Grafting of Ceramic Membranes :

Widely Broadening the Application Potential of Ceramic Membranes in Liquid Filtration

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VITO

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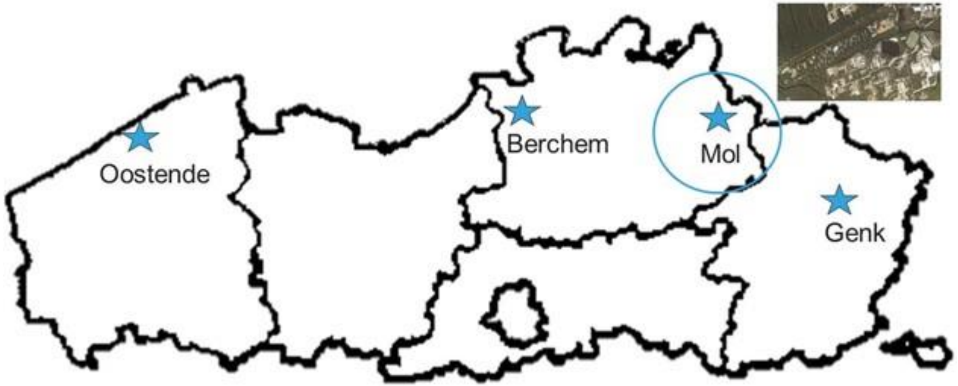
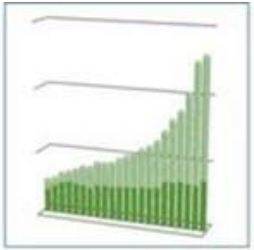


In 2021
~220 MEuro

Flanders based
Global focus

950 people
~45 nationalities

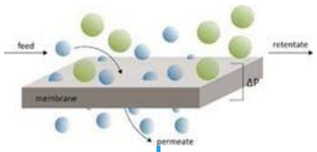
Central to industry - academia–government



Fast-growing
~75% external revenue

VITO

VISION ON TECHNOLOGY FOR A BETTER WORLD



THEMES

SUSTAINABLE CHEMISTRY

New value chains from renewable and circular resources

Process Transformation

SUSTAINABLE LAND USE

Air & climate

Water

Land use

Innovative technology

SUSTAINABLE HEALTH

I am my health

Sustainable health solutions

Environment, health & safety

SUSTAINABLE ENERGY

Buildings & Districts

Energy markets & strategies

Optimisation of thermal energy systems

Interfaces for electrical storage

SUSTAINABLE MATERIALS

Ceramics and powder metallurgy

Circular economy strategies

Getting value out of waste

Structured materials

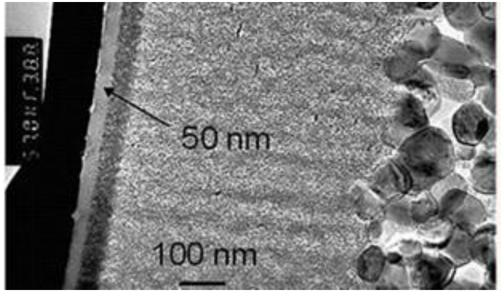
VITO

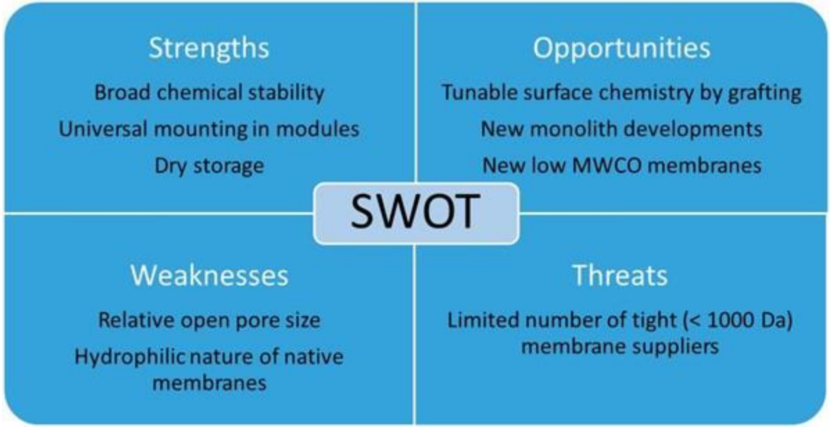
Membrane technology at VITO:

- Focus on liquid filtration
- Aqueous + organic solvent-based streams
- Pressure driven filtrations, membrane contactors, pervaporation
- Down-stream separation and coupling to (bio)reactors
- Process and membrane development
- From lab to pilot scale
- Techno-economic evaluation
- Collaborative projects and contract research

Ceramic membranes for liquid filtration

State of the art membranes: tubular, metal oxide or SiC, from NF to MF



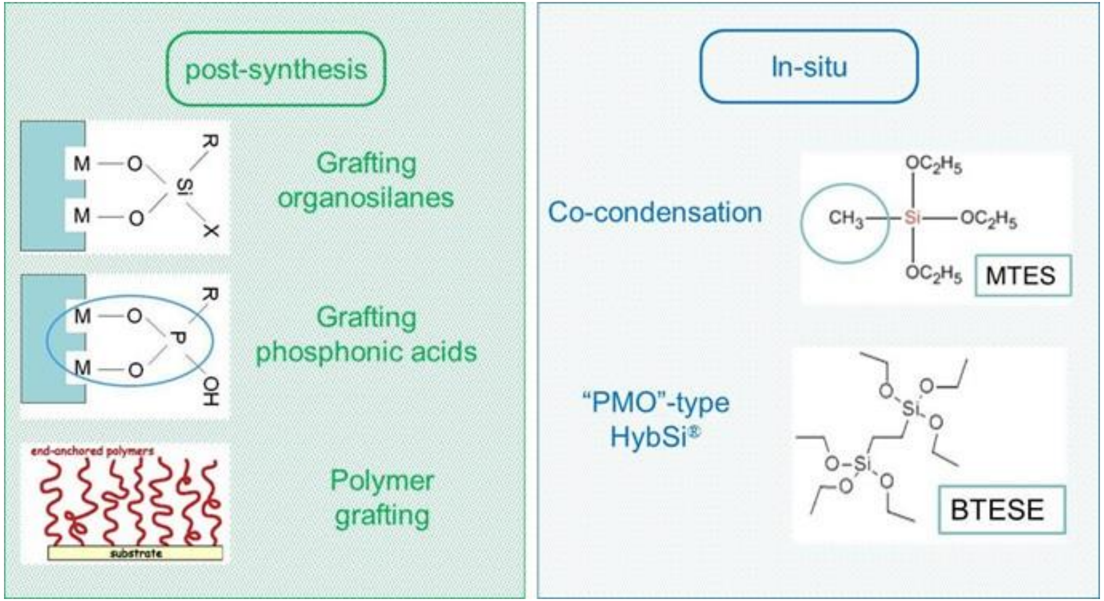


Grafting of ceramic membranes

Two methods for membrane functionalization: post-synthesis and in-situ

Incentives:

