MABMEM - A Toolbox for High Performance UF-Membranes

Frankfurt am Main 29.05.2018

Oliver Gronwald, BASF SE
MABMEM Team

MachWas
MATERIALIEN FÜR EINE NACHHALTIGE WASSERWIRTSCHAFT

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A Toolbox for Membranes

Outline

- Project details
- Objectives of the MABMEM project
- Results
- Conclusions
- Acknowledgements

Project details

Title: MABMEM – Materialauswahlbox zur Herstellung von Hochleistungs-membranen für die Wasseraufbereitung

Duration: 01.05.2016 - 30.04.2019

Members of the consortium:

BASF The Chemical Company

UNIVERSITÄT DUISBURG ESSEN
Offen im Denken

Prof. M. Ulbricht
Prof. S. Panglisch

Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

Prof. V. Abetz
P. D. U. Handge

inge heart of pure water

IWW
IWW Zentrum Wasser

enwor energie & wasser vor ort

OOWV gemeinsam · nachhaltig · transparent

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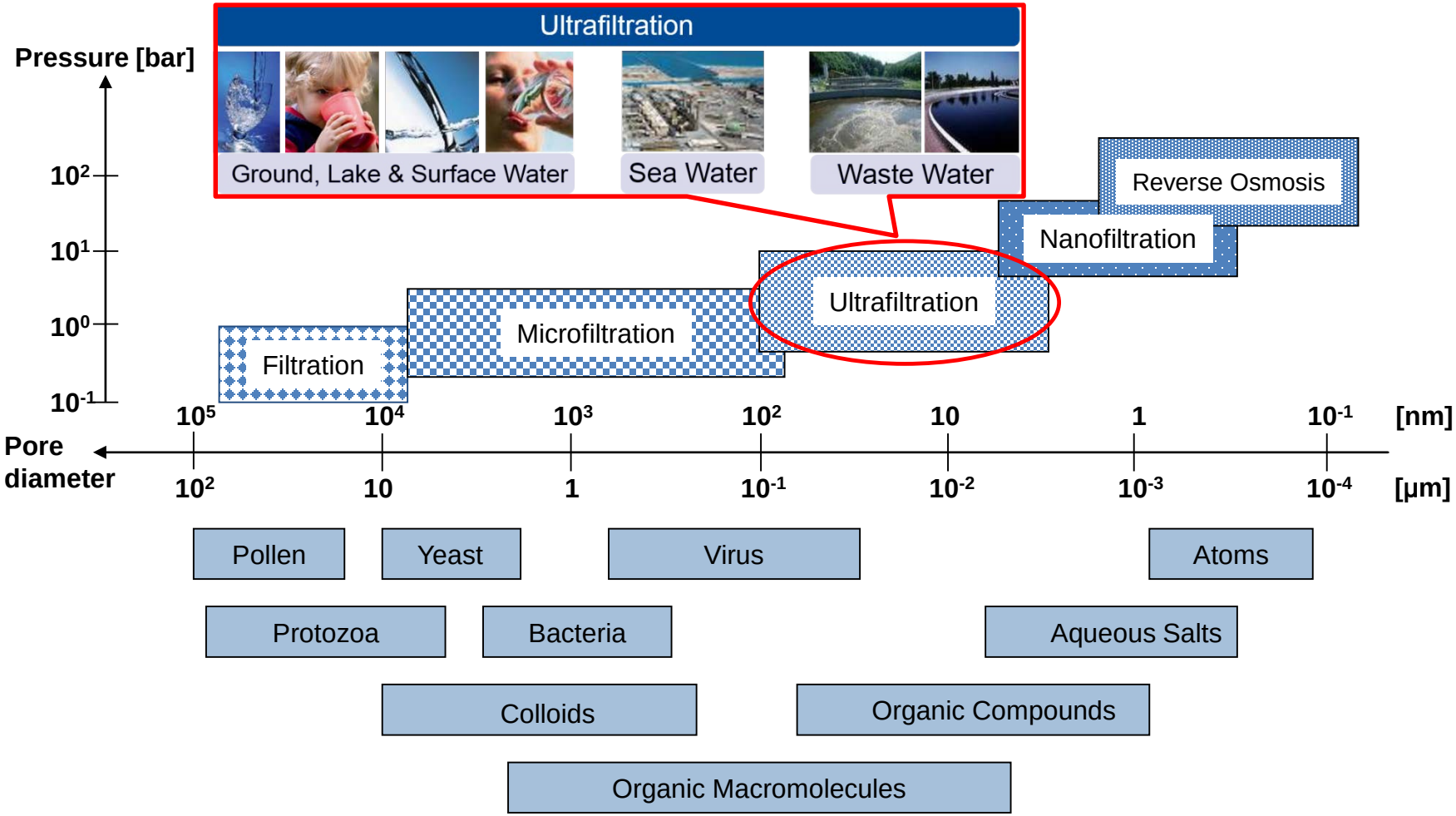
MABMEM objectives – filtration technologies



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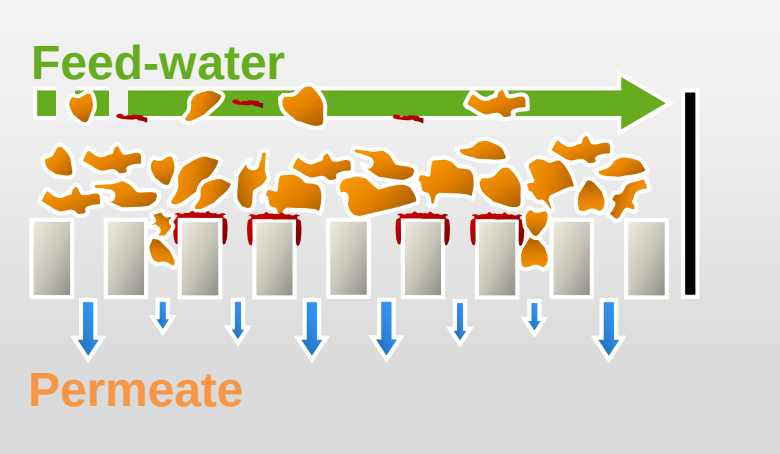
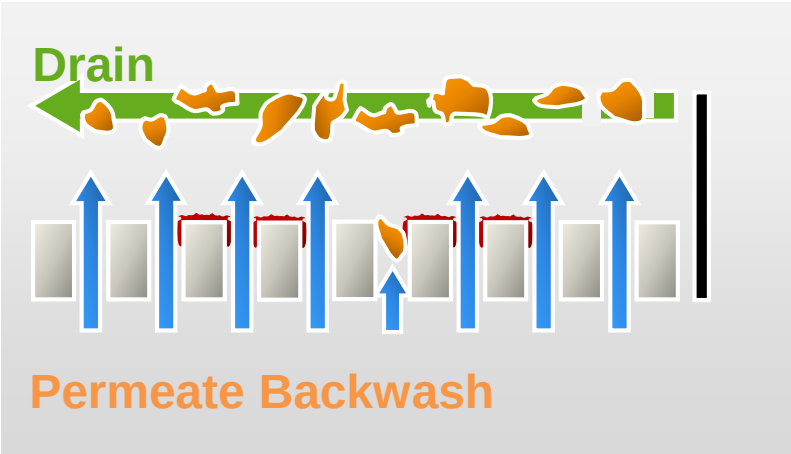
MABMEM objectives - fouling





