materials



- ~ 30 % of ultrafiltration membranes are based on PESU
- PPSU: Tight UF-membranes: lower permeability and cut-off compared to PESU
- But, compared to PESU, PPSU has improved stability against oxidation
- Currently, no PPSU membranes commercially available



<https://machwas-material.de>

GEFÖRDERT VOM



03XP0043A



MABMEM project: partners and project structure

New membrane materials

Project start 1.05.2016 Milestone M1 1.10.2017 Milestone M2 1.05.2018 Project end 30.04.2019



- Additive synthesis
- Testing in flat sheet membranes
- Optimization (structure, recipe)
- Hollow fiber membrane spinning
- Assembly to laboratory modules
- Module testing

- Multibore fiber spinning
- Demonstrator assembly

- Demonstrator testing
 - surface water
 - waste water



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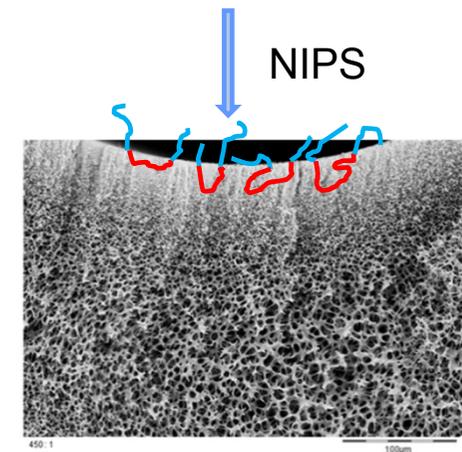
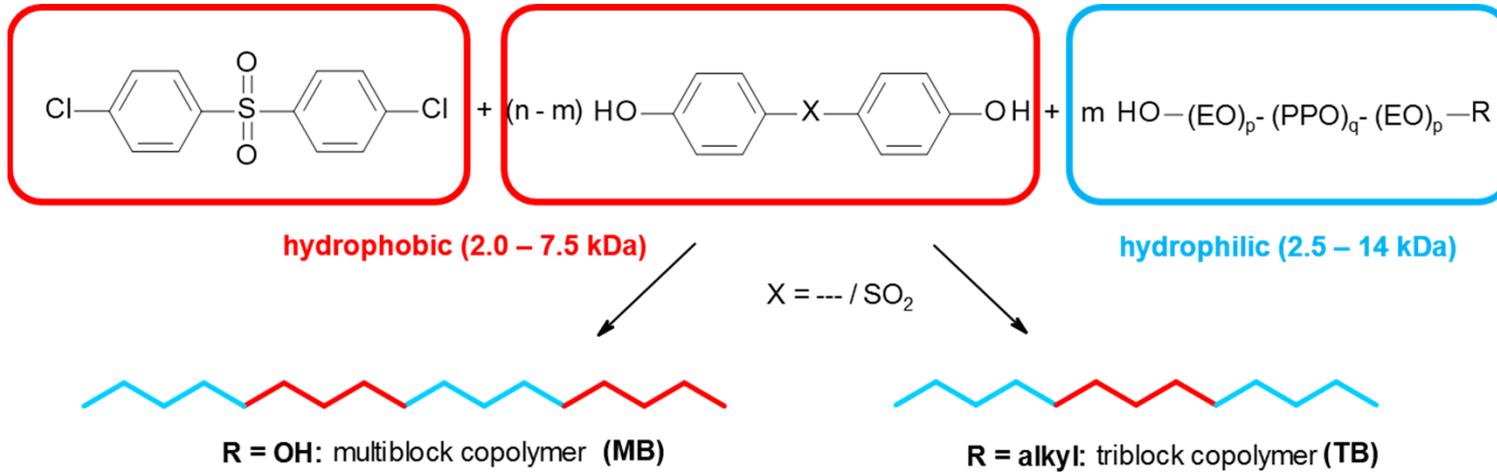
03XP0043A

- Funding measure "Materials for a sustainable water management - MachWas"
- Sponsored by German Federal Ministry of Education and Research (BMBF)



Results MABMEM project: additive synthesis

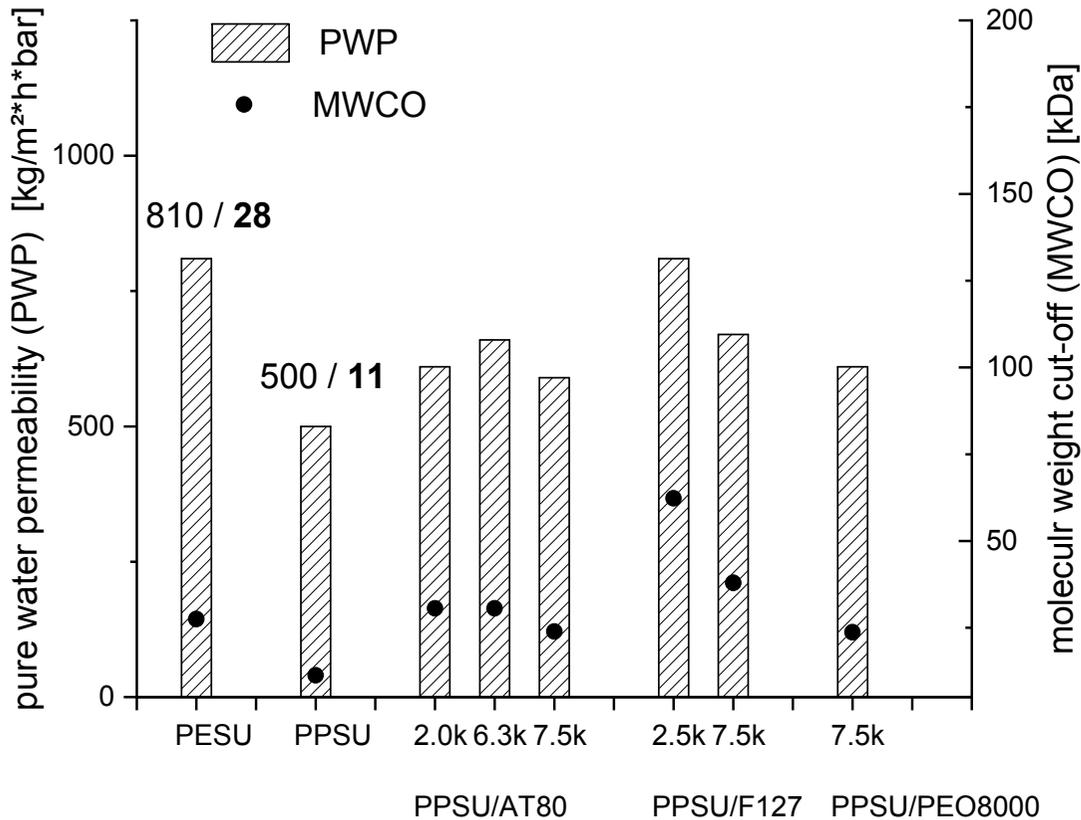
New membrane materials – UF membranes based on PPSU



