

Final MBR-Network Workshop

**“Salient outcomes of the European R&D
projects on MBR technology”**

Presentation handouts

31 March – 1 April, Berlin 2009 (Germany)



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6. DEVELOPMENT AND APPLICATION OF A PROTEINS AND POLYSACCHARIDES SENSOR FOR ON-LINE FOULING CONTROL IN MEMBRANE BIOREACTORS

*R. Mehrez, M. Ernst, V. Iversen, A. Drews, M.
Kraume, M. Jekel*

Development and application of a proteins and polysaccharides sensor for on-line fouling control in membrane bioreactors

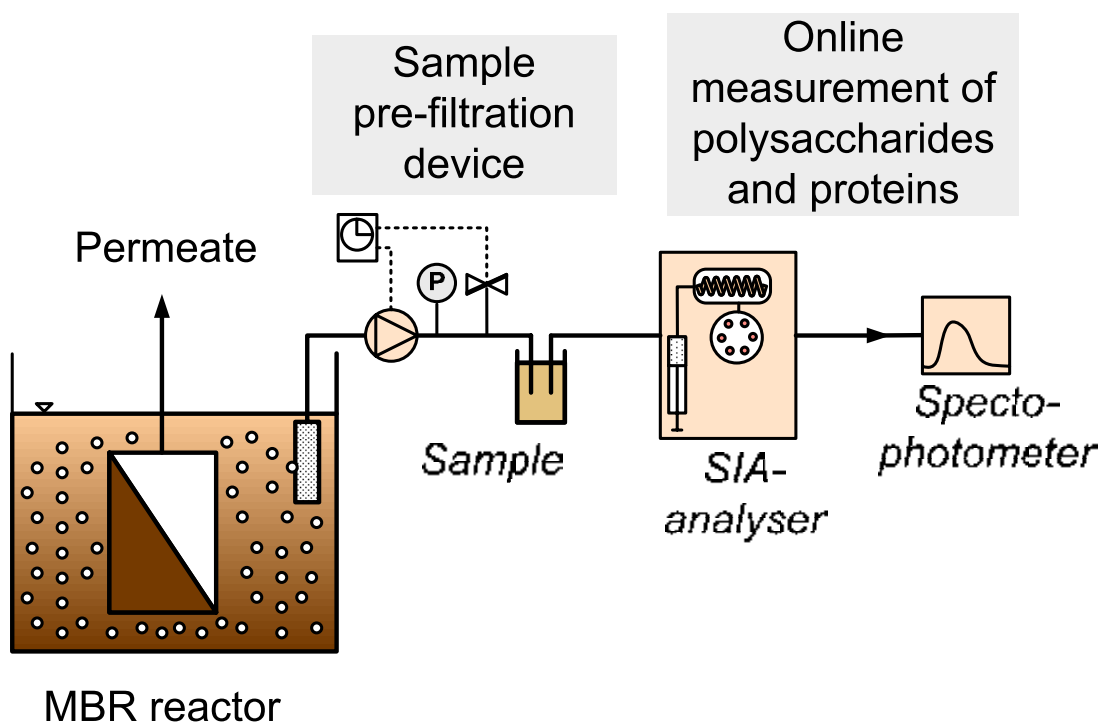
R. Mehrez*, M. Ernst**, V. Iversen***, A. Drews***, M. Kraume***, M. Jekel*

Technische Universität Berlin,
* Chair of Water Quality Control
** Centre for Water in Urban Areas
*** Chair of Chemical Engineering