- NOM: humic acid + polysaccarides
- Formation of filtration cake
- Adsorption of bio-polymers
- Partial pore size reduction and pore plugging

Improved membrane surface (e.g hydrophilicity) to reduce fouling

- Regular backwash to remove reversible foulants
- Irreversible fouling causes:
  - Reduced flux
  - Increased pressure
  - Reduced yield
- Chemical enhanced backwash (caustic, acid, active chlorine)

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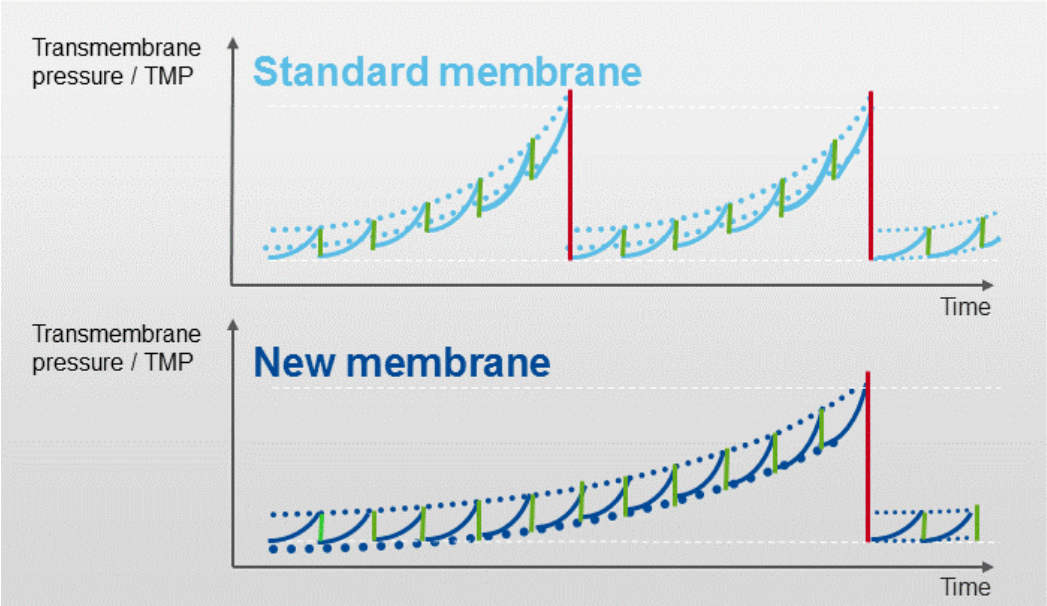
MABMEM objectives - fouling



Conditions

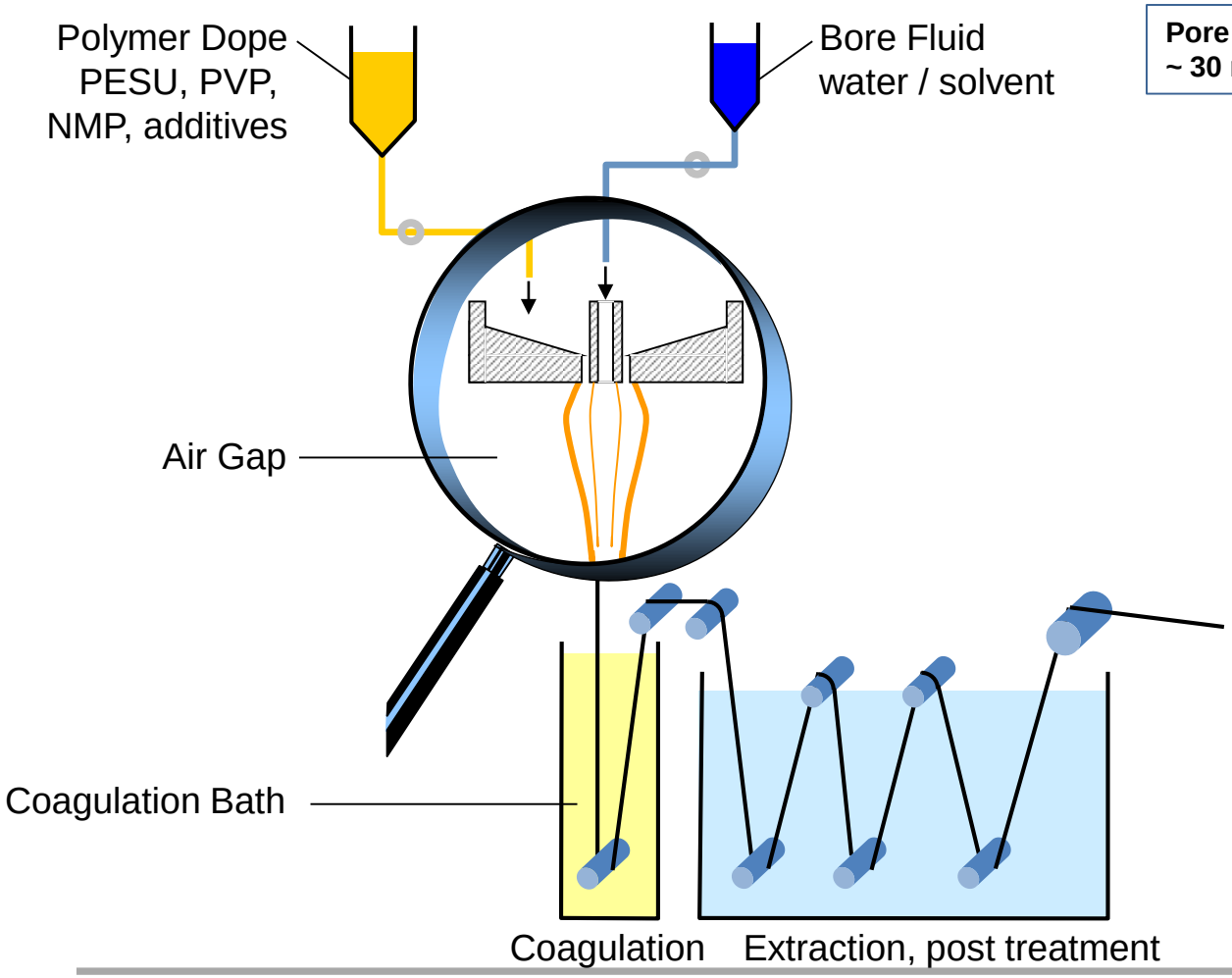
Constant flux
86 kg/m²/h

Permeate back-flush

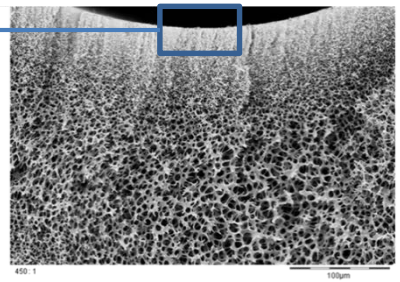
Chemical enhanced back-flush

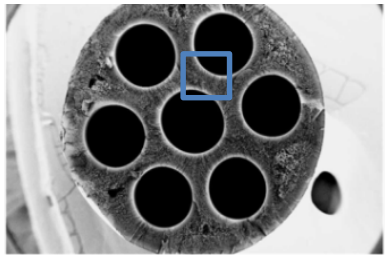
- Performance of UF-membranes limited by fouling issues
- Hydrophilic membrane materials show lower fouling tendency
- Additional functionalities of UF-membranes possible?