structure	type	molecular weight (M_n)	PEO share	polyethersulfone X = -SO ₂ - (PESU)			polyphenylsulfone X = --- (PPSU)		
				2.0 k	5.0 k	7.5 k	2.0 k	5.0 k	7.5 k
H(O-CH ₂ -CH ₂)-OAlkyl	Lutensol® AT80	~ 3500 g/mol	97 %	✓	✓	✓	✓	✓	✓
	Lutensol® AT50	~ 2500 g/mol	92 %	✓					
	Pluriol® A 5010 E	~ 5000 g/mol	99 %	✓	✓				
H(O-CH ₂ -CH ₂)-OH	Pluriol® E 8000	~ 8000 g/mol	100 %	✓		✓			✓
H[EO]-[PO]-[EO]-OH	Pluronic® F127	~ 14000 g/mol	73 %	✓		✓	✓		✓

Results MABMEM project – membrane properties

PPSU FS membranes with MABMEM additives: PWP, MWCO



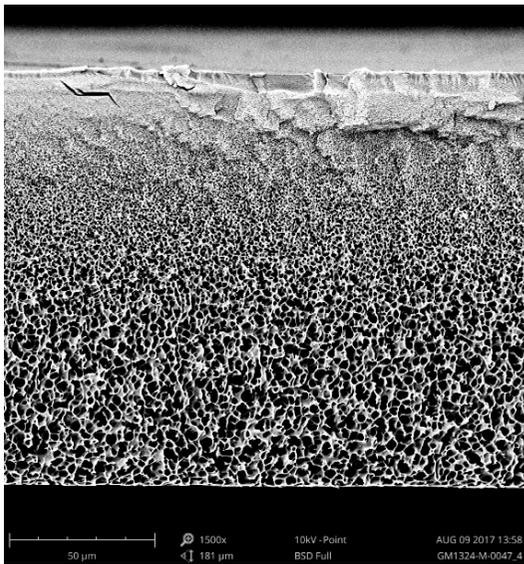
PPSU UF membranes with MABMEM additives

- 8.4 wt% additive relative to PPSU matrix polymer
- 18 – 62 % permeability increase compared PPSU ultrafiltration membranes
- Highest permeability of 810 $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ matches permeability of PESU standard membrane
- Molecular weight cut-off values with 23 – 62 kDa in ultrafiltration range

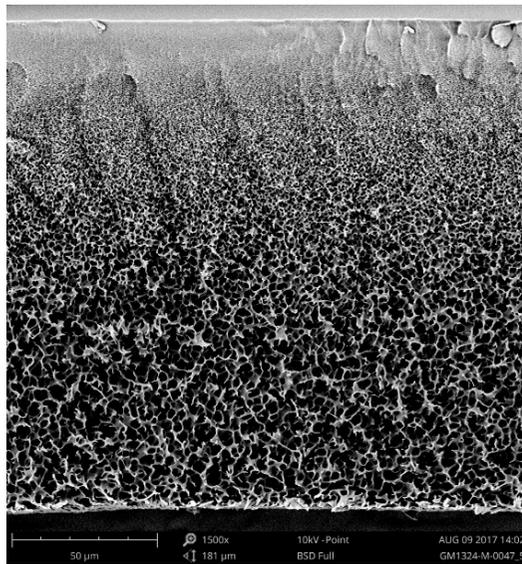


Results MABMEM project – membrane properties

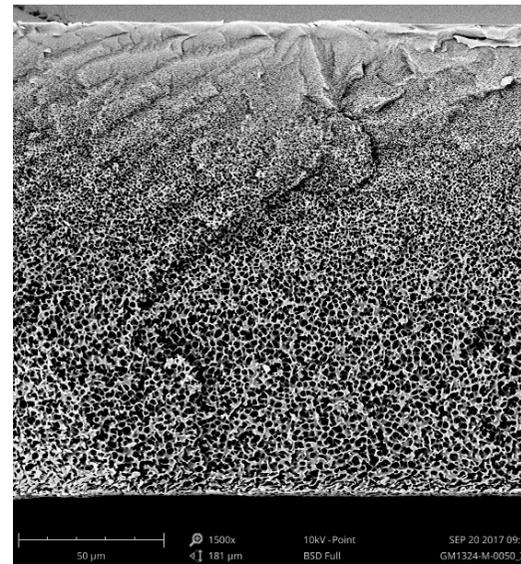
PPSU FS membranes with MABMEM additives: morphology SEM