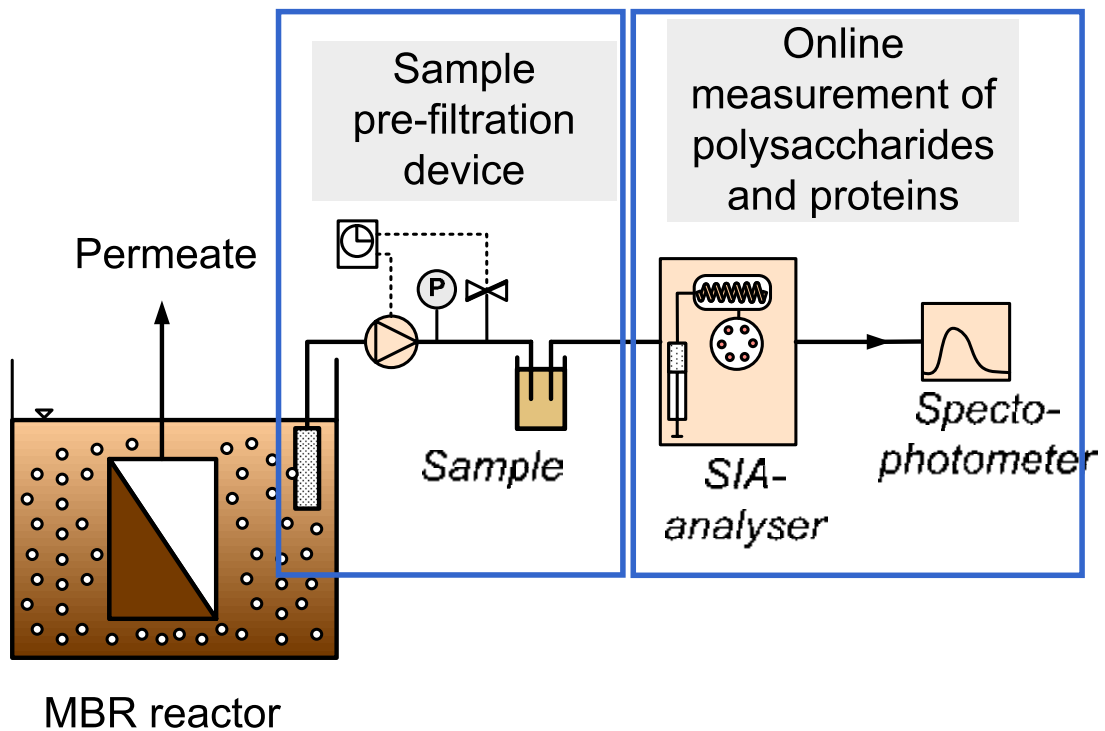
*Final Workshop MBR-Network
Membrane Technology for Wastewater Treatment
Wasser Berlin, 31st March - 1st April 2009*



On-line sensor



On-line sensor



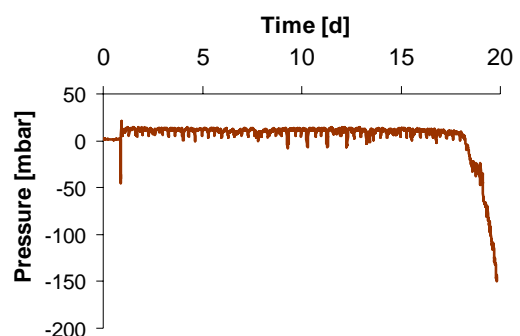
Sample pre-filtration device



- ▶ Filter: stainless steel, $\phi 1\mu\text{m}$, $\sim 50\text{ cm}^2$
- ▶ Filtration mode out / in
- ▶ Filtration/Relaxation: 10min/2min
- ▶ Comparable separation to manual sludge sample filtration (paper filter)

- ▶ Filter run-time $\sim 10\text{-}20$ days
- ▶ Sample volume 45-60 mL/h (measurement each 3 – 4h)

More details → see poster



Photometric methods

PROCEDURE

SAMPLE

+ REAGENT 1

MIXING

+ REAGENT 2

MIXING

MEASUREMENT OF ABSORPTION

PROTEINS

Modified method of Lowry

conc.: 15-30 mg/L

+ alkaline copper solution
with chelating agent (NTA)

+ Folin-Ciocalteu-phenol

750 nm



POLYSACCHARIDES

Method of Dubois

conc.: 5-20 mg/L

+ phenol solution

+ H₂SO₄ (97%)