MABMEM objectives – strategy



Pore size ~ 30 nm





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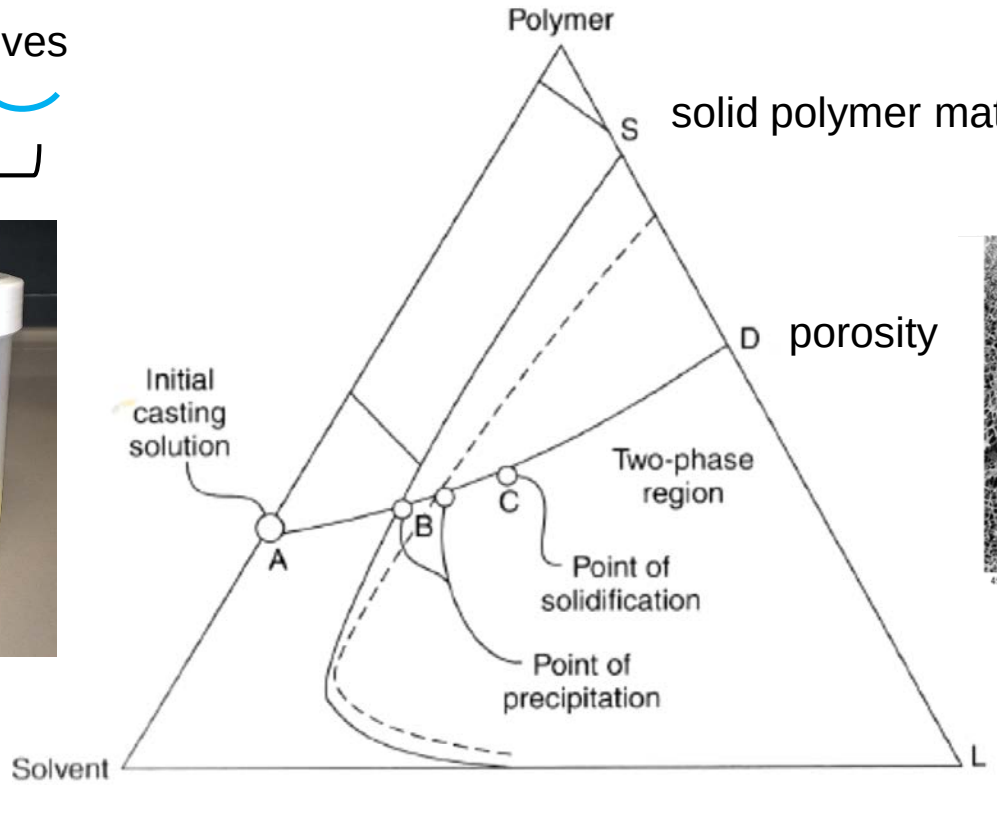
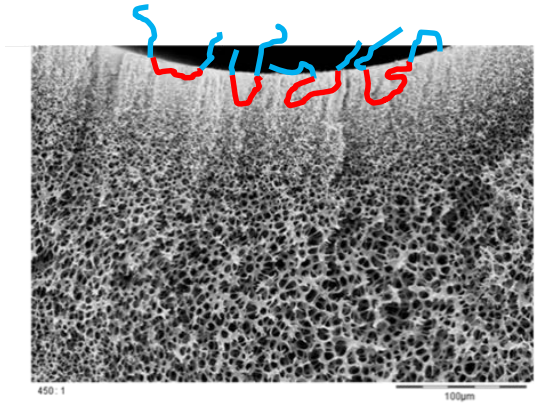
MABMEM objectives – new materials

PESU, PVP, solvent

MABMEM additives

Three component phase diagramm





R. T. Baker, Membrane Technology and Applications, 2nd Ed, John Wiley & Sons, 2004

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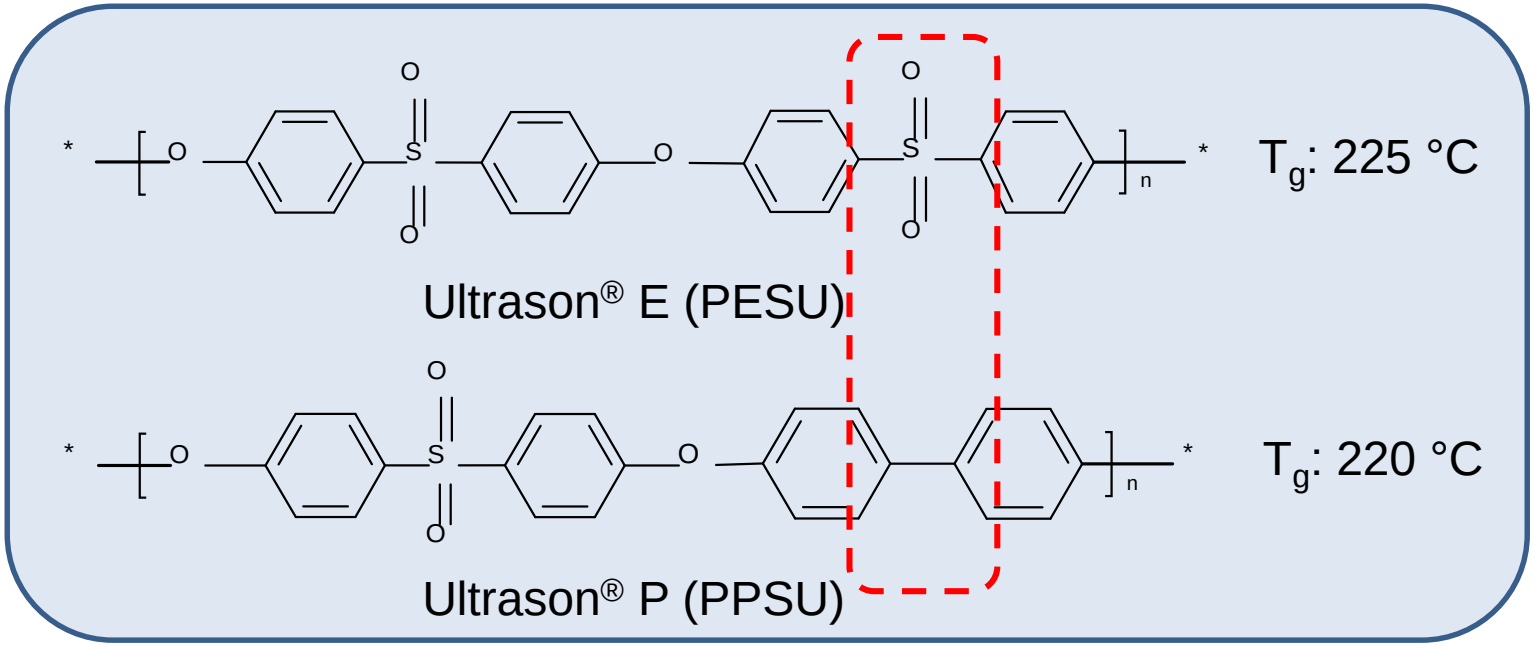
MABMEM objectives – new materials