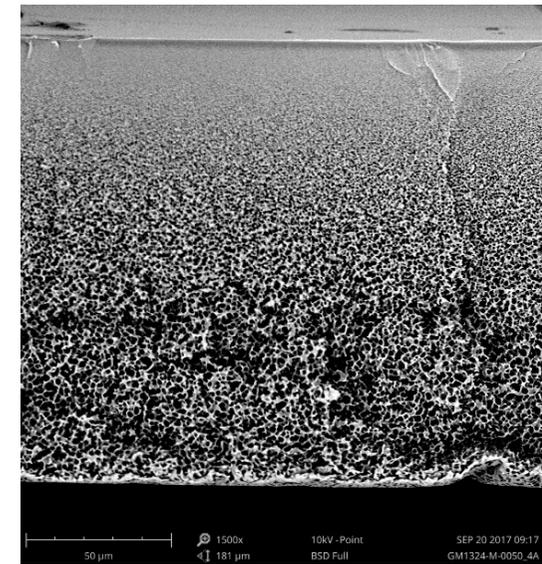
TB: 6.3 kDa PPSU/AT-80



TB: 7.4 kDa PPSU/AT-80



MB: 2.5 kDa PPSU/F 127

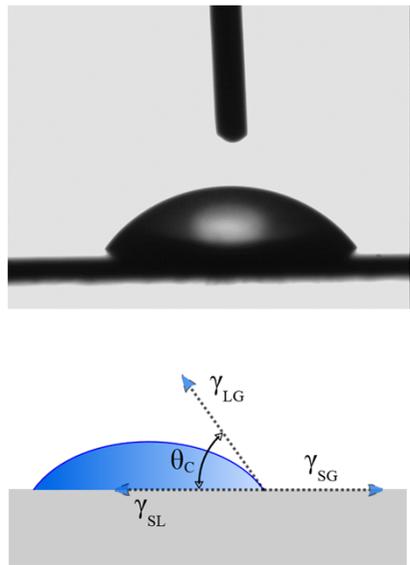


MB: 7.5 kDa PPSU/F 127

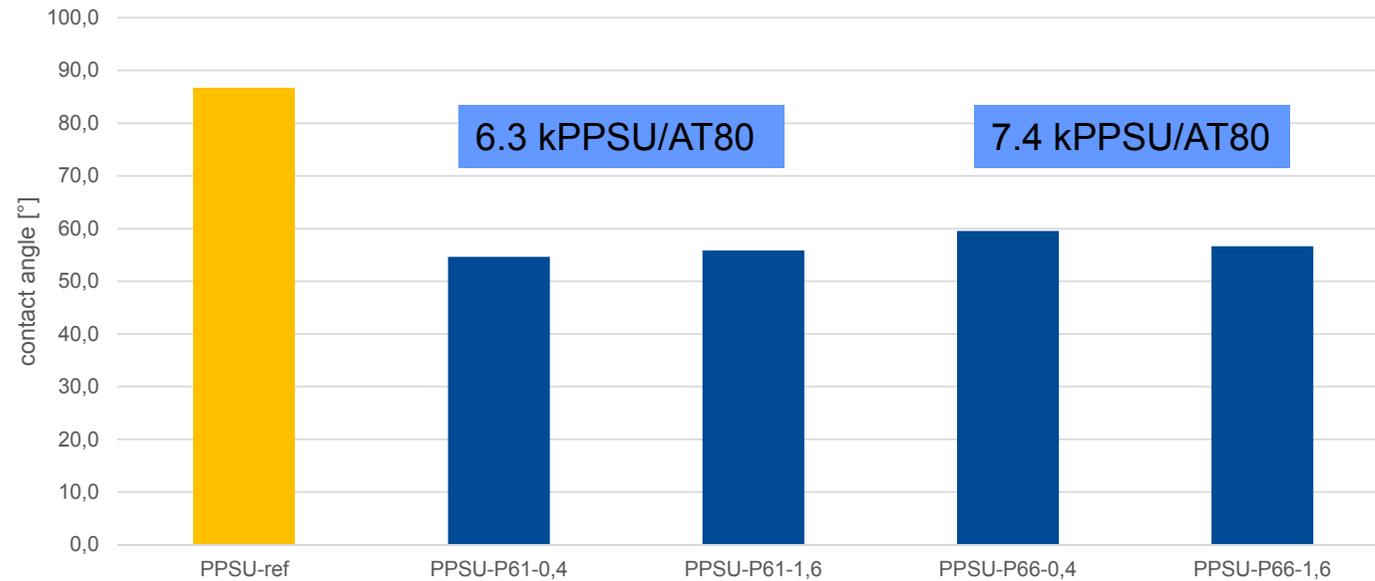
- Nano porous filtration layer, sponge type micro porous support layer
- No defects like macro voids