490 nm

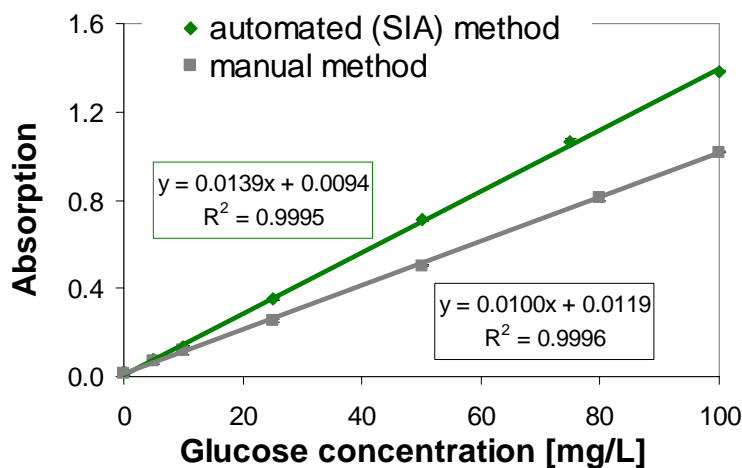


SIA - Sequential Injection Analysis



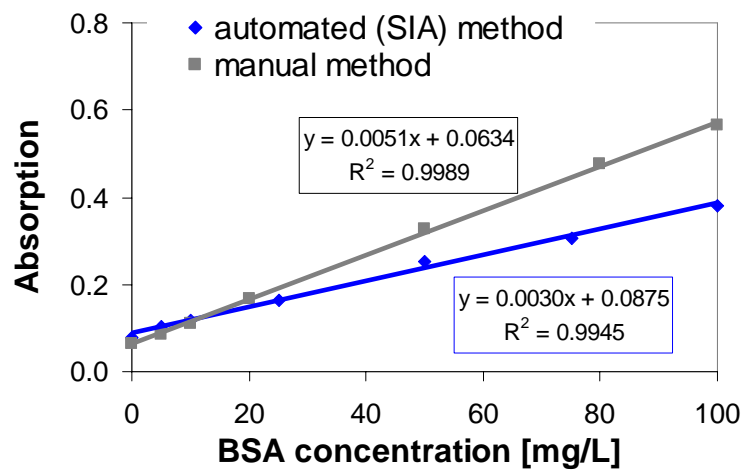
MEASUREMENTS WITH STANDARD SOLUTIONS

Polysaccharides - Calibration curve



| | SIA | Manual |
|---|------------|---------------|
| Detection limit | 0.9 mg/L | 1.2 mg/L |
| Quantification limit | 3.4 mg/L | 4.2 mg/L |
| Measurement error (SD) (glucose 10 mg/L) | ± 0.5 mg/L | ± 0.5 mg/L |