- Currently, no PPSU membranes commercially available
- Tight UF-membranes: lower permeability and cut-off compared to PESU
- But, compared to PESU, PPSU has improved stability against oxidation

MABMEM work packages

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Project start 1.05.2016

Milestone M1 1.10.2017

Milestone M2 1.05.2018

Project end 30.04.2019

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Universität Duisburg Essen – Offen im Denken

Helmholtz-Zentrum Geesthacht – Zentrum für Material- und Küstenforschung

inge – heart of pure water

enwor – energie & wasser vor ort

OOWV – gemeinsam · nachhaltig · transparent

IWW – IWW Zentrum Wasser

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

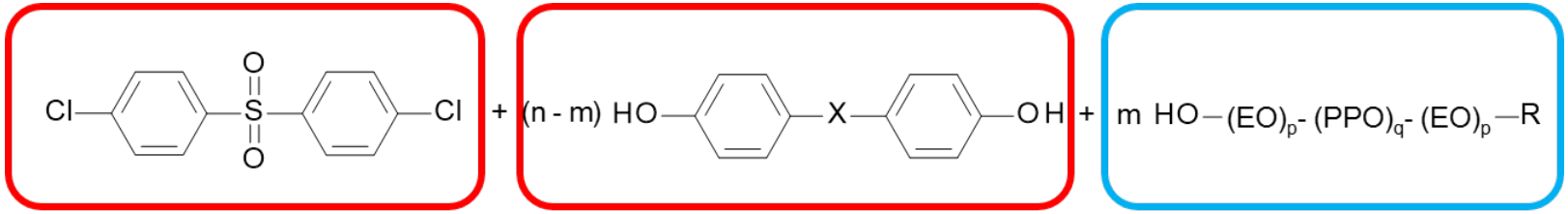
- Multibore fiber spinng
- Demonstrator assembly

- Demonstrator testing
- Surface water
- Waste water

MachWas – Materialien für eine nachhaltige Wasserwirtschaft

MABMEM – A Toolbox for Membranes

MABMEM results – additive synthesis



hydrophobic (2.5 – 7.5 kDa)

hydrophilic (2.5 – 14 kDa)

X = --- / SO_2

R = OH: multiblock copolymer

R = alkyl: triblock copolymer

structure	type	molecular weight (M_n)	PEO share	polyethersulfone X = -SO_2- (PESU)			polyphenylensulfone X = --- (PPSU)		
				2.5 k	5.0 k	7.5 k	2.5 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 %	✓		✓	✓		✓

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MABMEM results – surface enrichment

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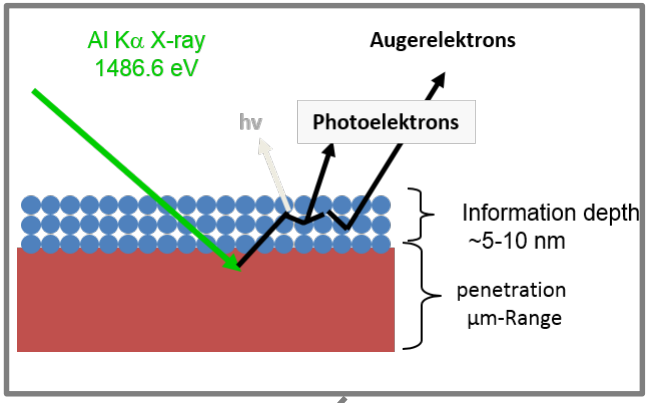
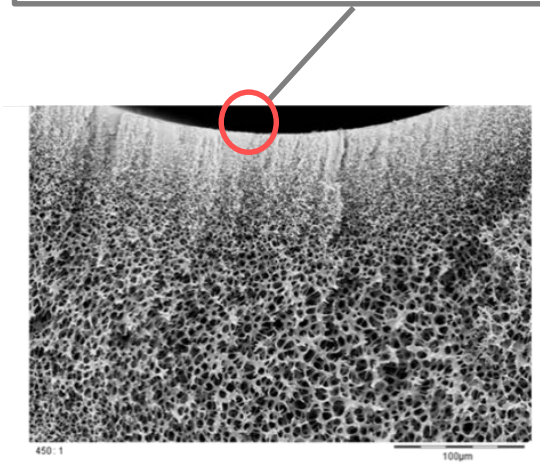
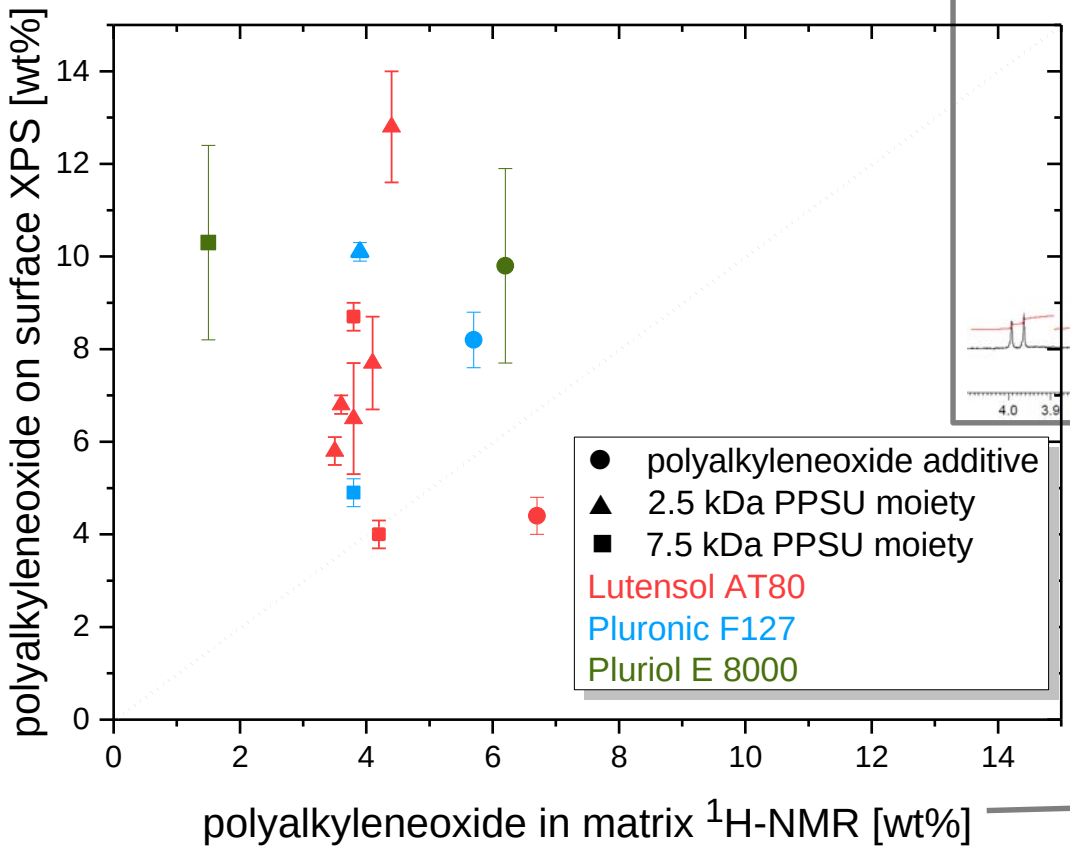
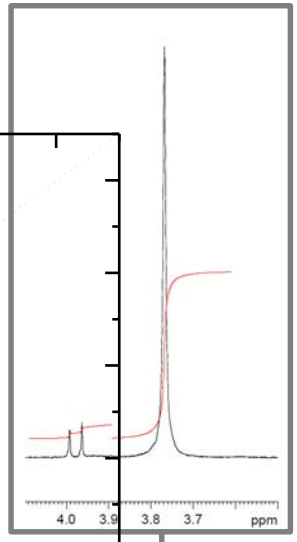
PPSU based additives in PPSU SB membrane separation layer