Results MABMEM project – membrane properties

PPSU FS membranes with MABMEM additives: water contact angle



sessile drop mode

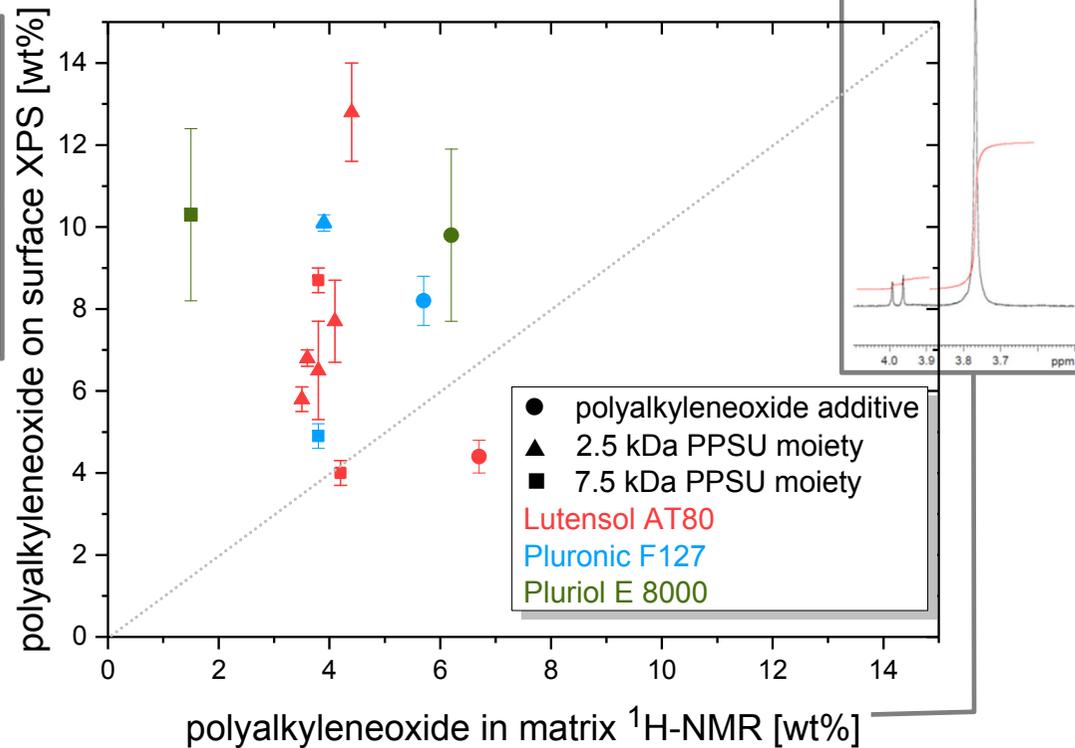
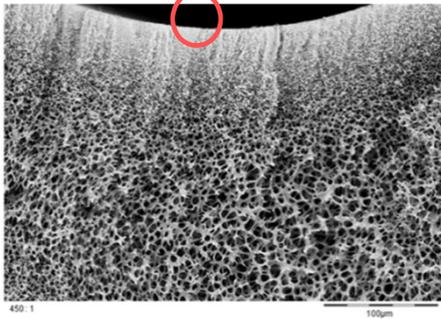
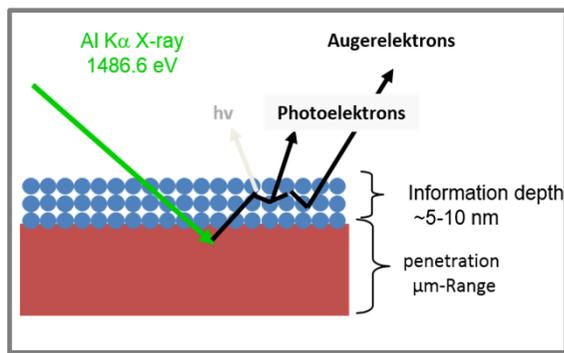


- PESU membranes: 70 – 75 °
- PPSU based additives in PPSU flat sheet membrane separation layer
- Presence of MABMEM additives lowers contact angle of separation layer