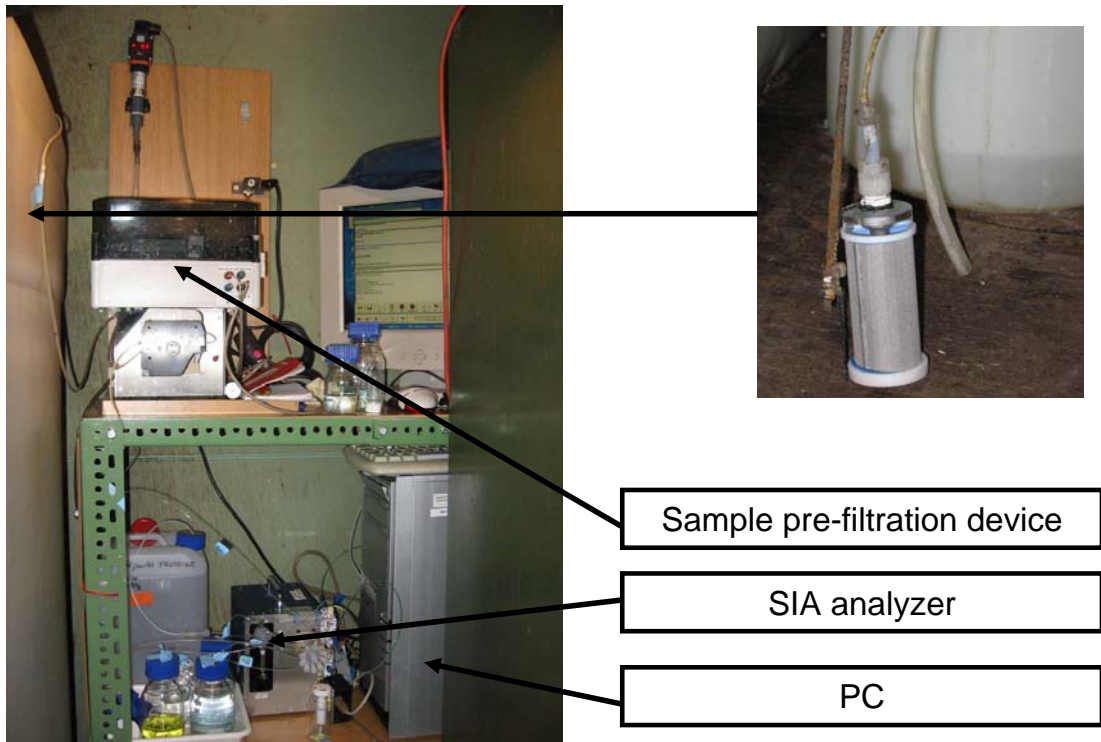
Proteins - Calibration curve



| | SIA | Manual |
|---------------------------------------|------------|------------|
| Detection limit | 3.9 mg/L | 1.0 mg/L |
| Quantification limit | 13.5 mg/L | 3.3 mg/L |
| Measurement error (SD) BSA 20 mg/L | ± 2.0 mg/L | ± 0.2 mg/L |