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MABMEM Results - Rheology

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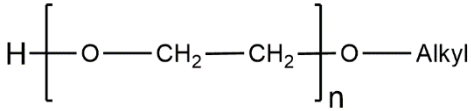
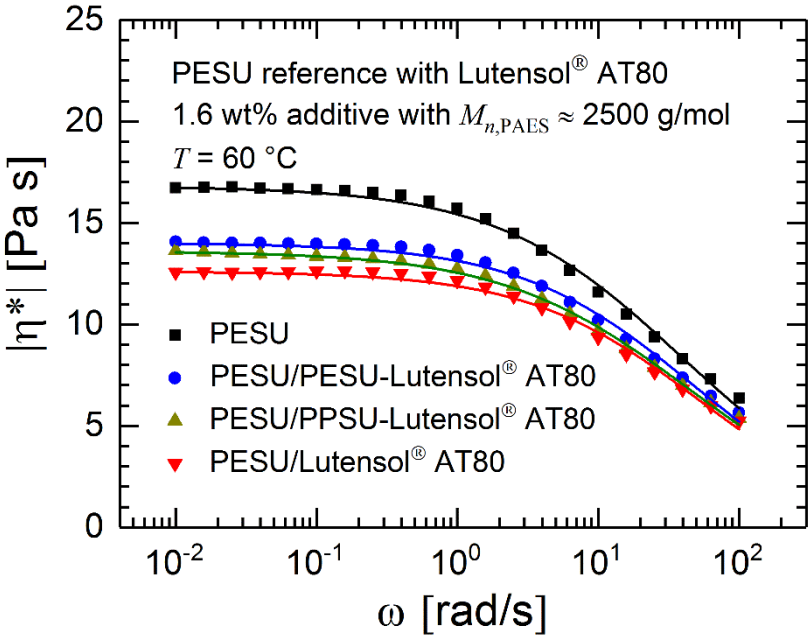
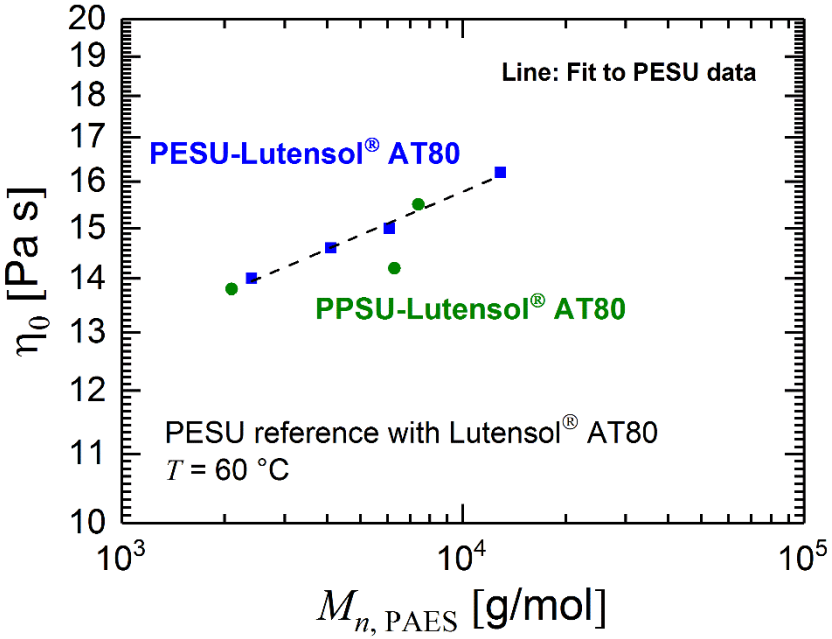
Centre for Materials and Coastal Research

Influence of additives on flow properties

Lutensol® AT80







Similar dependence of zero shear rate viscosity on molar mass

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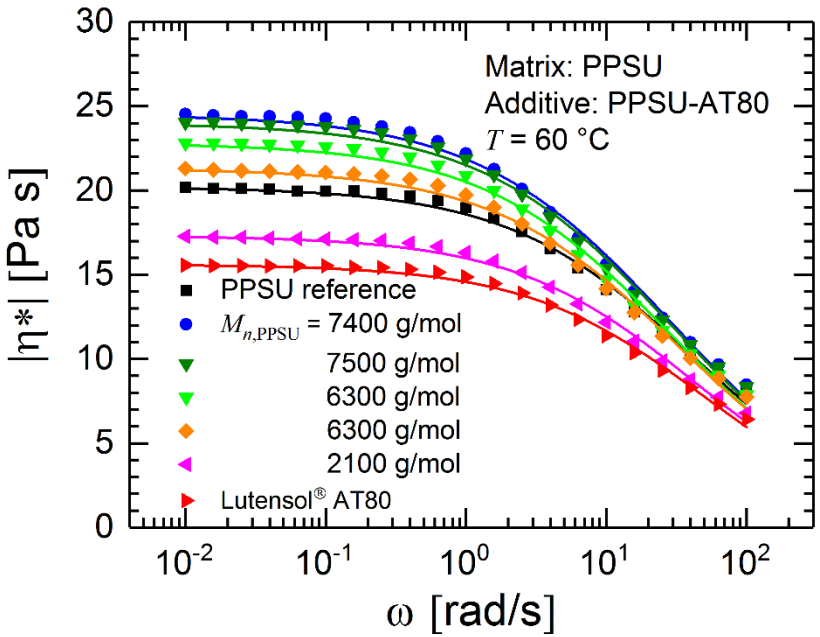
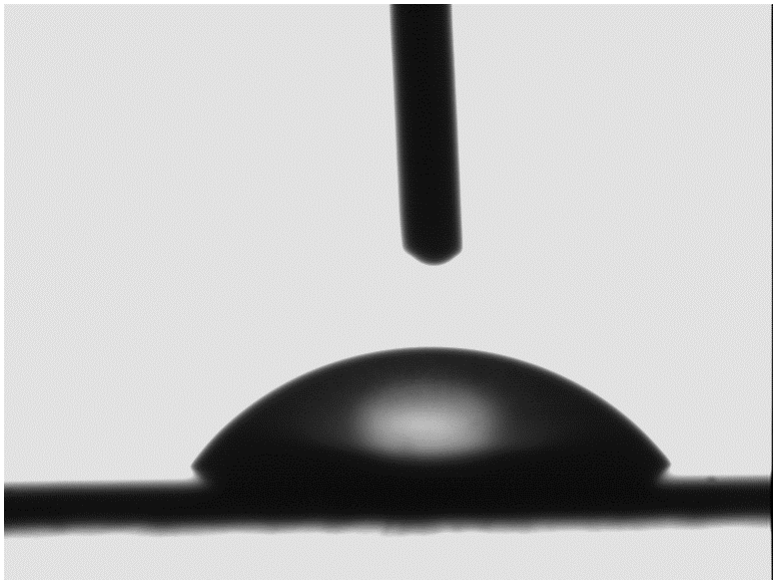
Influence of additives on flow properties of PPSU based solutions