Results MABMEM project – membrane properties

PPSU SB membranes with MABMEM additives: surface enrichment

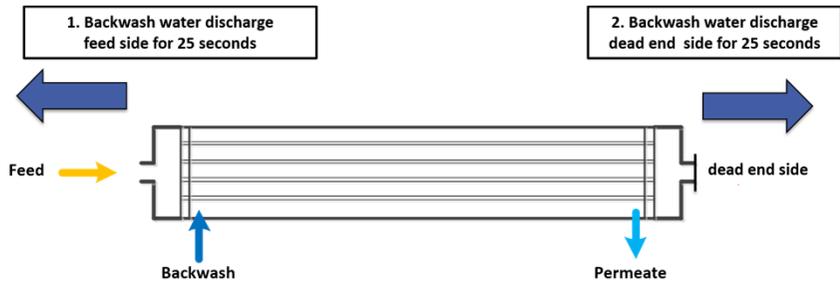
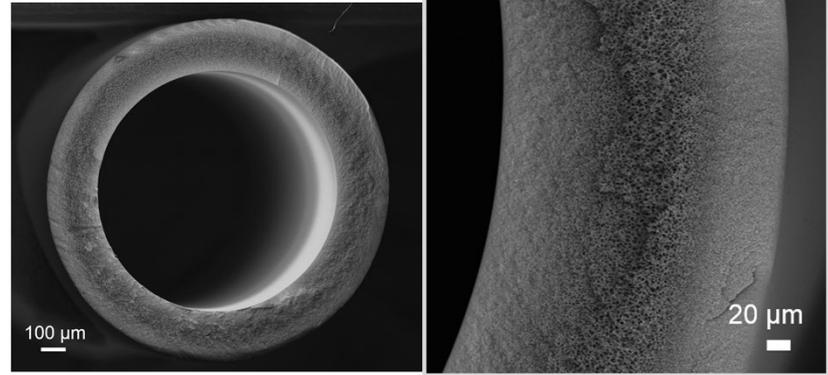
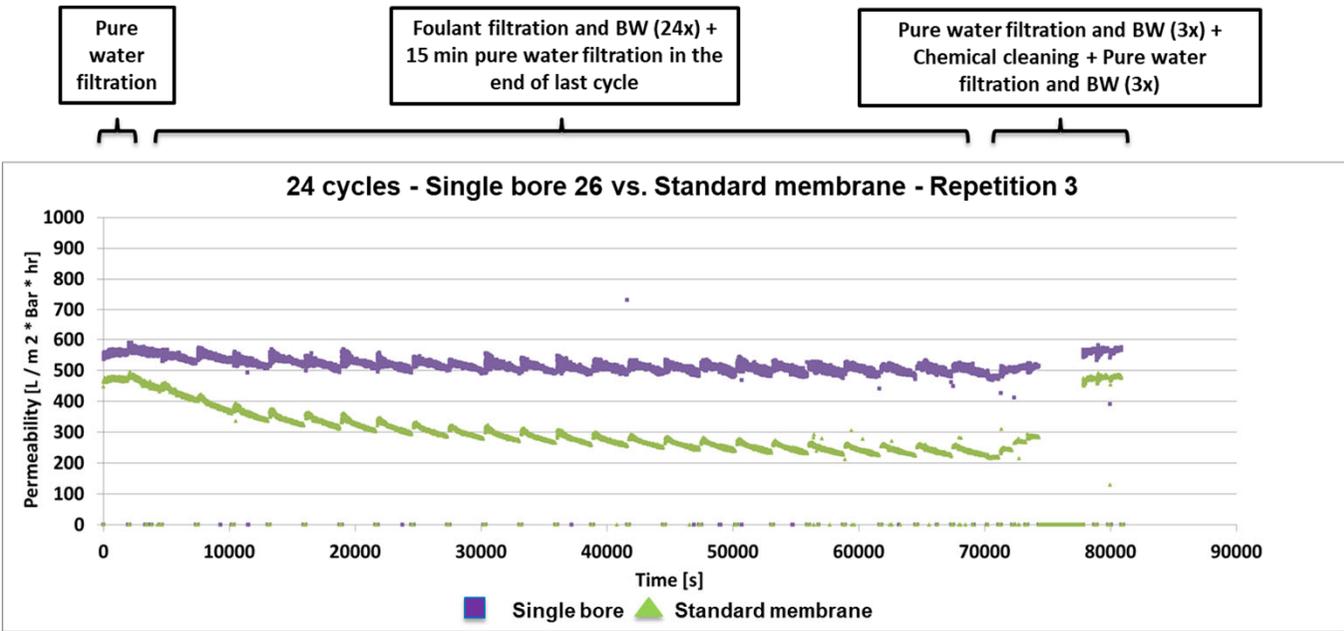
PPSU based additives in PPSU single bore (SB) membrane separation layer



Results MABMEM project – membrane surface properties

PPSU SB membranes with MABMEM additives: fouling propensity

Fouling with diluted flower soil (3.5 mg/l dry mass) with 100 l/h – PPSU SB with TB 6.3kPPSU/AT80



Significant reduced fouling propensity of modified PPSU membrane

Results MABMEM project – membrane surface properties

Upscaling of PPSU development candidates

PWP

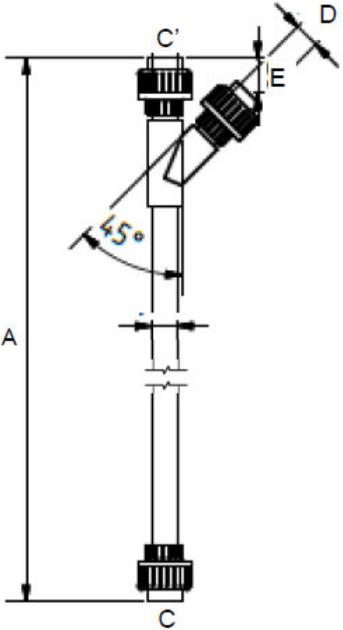
MWCO

Fouling

SB	matrix	additive
26	PPSU	TB: 6.3k PPSU/AT80
27	PPSU	TB: 7.4k PPSU/AT80
30	PPSU	MB: 2.5k PPSU/F127
31	PPSU	MB: 7.5k PPSU/F127