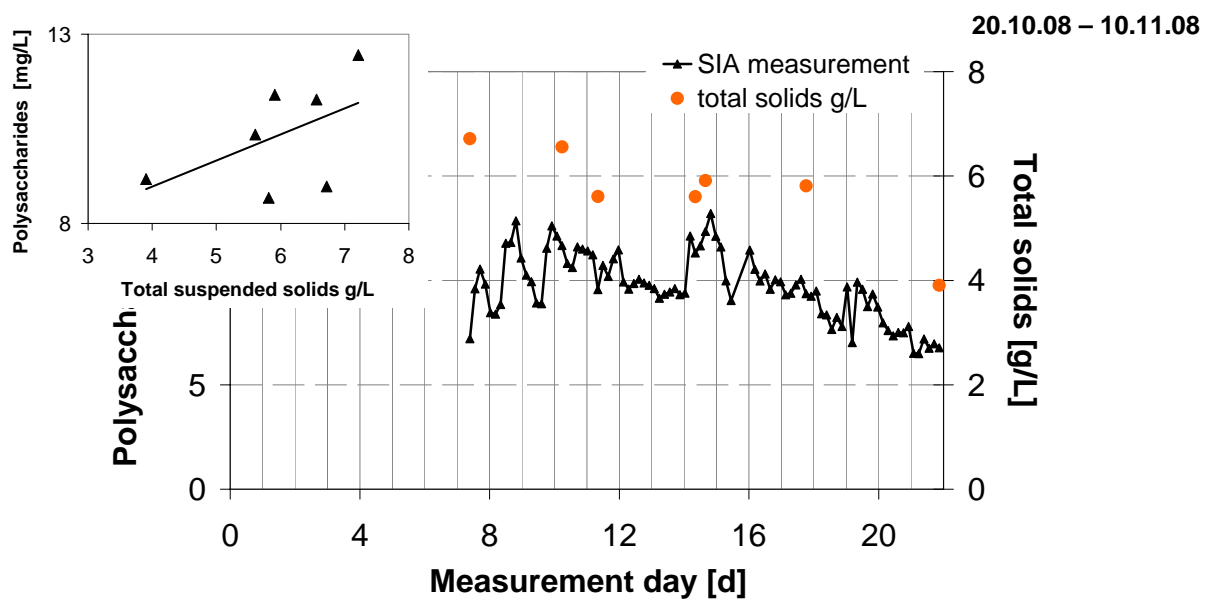
MEASUREMENTS ON THE PILOT PLANT

Sensor on the pilot plant



www.mbr-network.eu

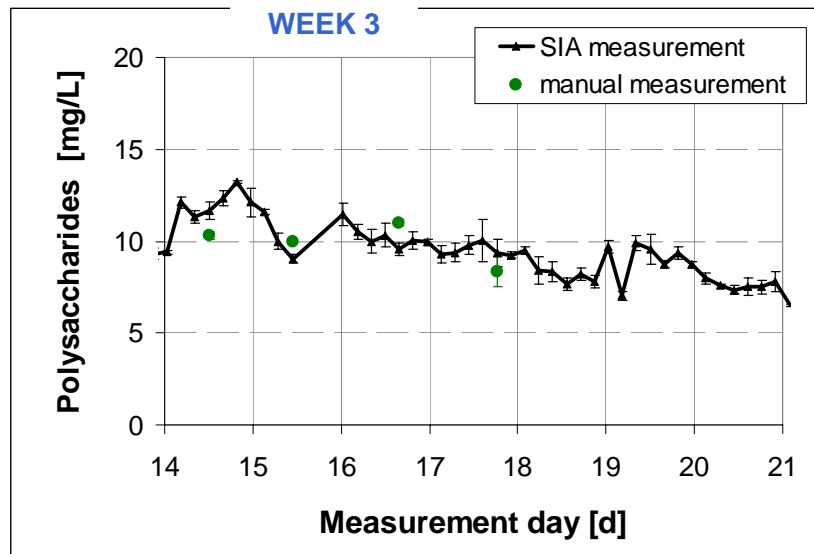
Polysaccharides – Pilot plant



- ▶ High variation of PS during 3 weeks of operation
- ▶ Decrease of PS correlates with the concentration of TS

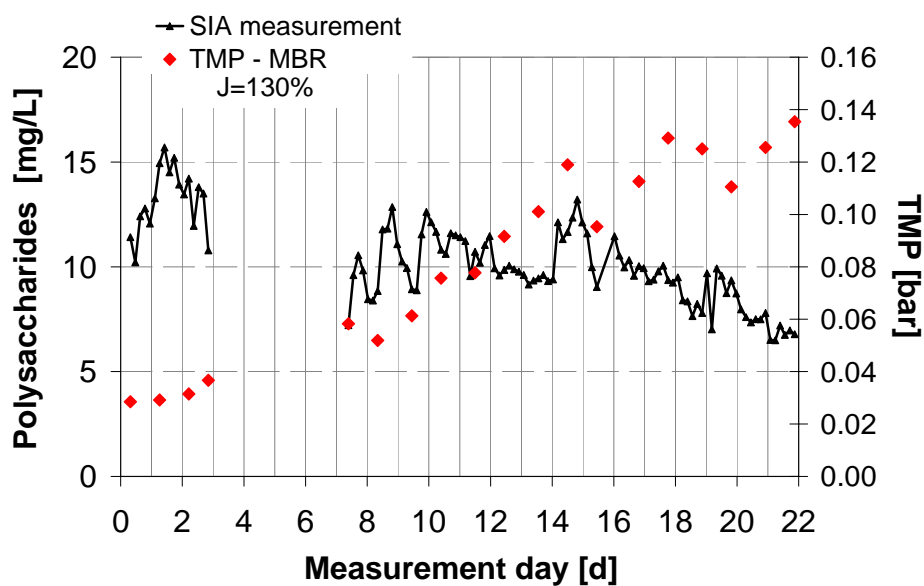
www.mbr-network.eu

Polysaccharides – Daily variation



- ▶ Daily PS fluctuation (~1-2 mg/L during day) but no characteristic weekly profile of PS concentration visible