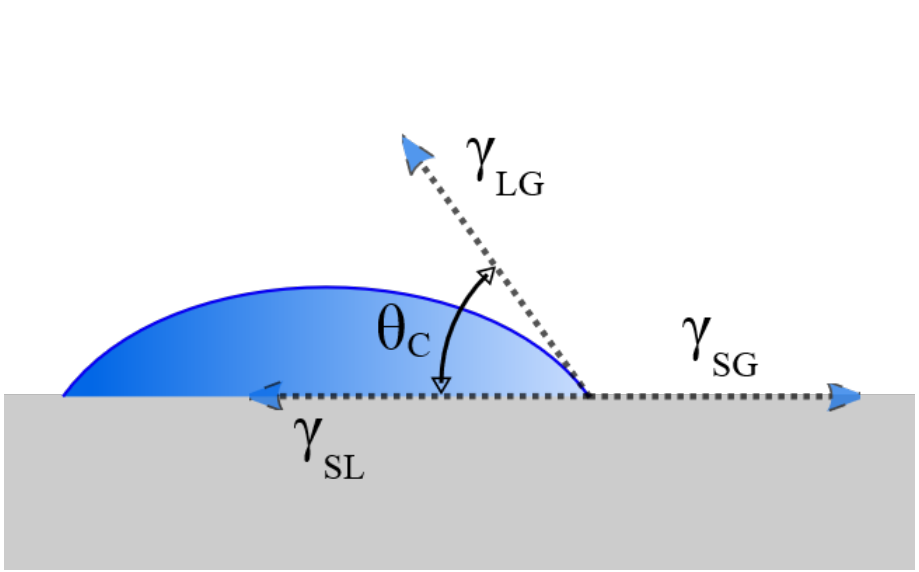


Solution	$\langle\tau\rangle$ [s]	η_0 [Pa s]
PPSU ref.	0.024	20.2
7.5 kg/mol	0.034	**24.0**
7.4 kg/mol	0.035	**24.5**
6.3 kg/mol	0.030	**21.3**
6.3 kg/mol	0.034	**22.8**
2.1 kg/mol	0.024	**17.3**
AT80	0.020	**15.6**

Increase of viscosity for PPSU/Lutensol® AT80 additives with high M_n

MABMEM results – water contact angle





- Water contact angle was measured in sessile drop mode
- Water is placed on membrane separation layer and contact angle determined
- After screening process is finished, surface energy will be determined for interesting samples

MABMEM results – water contact angle

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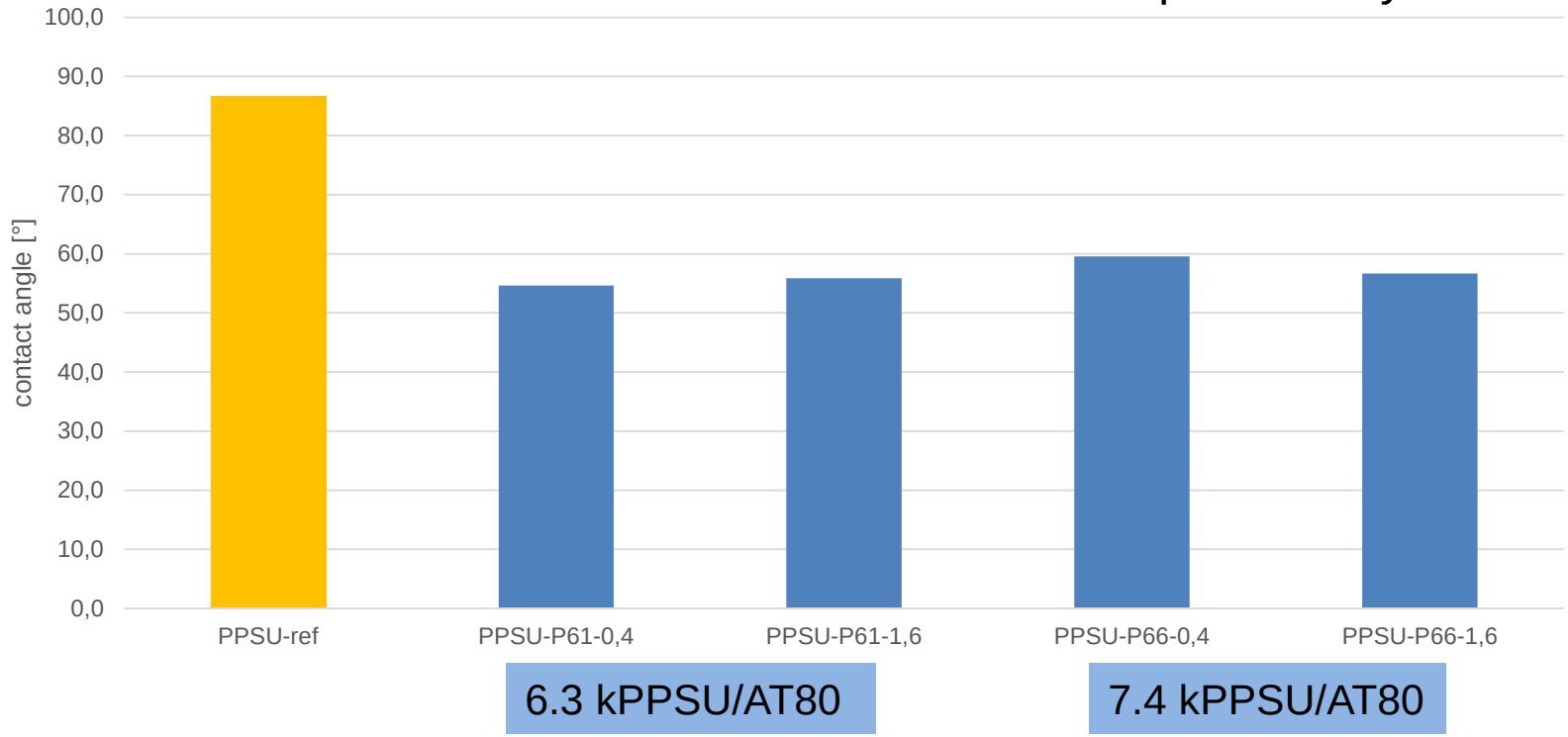
PPSU based additives in PPSU flat sheet membrane separation layer



Presence of MABMEM additives lowers contact angle of separation layer

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MABMEM results - fouling

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Filtration of pure water
(100 LMH – 30 min)

↓

Filtration of foulant
(100LMH – 45 min) & backwash (230 LMH-50 sec) (24 cycles)

↓

Filtration of pure water
(100LMH- 15 min) & backwash (230 LMH-50 sec) (3x)