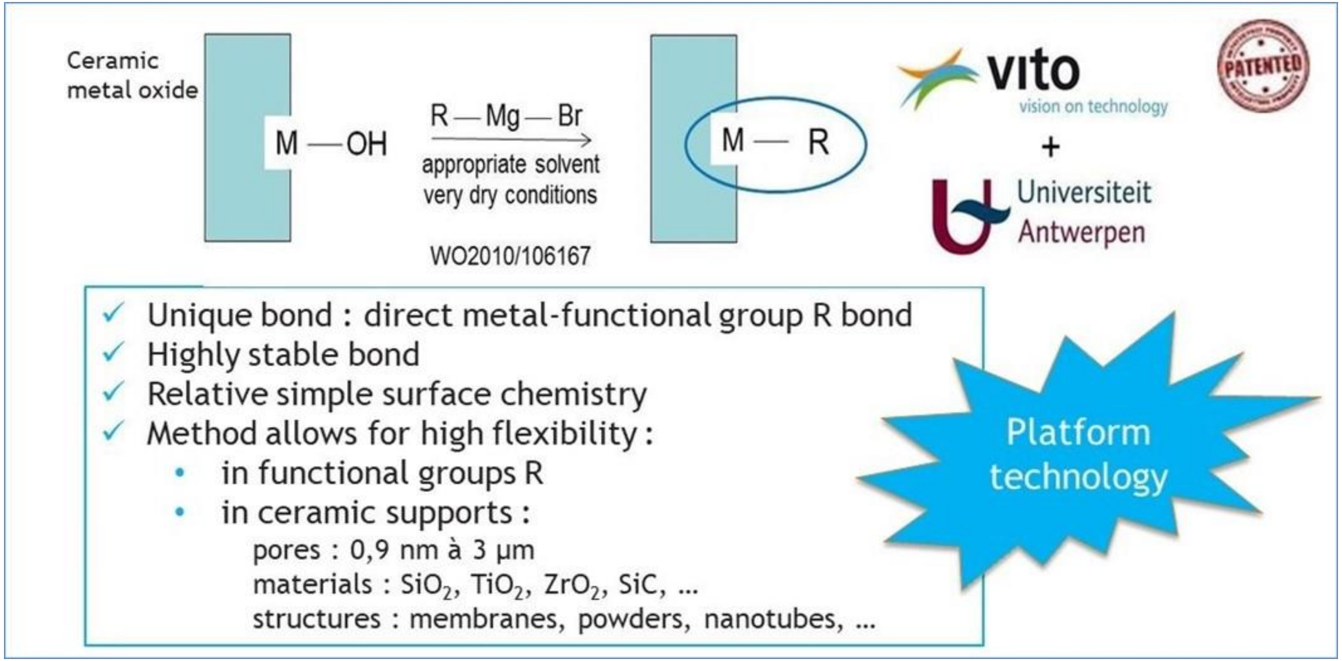
- Increase stability
- Decrease pore size
- Change surface polarity
- Change surface functionality/affinity



Grignard grafting

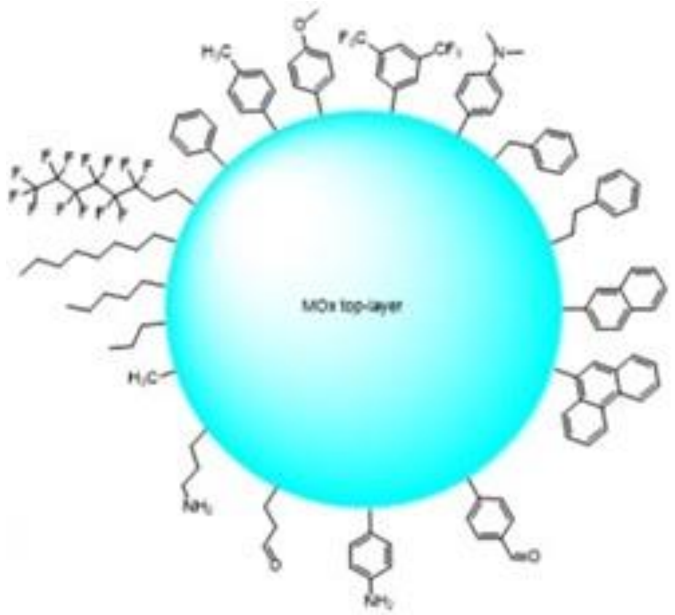
Innovative post-synthesis surface modification technique
On commercially available ceramic membranes/materials

FunMem®



Grignard grafting

Variety of groups already grafted using this technology



Membranes used for liquid filtrations

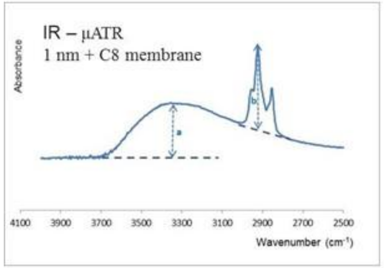
Grignard grafting

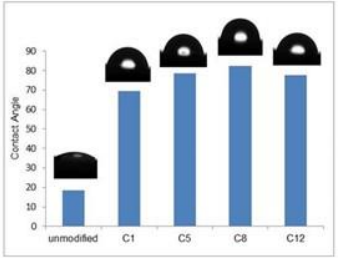
Alkyl modification of 1 nm TiO_2 membranes : amphiphilic, idem MWCO

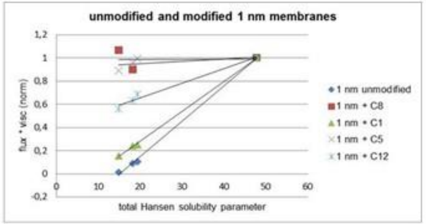
Partial coverage:
~1 alkyl/nm^2
~30%

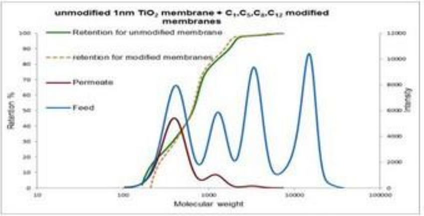
J. Van Dijck et al., Appl. Surf. Sci. 527 (2020) 146851

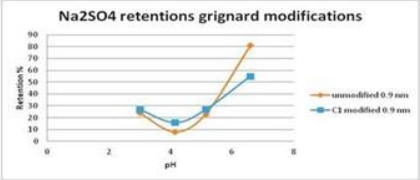
- Alkyl FunMem
  Amphiphilic membranes
- Increased fluxes for apolar solvents
- MWCO not altered
- Decreased surface charge