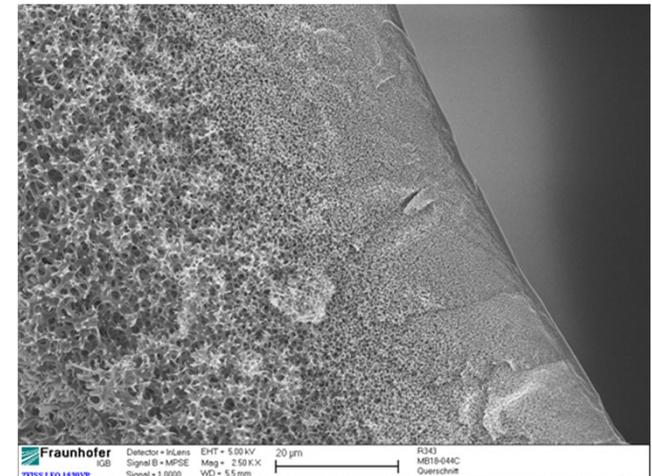
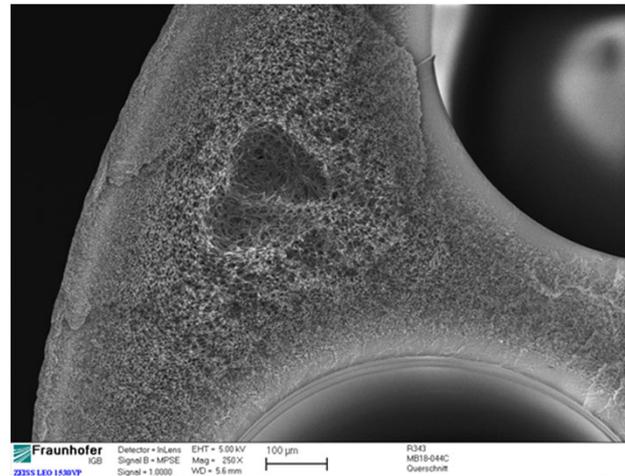
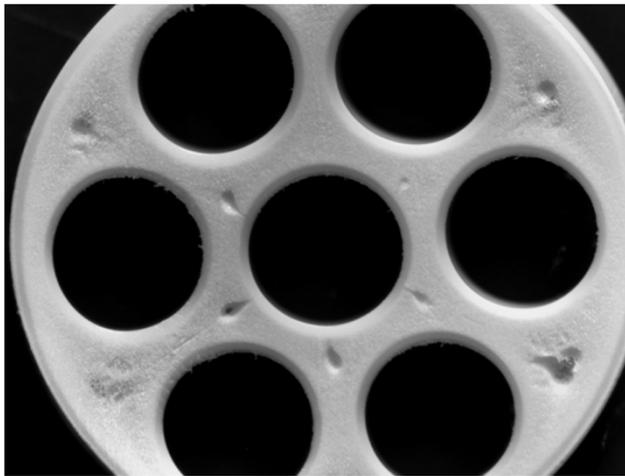
Dizzer Lab modules
LAB 0.9 MB 0.2 Y



Length: 1558 mm
Area : 0.2 m²

Results MABMEM project – membrane surface properties

Upscaling of PPSU development candidates



SEM cross-section of SB 27

SB	matrix	additive	PWP [kg/h*m ² *bar]	MWCO [kDa]
27	PPSU	TB: 7.4k PPSU/AT80	972	31
	PESU	Standard	1090	37

Results MABMEM project – membrane surface properties

Testing of dizzer lab modules

Location: Varel
Waste water
4th cleaning step

Location: WAG Roetgen
Surface water 6800 m³/h
From July 2018 (KW 28)

Triflux Demonstrator testing equipment

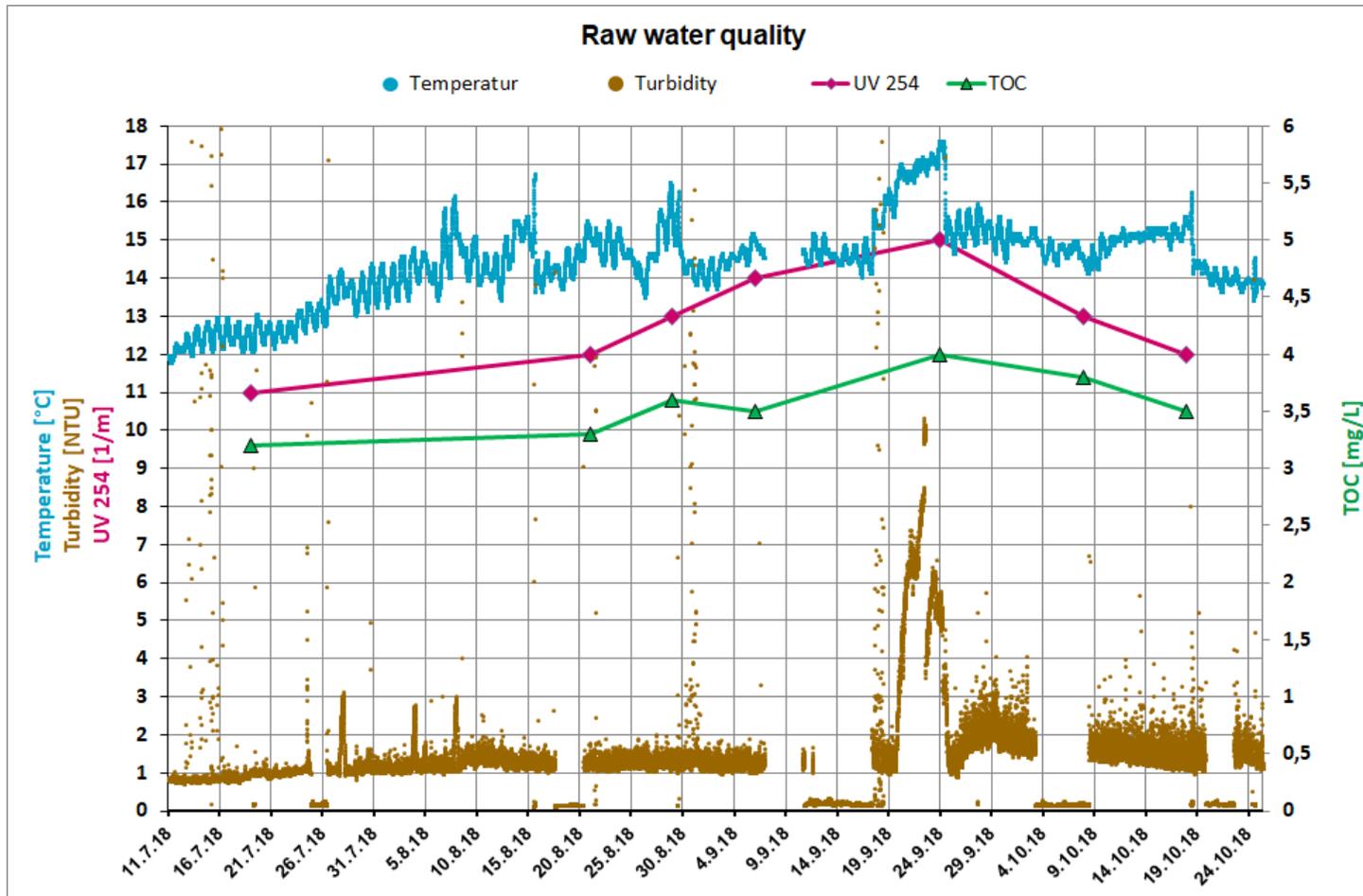


WAG Roetgen
Surface water 6800 m³/h
From July 2018 (KW 28)