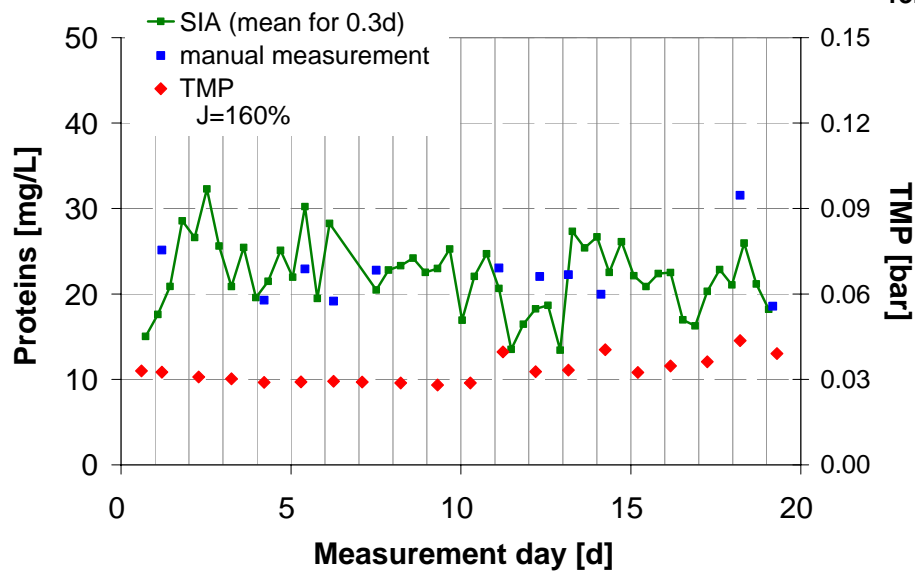
Polysaccharides versus TMP



- ▶ TMP increases during the monitoring time but not PS

Proteins – Pilot plant

13.11.08 – 02.12.08



- ▶ PR concentration as mean for 8 h
- ▶ Variation of PR between ~13–30 mg/L
- ▶ No trend can be observed
- ▶ Stable TMP

Conclusions

On-line sensor for continuous photometric measurement of PS and PR was developed and tested in MBR pilot (Berlin, Mitte)

- **Automated method for PS** is suitable for monitoring in MBR
 - low LOD, small measurement error and good robustness
 - variation of PS can be recognised due to comprehensive data set
 - Aggressive reagents (conc. H₂SO₄) requires caution and frequent maintenance



Conclusions

- **Automated method for PR**
 - monitoring of trends especially at high PR concentration (calculation of 8h mean)
 - sensitive measurement in MBR limited due to relative high LOQ and measurement error
 - **potential for method optimisation**



Currently no positive correlation of measured PS / PR vs. TMP

Acknowledgement

AMEDEUS is a research project supported by the European Commission under the Sixth Framework Programme (Priority “Global Change and Ecosystems”)



Contract No. 018328 - AMEDEUS
Duration: 01/10/05 - 30/09/08
AMEDEUS is part of the MBR-NETWORK Cluster



More info: www.mbr-network.eu

7. THE EUROPEAN MBR TOUR OF THE DELFT FILTRATION CHARACTERISATION METHOD

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Krzeminski*

The European MBR tour of the Delft Filtration Characterisation method

Jaap H.J.M. van der Graaf, Arjen F. van Nieuwenhijzen, Stefan Geilvoet, Adrien A.
Moreau, Maria Lousada Ferreira, Pawel Krzeminski

(Final MBR-Network workshop, Berlin, 31st March 2009)