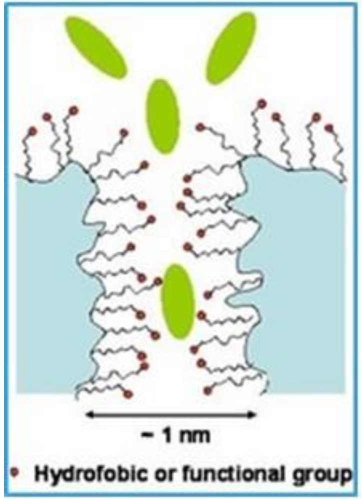


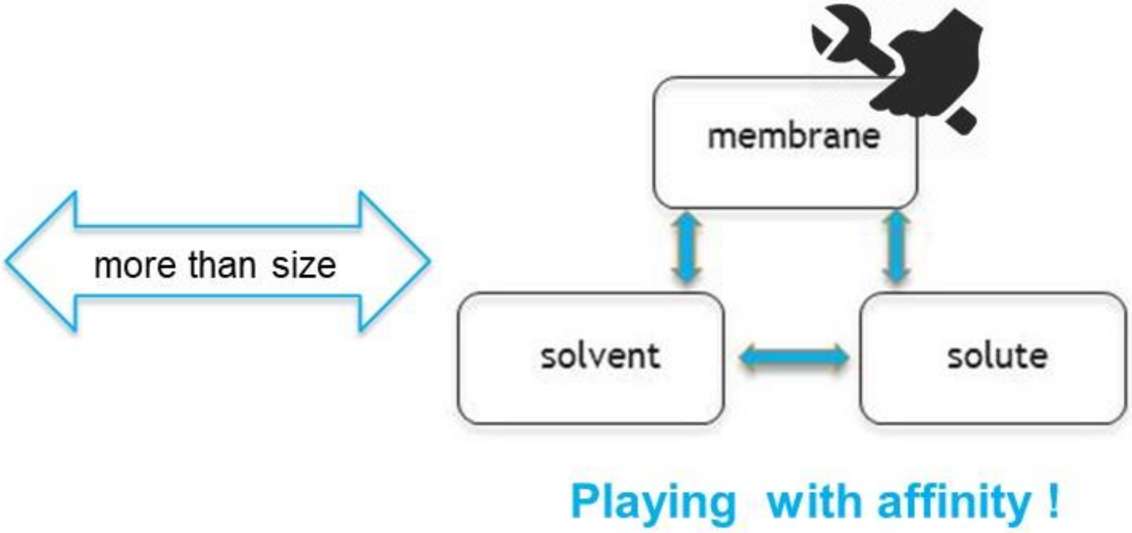


S. Rezaei et al., JMS, 454 (2014) 496-504

Grignard grafting

Grafting ceramic membranes : tuning chemistry of membrane pore surface

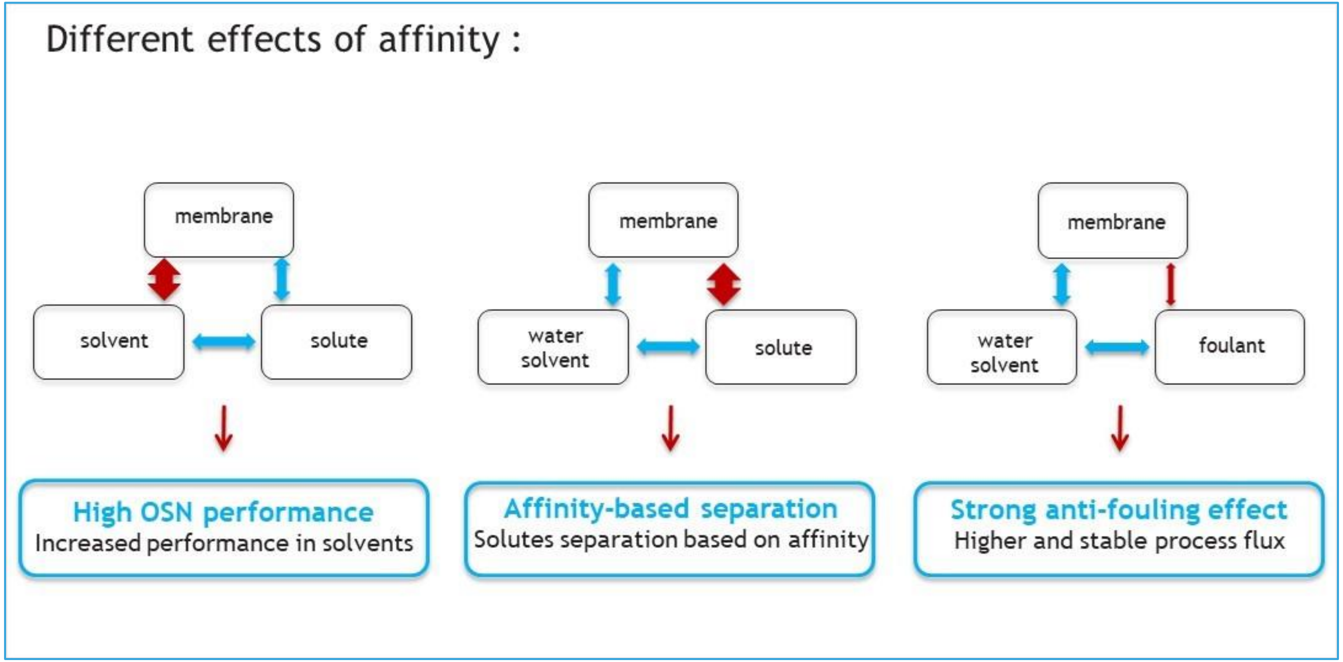




Expanding potential of membrane filtration

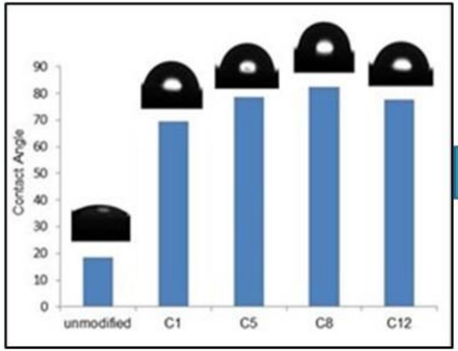
Grignard grafting

Grafting ceramic membranes : increasing application potential of ceramic membranes

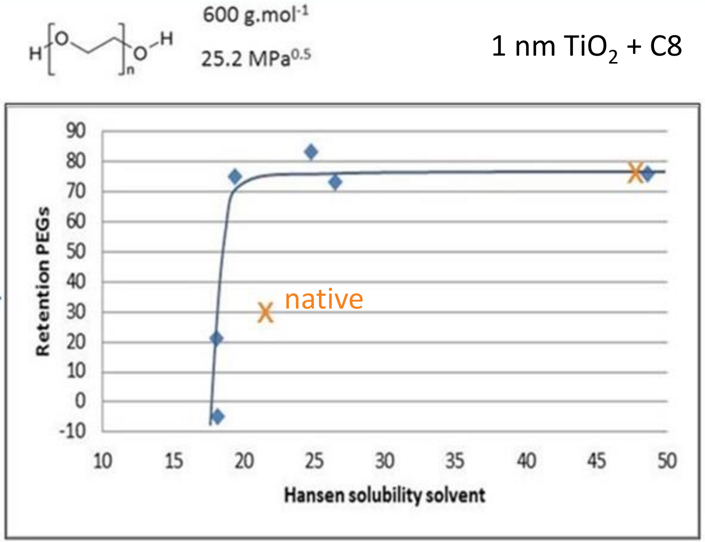


OSN performance FunMem

Increasing nanofiltration in organic solvents = OSN



Increased membrane-solvent affinity



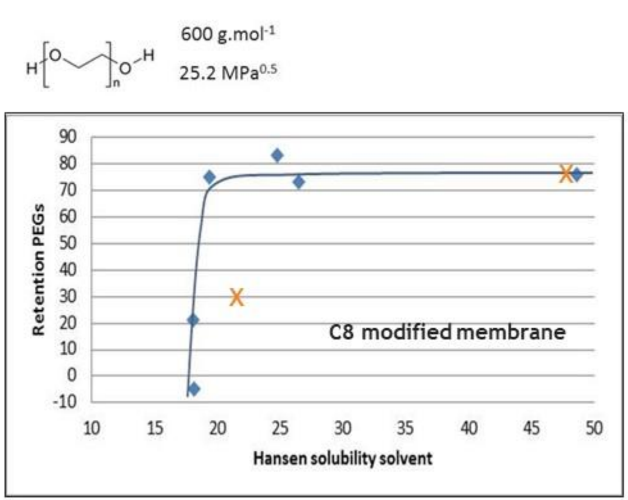
S. Rezaei et al., JMS, 513 (2016) 177-185

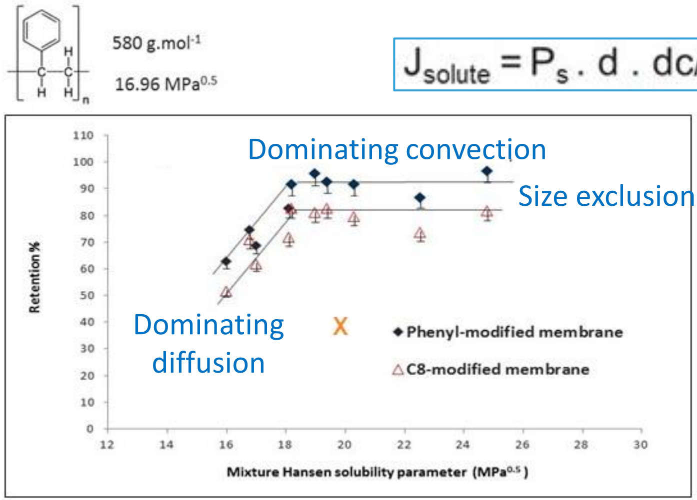
OSN performance FunMem

High retentions for many different solutes and solvents

Spiegler-Kedem theory

$$J_{solute} = P_s \cdot d \cdot dc/dy + (1 - \sigma) \cdot J_{solvent} \cdot c$$