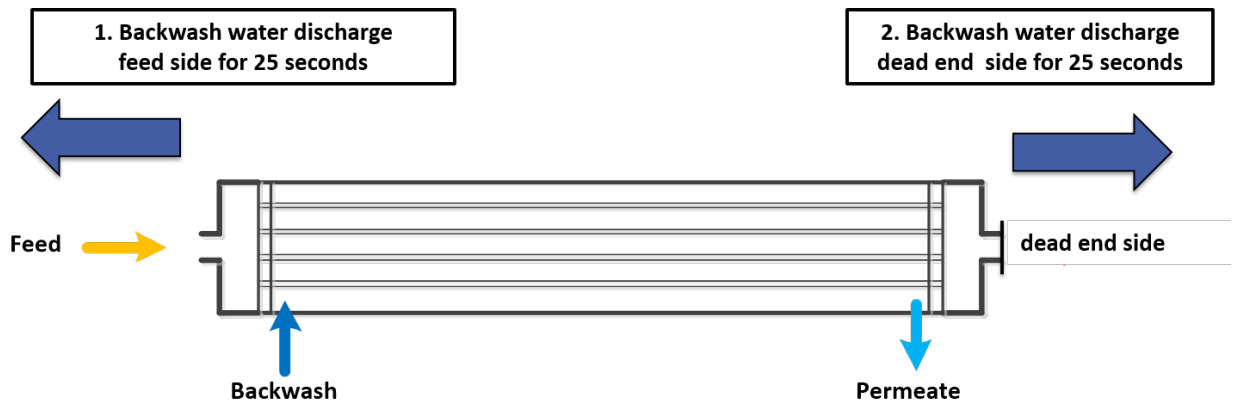
↓

Chemical cleaning
(NaOH pH:12 + 50ppm free CL)

↓

Filtration of pure water
(100LMH- 15 min) & backwash (230 LMH-50 sec) (3x)

- Three (3) repetitions
- Feed (1:6000 diluted FS extract, ~ 3.5 mg/L dry mass)
- Fully automated plant enables us to perform filtration with:
  - exact same feed solution
  - exact same operational parameters
  - enables the direct comparison of two different membrane materials



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MABMEM results - fouling

inge heart of pure water

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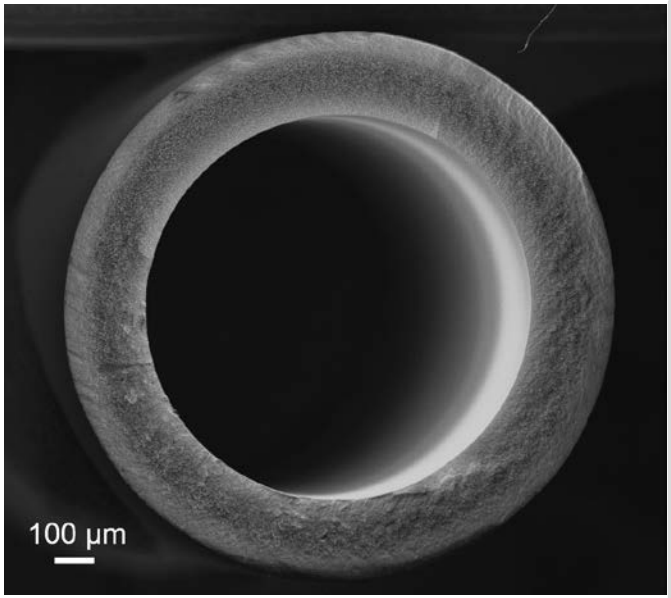
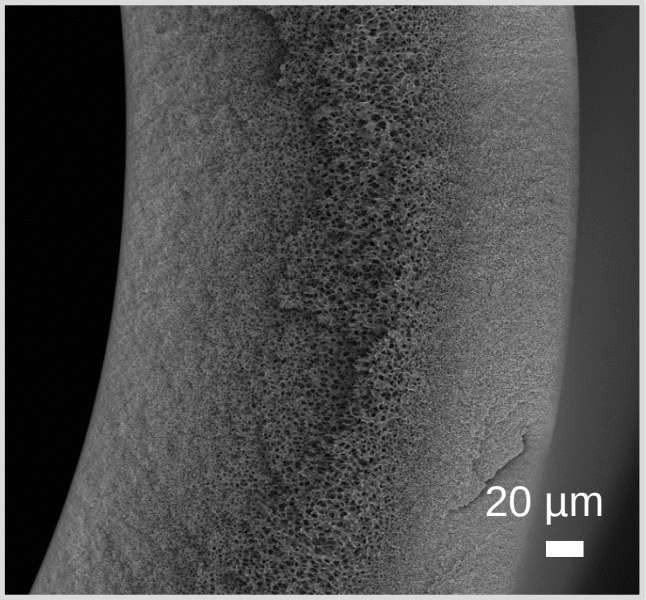
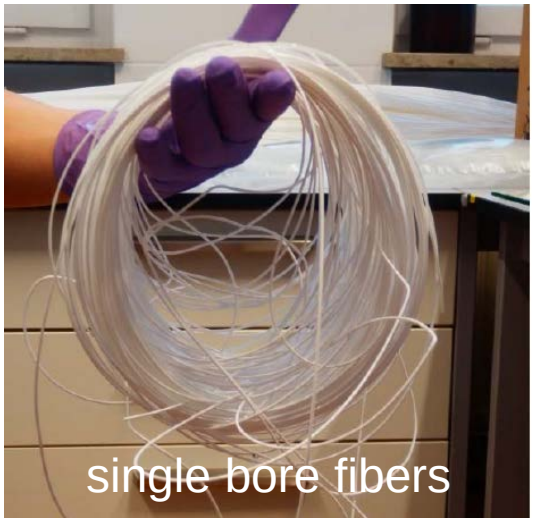
Centre for Materials and Coastal Research

PPSU SB with 6.3kPPSU/AT80 additive (SB 26)