Content

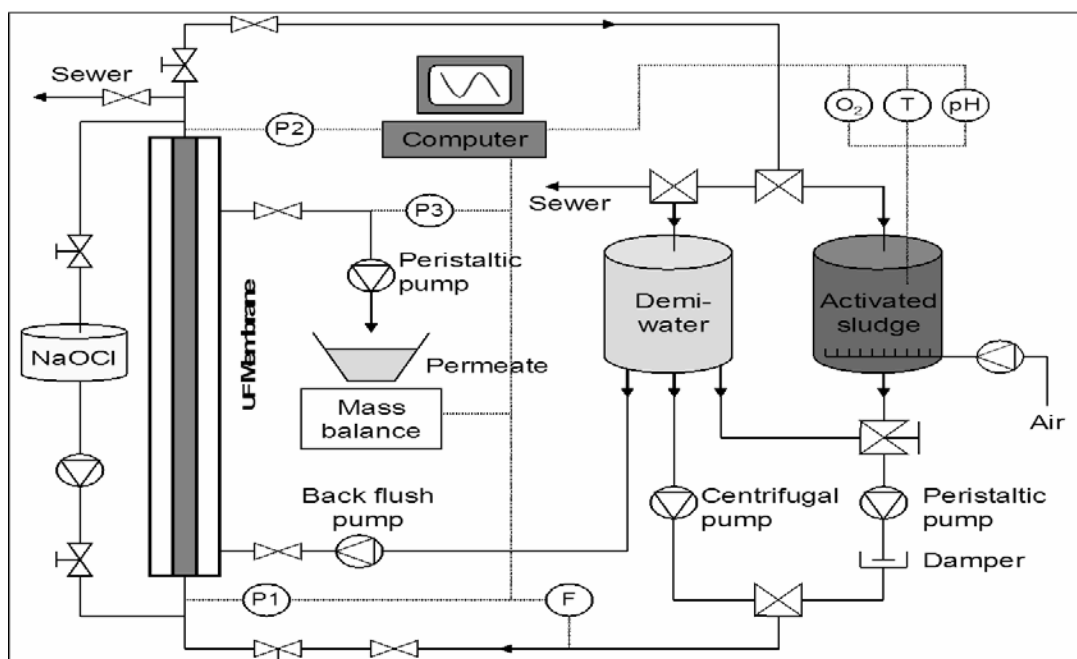
- ▶ MBR sludge tour
- ▶ Delft Filtration Characterisation method
- ▶ comparison of MBR's
- ▶ sludge instability
- ▶ sludge concentration
- ▶ temperature
- ▶ filterability model