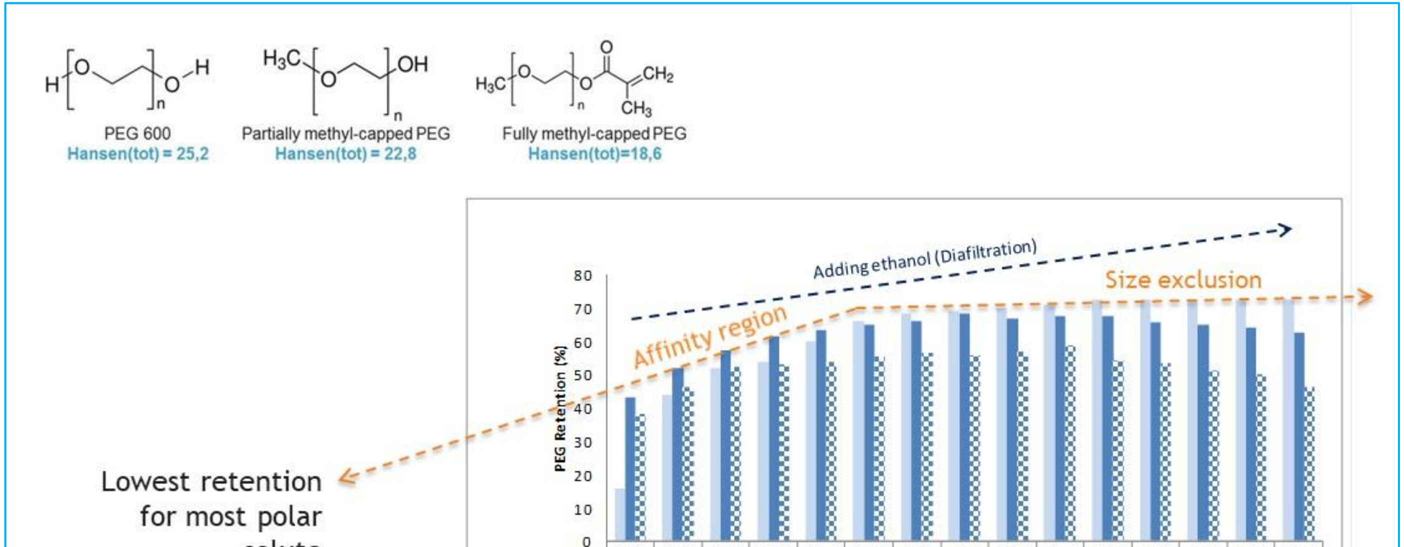
X : native

High retentions for a wide range of solvents

S. Rezaei et al., JMS, 513 (2016) 177-185

OSN performance FunMem

Performance as function of solvent polarity: diafiltration EtAc → EtOH



	18,1	18,4	18,8	19,1	19,4	19,8	20,1	20,6	21,0	21,4	21,8	22,3	22,6	22,9	23,4
PEG	15,82	43,8	52,0	53,7	60,0	66,1	68,1	69,0	70,0	71,1	72,5	72,5	72,1	72,6	72,6
PEG-partially	43,24	51,9	57,3	61,5	63,4	64,8	65,9	68,3	66,9	67,5	67,7	65,8	64,8	64,1	62,5
PEG-fully	38,24	46,0	52,2	53,0	53,8	55,4	56,3	55,6	56,9	58,5	54,1	53,3	50,9	50,0	46,2

S. Rezaei et al., JMS, 513 (2016) 177-185

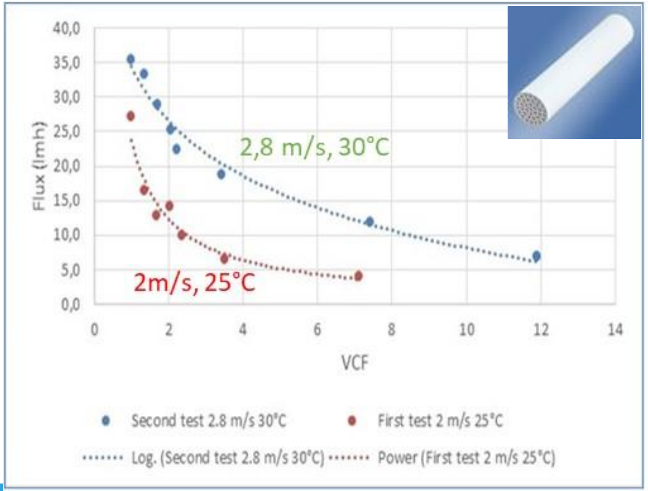
OSN performance FunMem

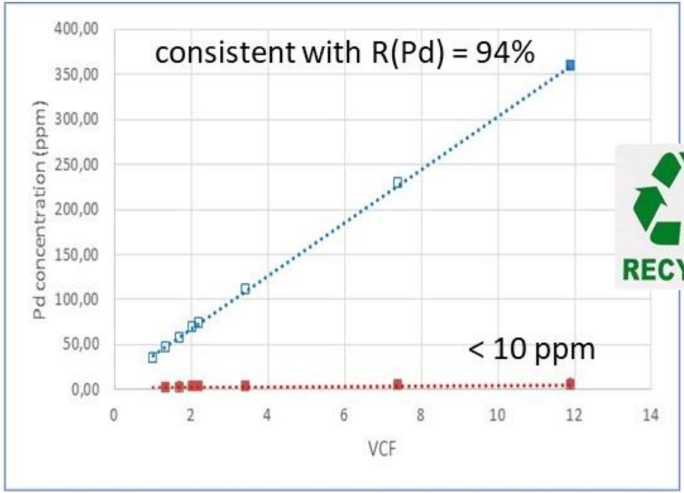
SuMems

Pd removal from mother liquor methanol-based (97%)

- ✓ ~ 7 g/L succinic acid + traces K-salt
- ✓ small amount of toluene
- ✓ API (400 Da) ~ 1g/L
- ✓ 60 à 100 ppm Pd

Membrane	TMP (bar)	Flux (L/hm2)	R(Pd) in %
0,9 nm C1	20	9,8	92,8
0,9 nm native	10	62,0	22
Koch MPF 34	20	1,1	85





POC at 0,1 m^2 (19ch 50 cm)

Membrane cleaning: MeOH rinse + pH10

OSN performance FunMem

Many different demonstrations at pilot scale

Solute in DMSO with poor thermal stability → diafiltration + concentration → Solute in water/n-butanol

Grafted membranes better than alternatives

Present method: 9 L/L extractions & vacuum distillation

Solute: Chiral molecule ~1500 g mol^{-1}

Task: solvent exchange & solution concentration

Membrane: 0.9 nm C_1 TiO_2 (0.75 m^2)

Membrane performance

Permeance:	1.4 – 2.9 $Lm^{-2}h^{-1}$ bar^{-1} diafiltration 1.5 – 0.15 $Lm^{-2}h^{-1}$ bar^{-1} conc^n	
Rejection:	98.1% – 99.1% 99% - 92%	diafiltration conc^n

OSN performance FunMem

Different demonstrations at pilot scale

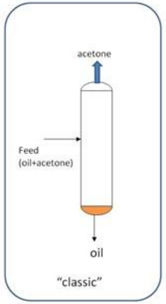
Robust, long-term behavior

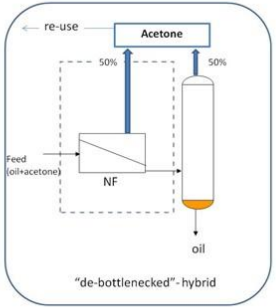
Economic feasibility

- **EEMBAR/ISRO** : Energy-efficient membrane-assisted recovery of acetone
- Acetone recovery from different edible oils (palm or shea nut oil)
- Demonstrate techno-economical feasibility of OSN process through long term pilot testing in industrial environment (TRL 7)
- Comparison membranes : FunMem) ↔ polymeric SolSep membranes

FunMem performance at pilot-scale :