SEM cross section



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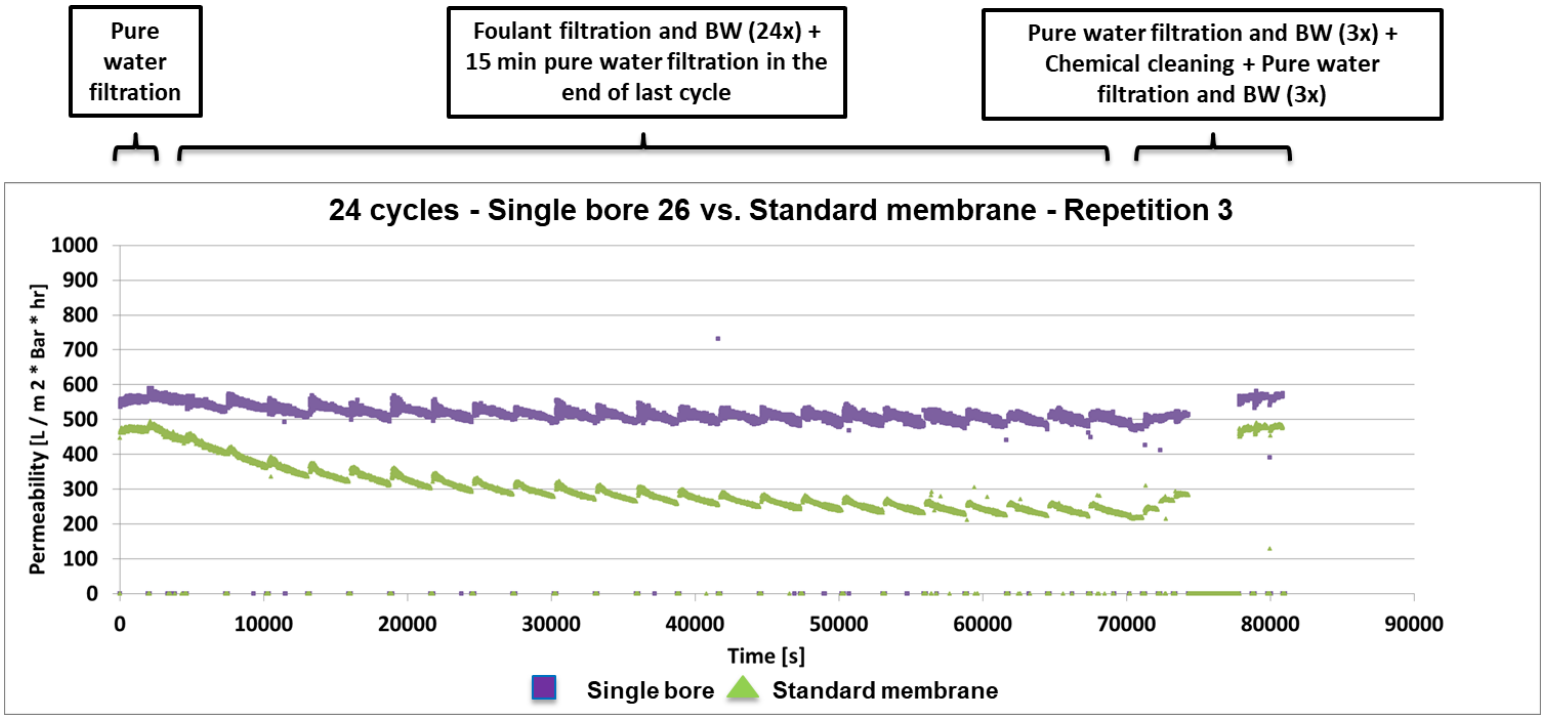
Fouling with flower soil – PPSU with 6.3kPPSU/AT80 additive (SB 26)



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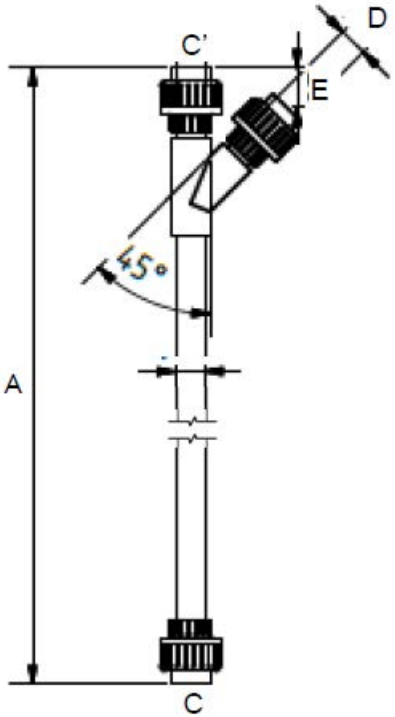
MABMEM results - upscale

Dizzer Lab modules LAB 0.9 MB 0.2 Y

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



Length: 1558 mm
Area : 0.2 m²

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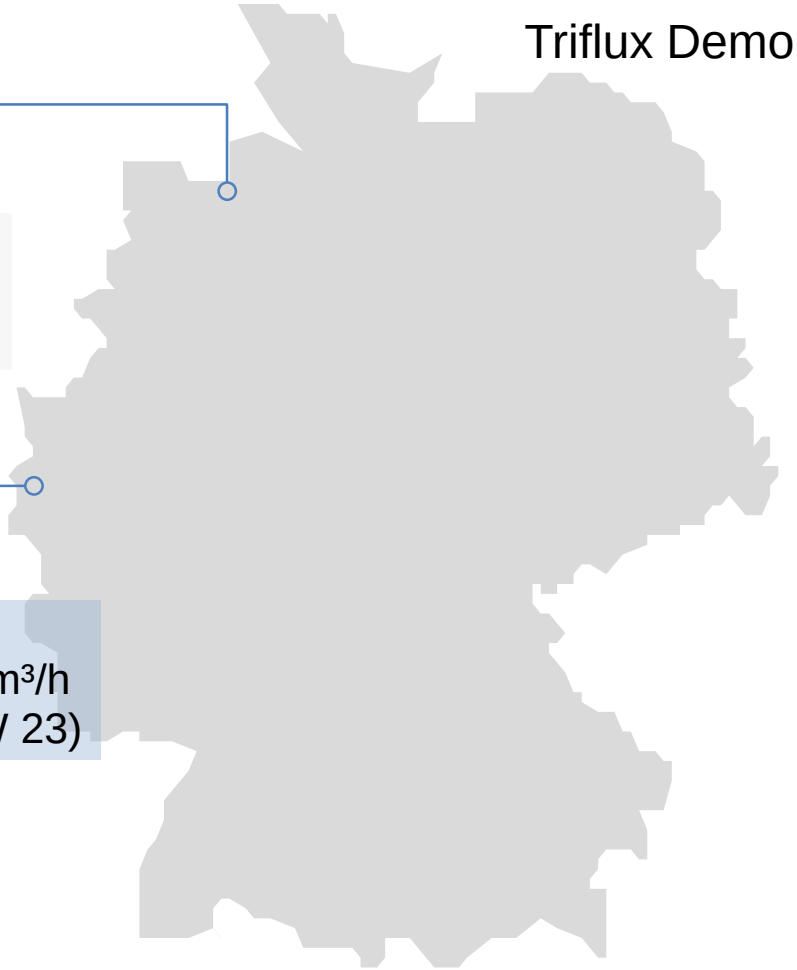
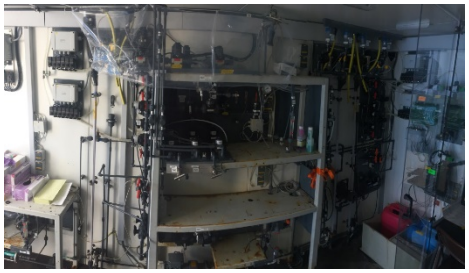
MABMEM next steps

Location: TBD
Waste water



WAG Roetgen
Surface water 6800 m³/h
From June 2018 (KW 23)

Triflux Demonstrator testing equipment



MABMEM conclusions

- Large number of new additives prepared, characterised and tested in PESU and PPSU ultrafiltration membranes
- Additive surface agglomeration proven by XPS and contact angle
- Fouling screening with flower soil extract conducted
- PPSU based additives in PESU and PPSU matrix as development candidates selected
- Demonstrator testing with surface water from June 2018

Acknowledgements

- BMBF for funding

GEFÖRDERT VOM

Bundesministerium
für Bildung
und Forschung

- PTJ for support

Projektträger Jülich
Forschungszentrum Jülich

- MABMEM-Team (UDE, IWW, HZG, inge, BASF SE)

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