Results MABMEM project – membrane surface properties

Testing of dizzer lab modules: quality of raw water



Dreilaegerbach reservoir

- 11.7 – 25.10.2018
- average surface water
- Typical seasonal fluctuations in raw water quality
- demanding for membrane process

Results MABMEM project – membrane surface properties

Testing of dizzer lab modules: process performance

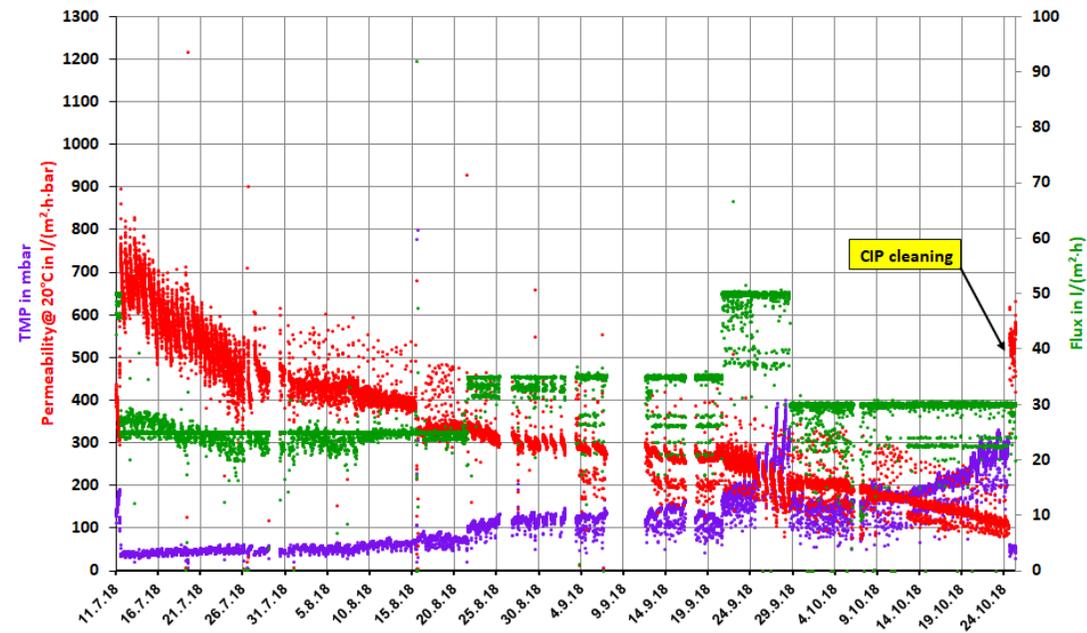
SB 27 - 7,4 kDa PPSU/AT80 in PPSU

● TMP in mbar ● Permeability@ 20°C in l/(m²·h·bar) ● Flux in l/(m²·h)