Oil retentions	~90 %
Fluxes	20 à 40 l/hm²





3x 120 cm 19 ch elements

SolSep BV

vito

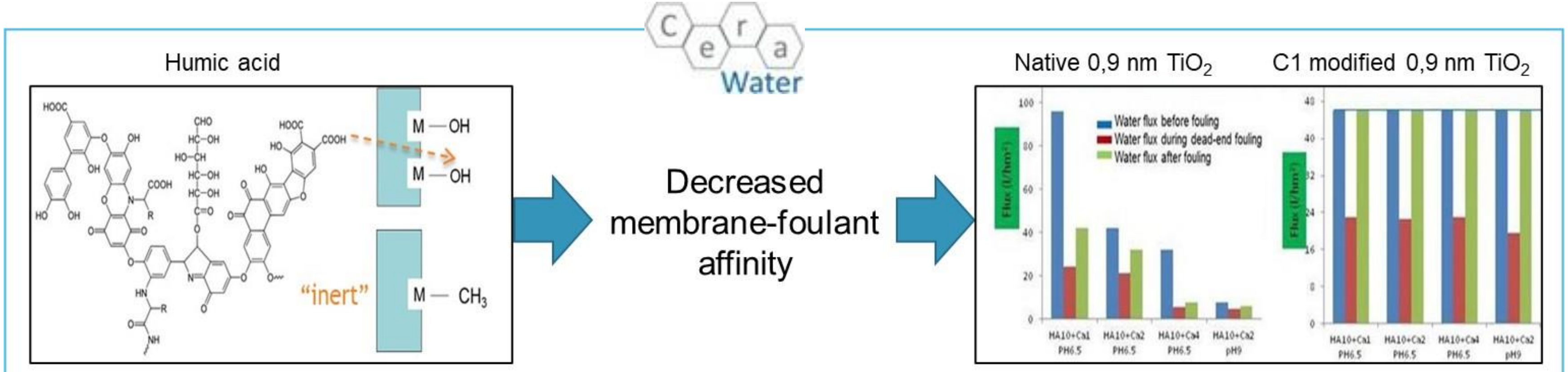
ISPT

IOI Loders Croklaan

HOGESCHOOL ROTTERDAM

Anti-fouling performance FunMem

Strongly reduced fouling for C_1 grafted membranes in a variety of waste waters



G. Mustafa et al., JMS, 470 (2014)369-377

No to low irreversible fouling for a wide range of foulants

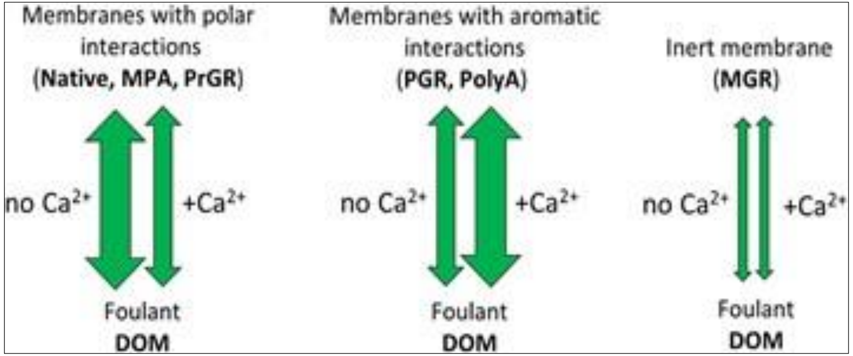
For non-aromatic foulants: also Ph grafted membranes anti-fouling

WO2015/124784A1 PATENTED

Anti-fouling performance FunMem

Effect of Ca on humic acid fouling unraveled:

- Decrease of polar groups by complexation
- Relative increase of aromaticity by complexation

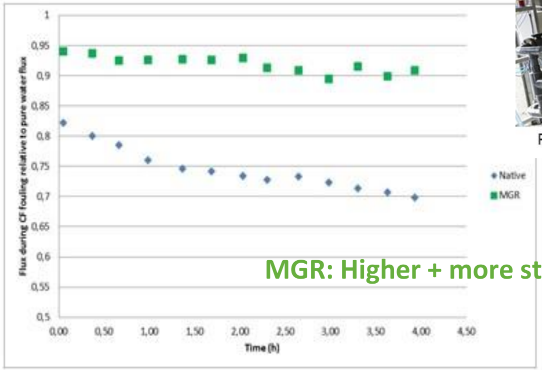


G. Mustafa et al., Water Research, 93 (2016)195-204

Anti-fouling performance FunMem

Higher and more stable process flux + sometimes higher retentions

Cross-flow filtration real surface water



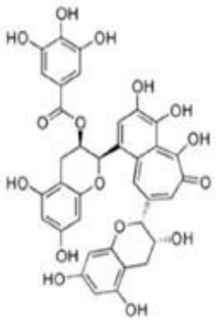
Piloting during 1 month

MGR: Higher + more stable flux

Humic acid retentions	
MGR	95%
Native	91%

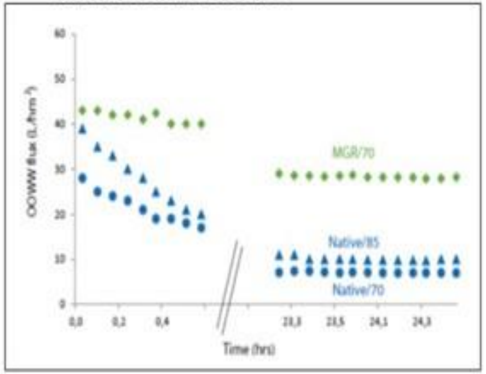
Water flux recovery after forward flush	
MGR	100%
Native	84%

Fouling solution :
real olive oil waste water (ES)



Foulants :
e.g. polyphenols

24h filtration in cross-flow



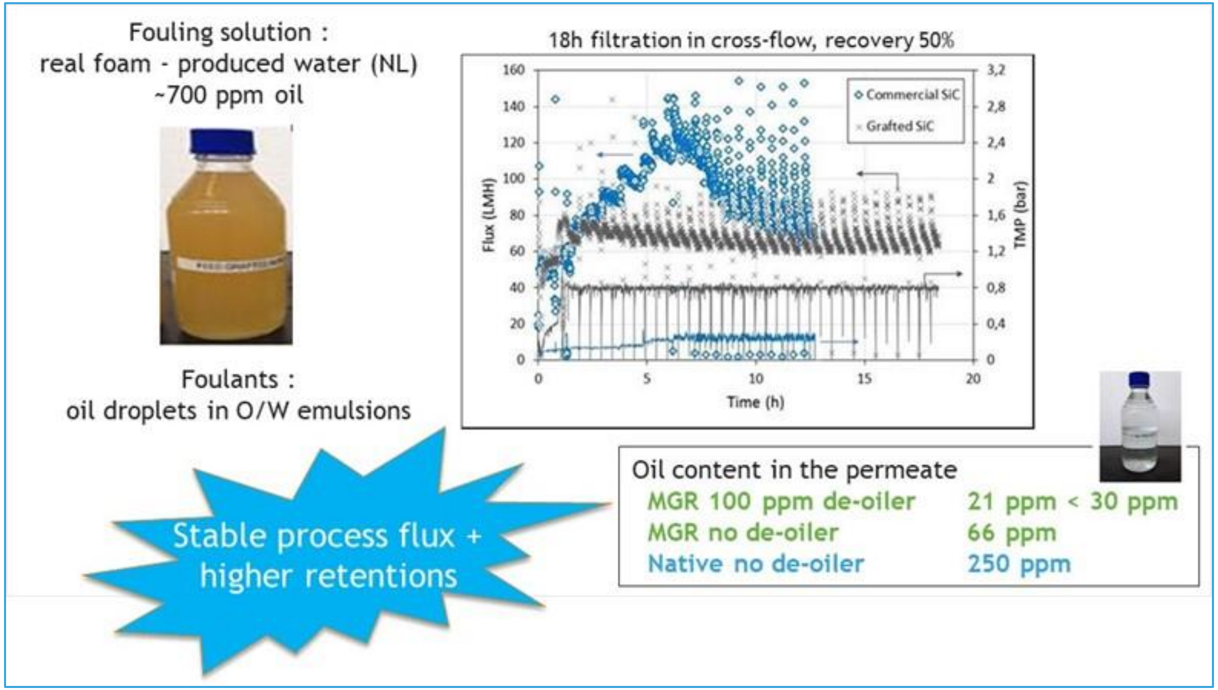
COD retentions	
MGR	48%
Native	11%

Water flux recovery after forward flush	
MGR	100%
Native	42%

G. Mustafa et al., Water Research, 104 (2016) 242-253

Anti-fouling performance FunMem

Demonstration for MF (SiC) membranes for real oil produced water



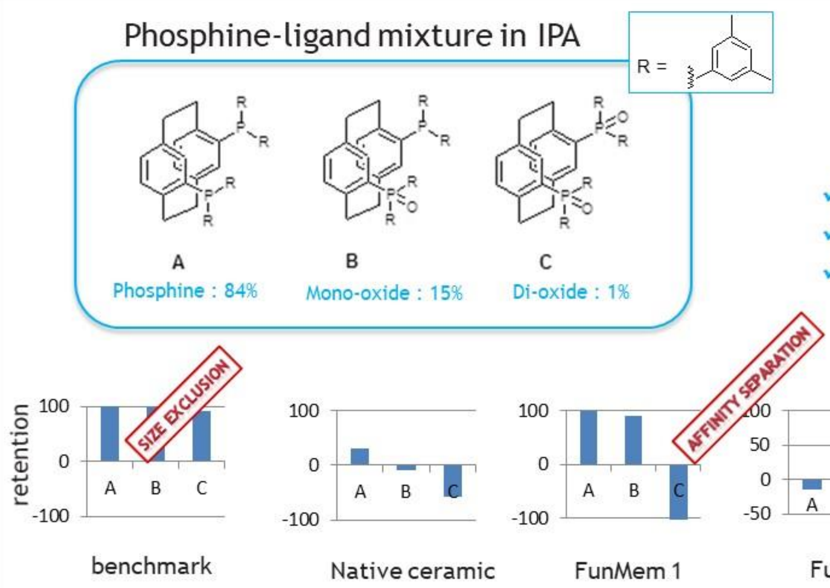
ISPT Institute for Sustainable Process Technology

LiqTech

AMK proceedings 2016

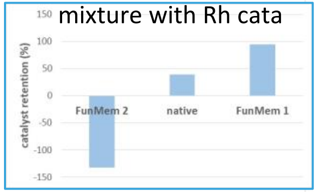
Affinity separations with FunMem

Separations based on membrane-solute affinity: NF



- ✓ Like chromatography
- ✓ But continuous processing
- ✓ Shown also for bioaromatics

Confirmed in real reaction mixture with Rh cata



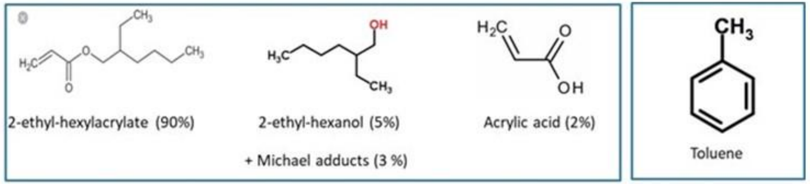
S. Rezaei et al., Sep. Purif. Techn., 147 (2015) 320-328

Affinity separations with FunMem

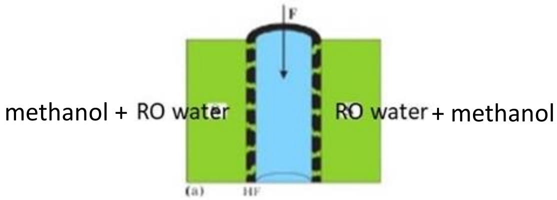
EasiChem

Separations based on membrane-solute affinity : membrane extraction (ME)

Removal of alcohol (< 1%) + acid (as low as possible) from acrylate :



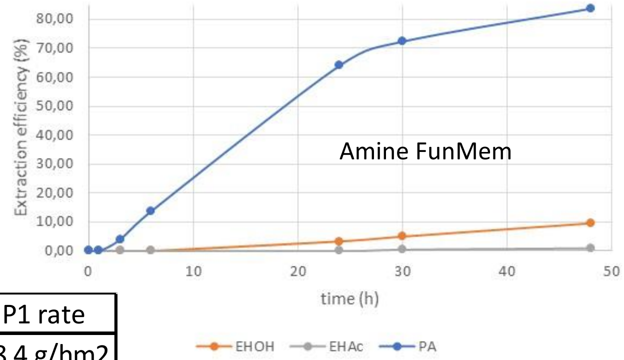
Active component = 80 %   Solvent = 20 %



Fine-porous hydrophilic membrane (FunMem) wetted with optimal extractant

Feed : 10 g/L each in toluene

Molecule	MW	LogP
2-ethyl-hexylacetate	172	3,72
2-ethyl-hexanol	130	2,74
propionic acid	74	0,33



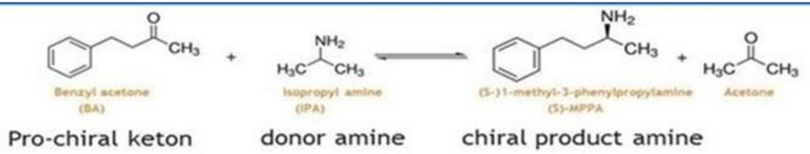
Membrane	P1 rate
native	18,4 g/hm2
amine FunMem	33,8 g/hm2

Affinity separations with FunMem

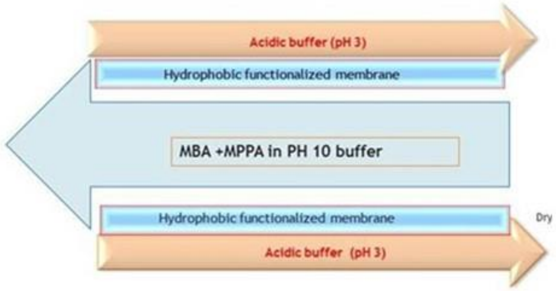
EasiChem

In-situ product recovery by membrane extraction (ME)

Separation of donor amine and chiral product amine in transaminase reaction



- ✓ High selectivity
- ✓ Low yield
- ✓ Yield increase by ISPR



Charged amines
No back extraction

Dry membrane !

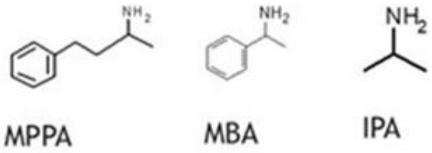
Dry fine-porous hydrophobic membrane (FunMem)
to avoid solvent leaching of open-porous membrane (e.g. PTFE or PP)

Rehn et al., J. Biotechn., 179 (2014)

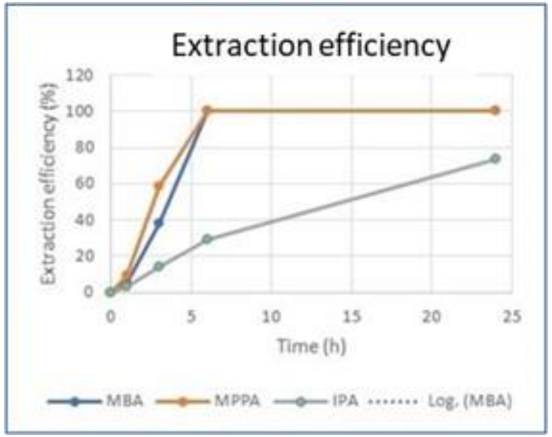
EasiChem

In-situ product recovery by membrane extraction (ME) : membrane-solute affinity driver

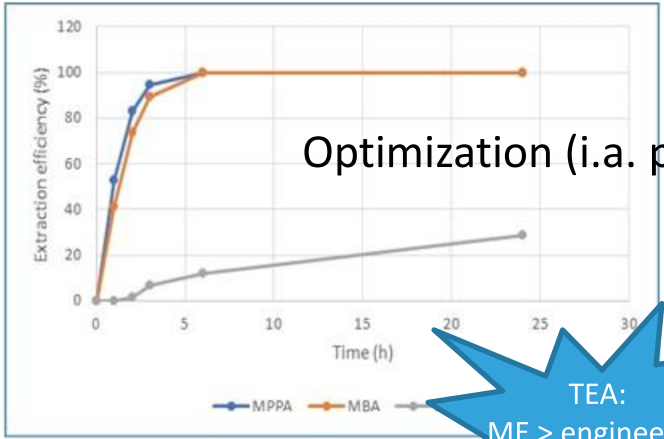
Feed :
1g/L each



Property	MPPA	MBA	IPA
Log P	2,26	1,52	0,39
pKa	10,63	9,54	10,73
% uncharged at pH=10	19	74	16