Standard PESU

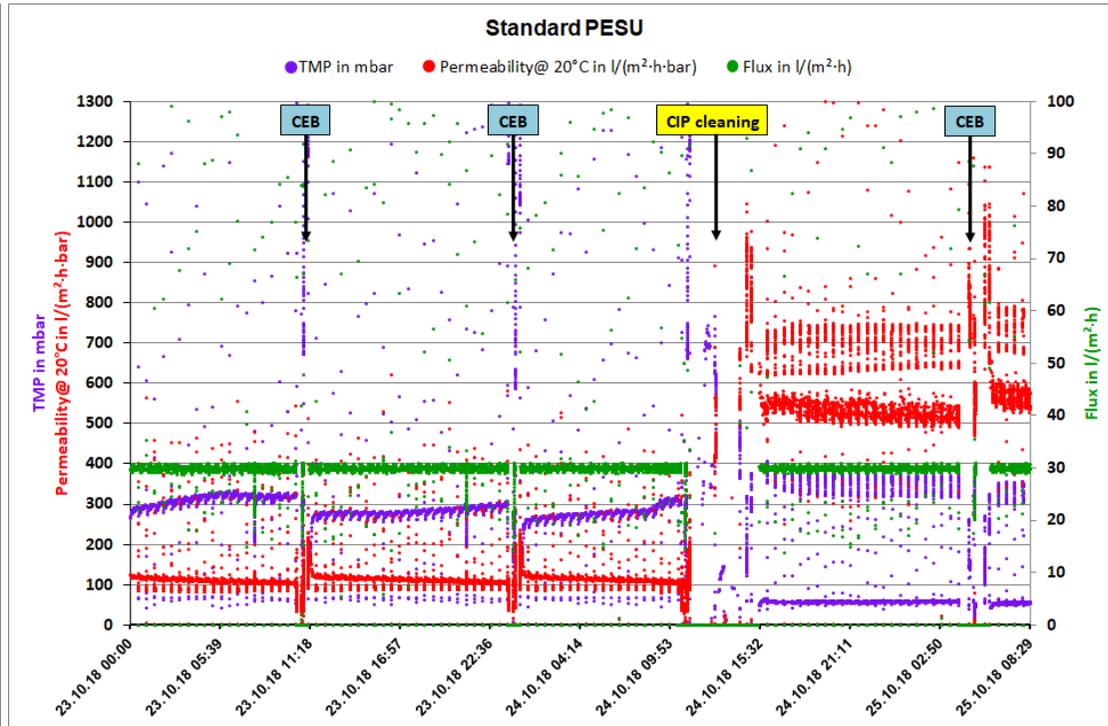
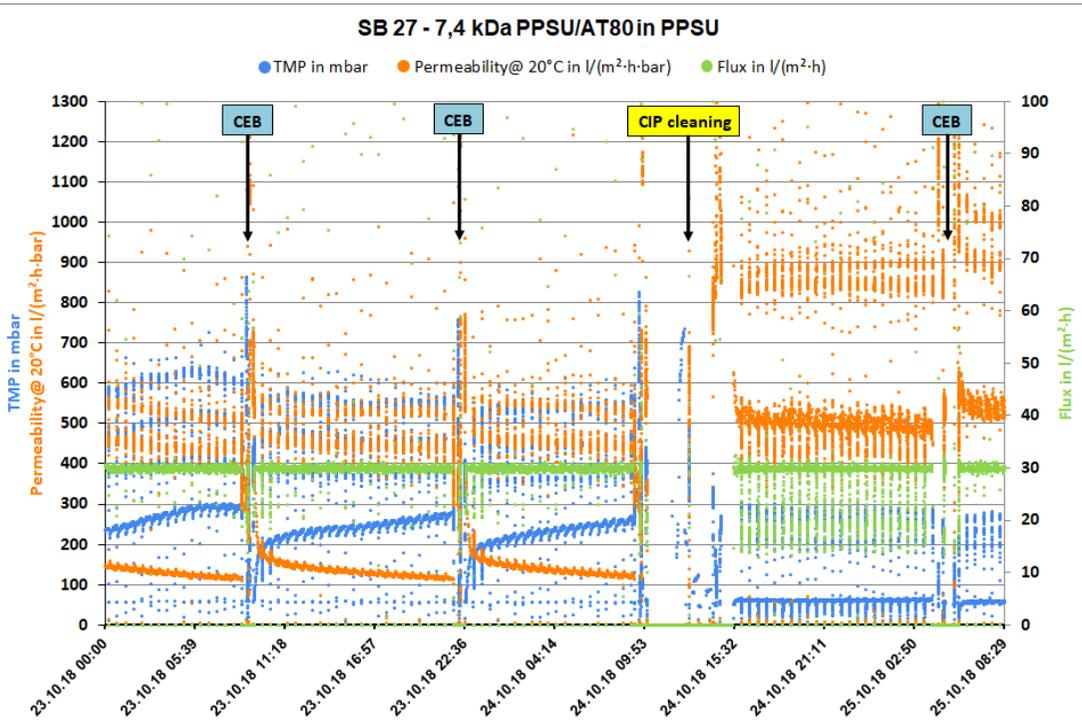
● TMP in mbar ● Permeability@ 20°C in l/(m²·h·bar) ● Flux in l/(m²·h)



- without upstream flocculation
- flux 25 / 30 / 35 / 50 kg/m²·bar·h
- in average 20 – 25 % higher permeability of SB27 compared to PESU

Results MABMEM project – membrane surface properties

Testing of dizzer lab modules: Cleaning in detail



- Cleaning steps in detail
- CEB: NaOH (pH12.3) / H₂SO₄ (pH 2.0) – twice per day
- CIP: 200 ppm NaOCl / NaOH (pH12), 30 min flush forward / 30 min filtration (70 l/h)

Results MABMEM project – membrane surface properties

Testing of dizzer lab modules of PPSU development candidates: summary

	7.4 kDa PPSU / AT80 in PPSU	Standard PESU inge
Experimental period	11.07.18 – 25.10.2018	
Flocculation	None	
Flux [l/m ² /h]	25 / 30 / 35 / 50	
Filtration time [min]	30	
CEB	Combined regime: NaOH (pH12,3) / H ₂ SO ₄ (pH 2,0) – 2x per day	
Average permeability@20 [l/m ² /h/bar]	800 - 140	700 - 110
Deviation of average permeability in reference to standard PESU [%]	+ 20 - 25	-
CIP	NaOCl (200 ppm) + NaOH (pH 12) 30 min Forward Flush / 30 min Filtration (70 l/mh)	



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Conclusion

- TB and MB Lutensol AT80 and Pluronic F127 PPSU additives with 8.4 wt% in PPSU FS matrix:
 - ▶ 18 – 62 % permeability increase compared PPSU ultrafiltration membranes
 - ▶ molecular weight cut-off values with 23 – 62 kDa in ultrafiltration range
 - ▶ defect free membrane morphologies in SEM cross-section
 - ▶ contact angle of 55- 60 ° compared to 85 ° (PPSU reference): improved hydrophilicity
- TB and MB Lutensol AT80 and Pluronic F127 PPSU additives in PPSU SB matrix:
 - ▶ additive surface agglomeration indicated by ¹HNMR and XPS
 - ▶ reduced fouling propensity with flower soil extract as testing model
- PPSU MB demonstrator testing with TB 7.4k PPSU- Lutensol AT80 additives Dreilägerbach reservoir
 - ▶ 20- 25 % higher permeability in average compared to PESU standard (without flocculation)

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