Polar component slowest



Optimization (i.a. pH ↓)

TEA:
ME > engineered enzyme

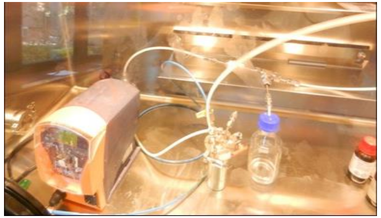
Yang et al., OPRD, (2022)

Development of FunMem

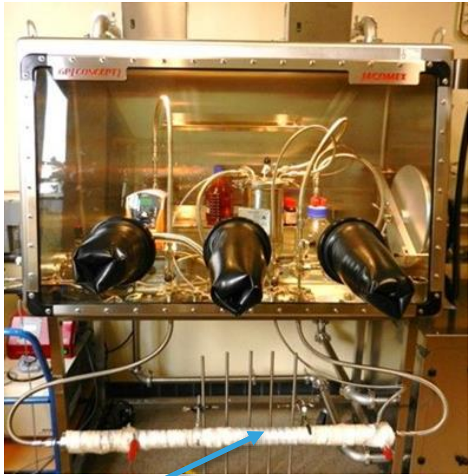
From stirring + shaking towards grafting at large scale in filtration conditions

2011

2013



2014



2017

From 12 cm single tubes towards 120 cm long multichannel elements

Production for different piloting campaigns

Further upscaling FunMem production

Next step in 2021-22 : upscaling/upgrading existing grafting pilot line

INNOMEM

Open Innovation Test Bed for nano-enabled Membranes

Our Pilot is one out of 14

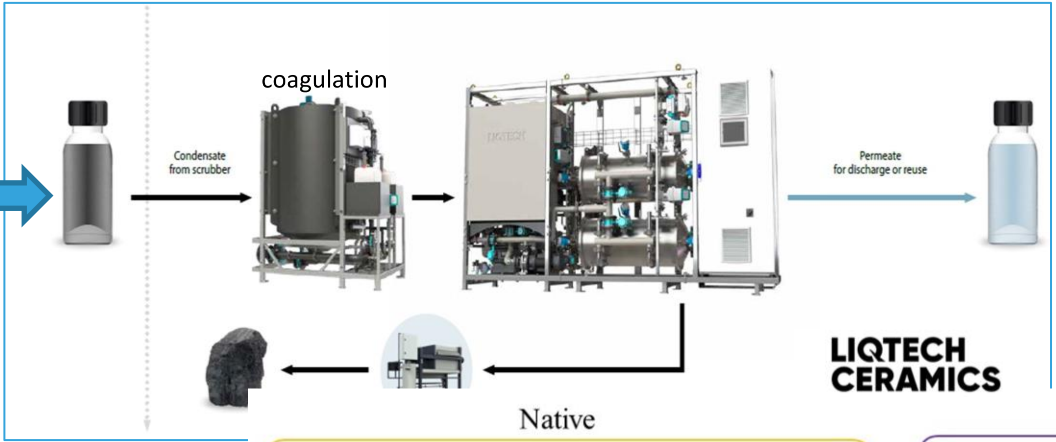
	Actual system	Upscaled system
	Fixed size of multichannels	Flexible length 120/118 cm
Production capacity increase	Production of 5 membranes/week	Production of 10 membranes/24h
	High vacuum pre-treatment	Easier pre-treatment

Further upscaling of FunMem production

Same skid, two layers of membranes; modules for membranes of flexible lengths

Show Case of anti-fouling action FunMem

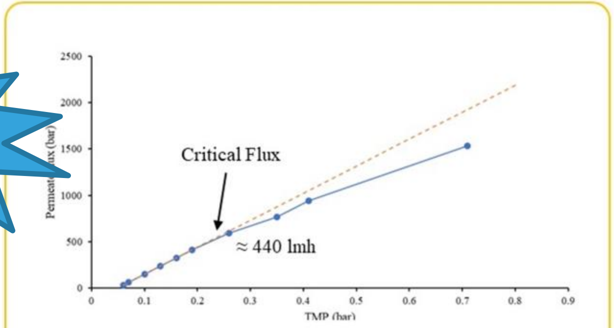
Demonstration of FunMem: metal removal from scrubber water from power plants (DK)



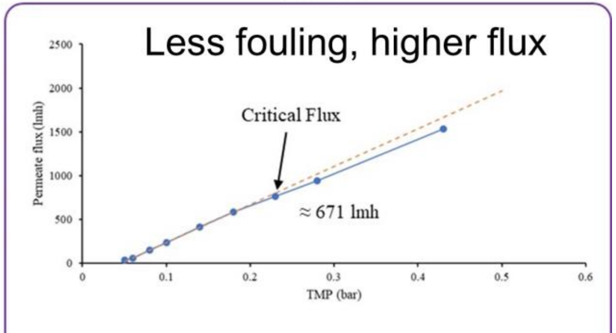
13 multichannels

Decreasing CAPEX + OPEX

Native

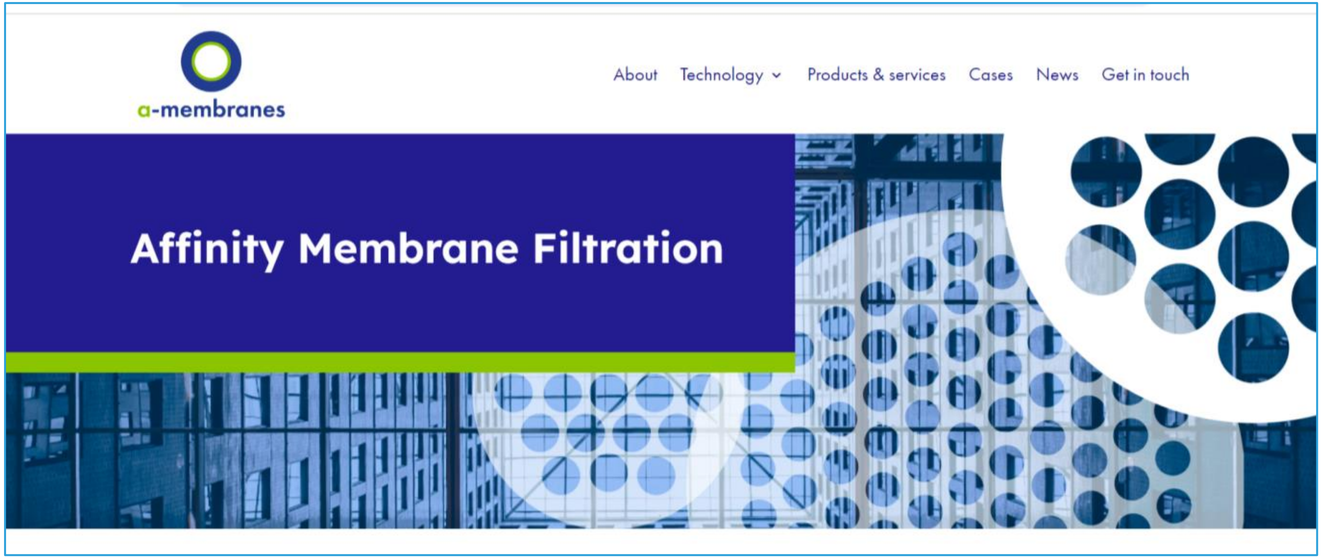


Grafted



Commercialization of FunMem

Creation of a spin-off : 01 December 2021



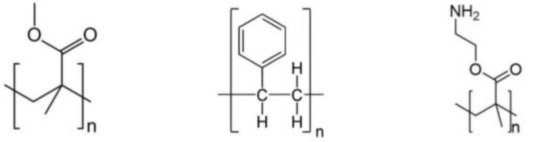
Bart Coen

Systematic production of large amounts of grafted membranes

Further exploration of possibilities

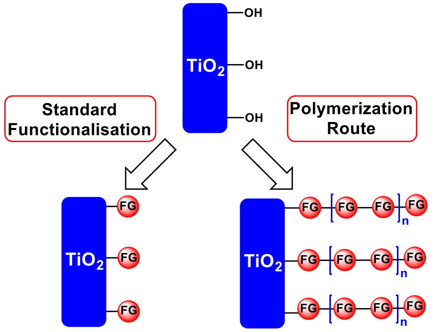
Multiply amount of functional groups

- ✓ Using SI-ATRP : surface-initiated atom transfer radical polymerization
- ✓ Different chemistries realized on tubular 5 nm TiO_2 membranes

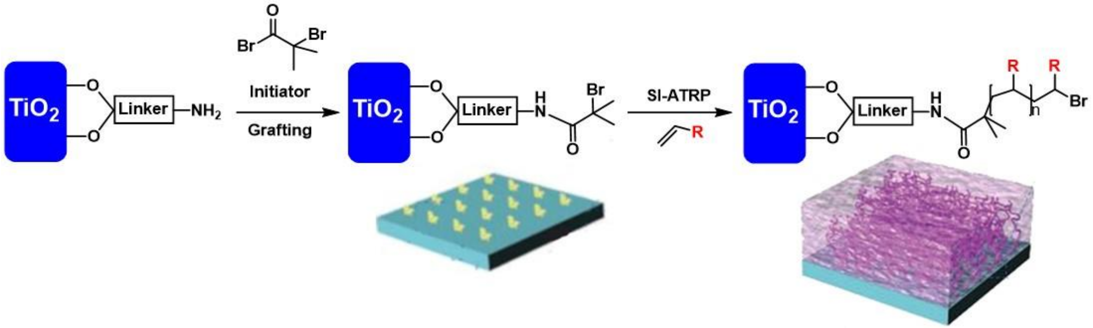


PMMA : Polymethylmethacrylate   PS : Polystyrene   PAEM : Poly(2-aminoethyl methacrylate)

- ✓ PS NF membrane : R (DPA, 330 Da) in toluene = 91%



SI-ATRP technique



WO2020/016068A1

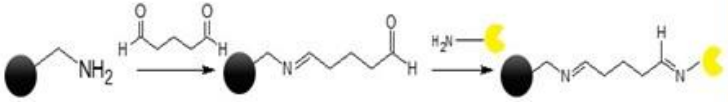
Further exploration of possibilities

EasiChem

MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

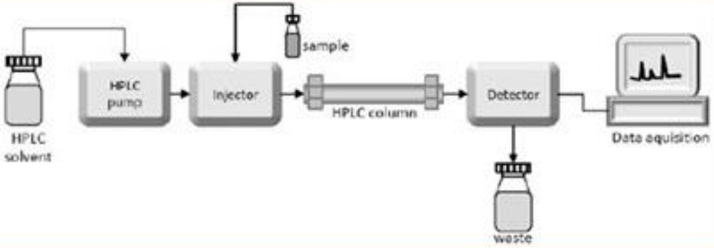
Enzyme immobilization

- ✓ On PAEM modified TiO_2 powder (+ membranes)
- ✓ Covalent binding enzyme via glutaraldehyde
- ✓ Esterification activity : 645 ester/g compared to 891 ester/g for beads with higher surface area



Chromatography

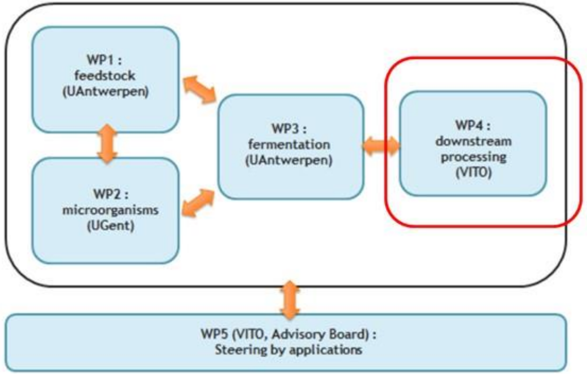
- ✓ ZirChrom TiO_2 + C12 powder
- ✓ Partition coefficients: K(MPPA) = 92 > K(IPA) = 8
- ✓ Comparable to ME results



Further exploration of possibilities

Waste Oil to Long-chain Di-Carboxylic Acids = WODCA project

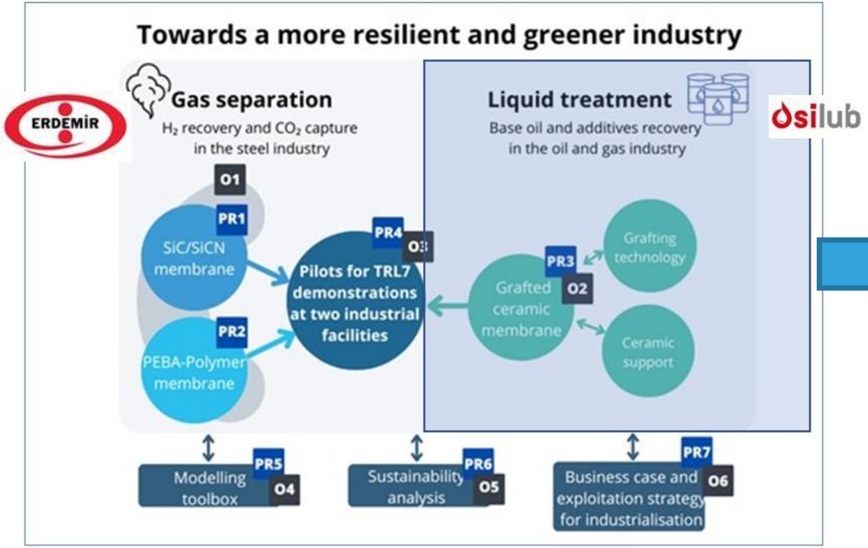
Goal DSP
1. Product recovery
2. Product concentration / purification
3. Avoid product inhibition (ISPR)

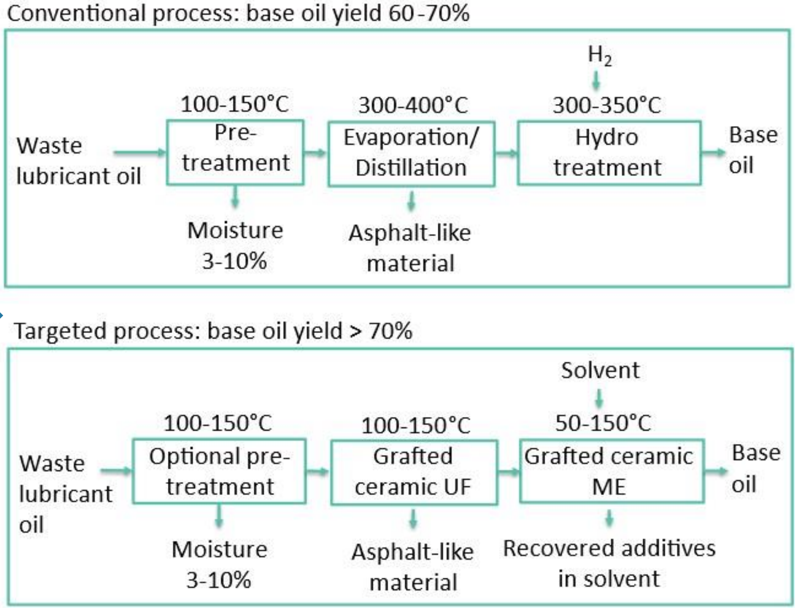


Further exploration of possibilities

CUstomised MEmbranes for green and Resilient Industries

CUMERI





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- EasiChem (BE)
- Innomem (EU)
- MacBeth (EU)
- WODCA (BE)
- CUMERI (BE)
- …

Thank you for your attention !