MBR test sites



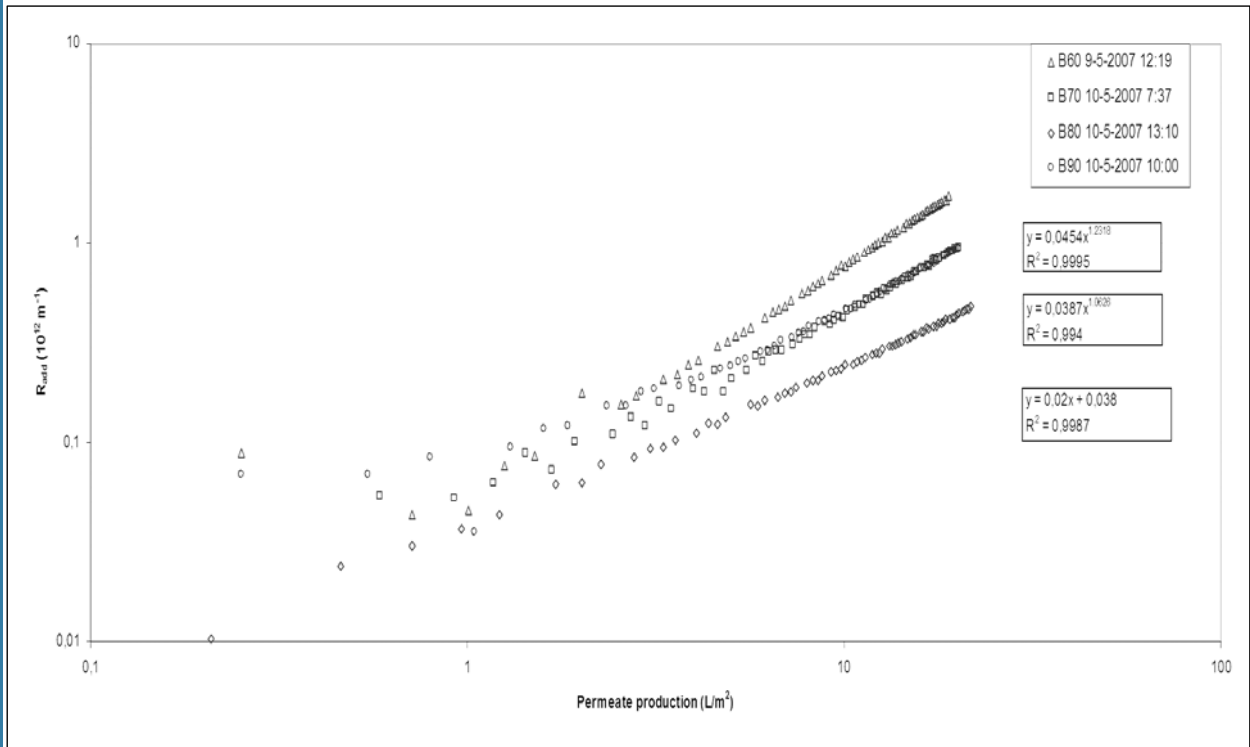
www.mbr-network.eu

The Delft Filtration Characterisation installation

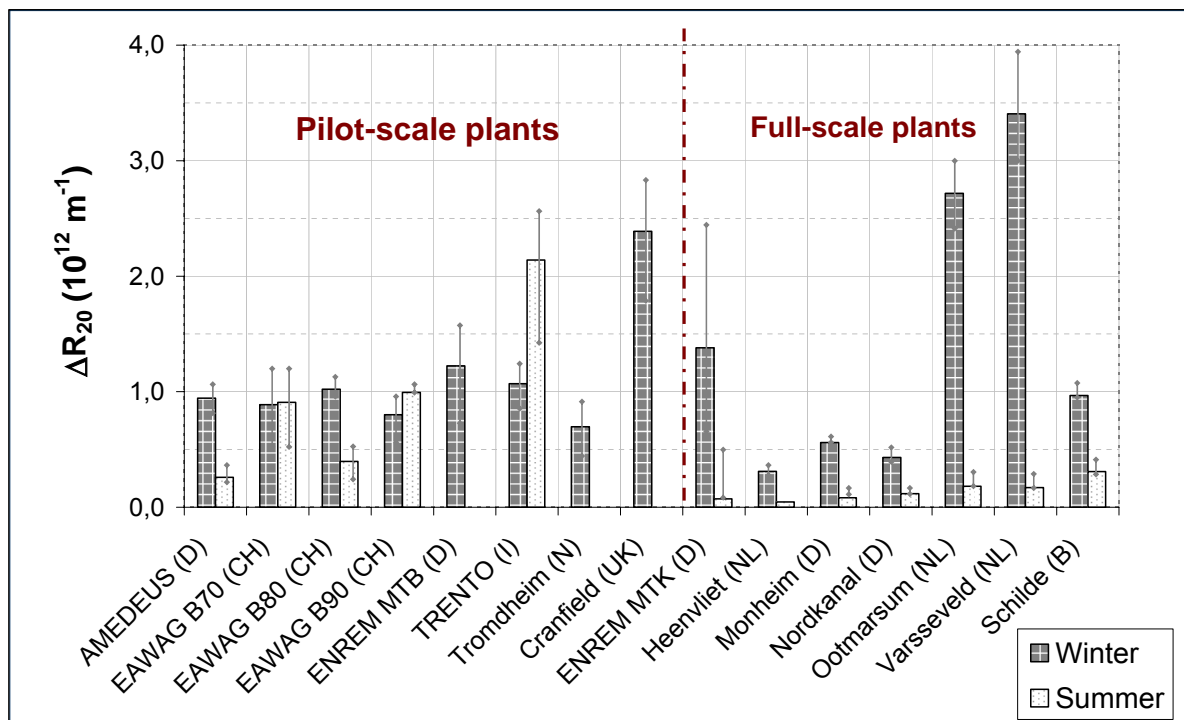


www.mbr-network.eu

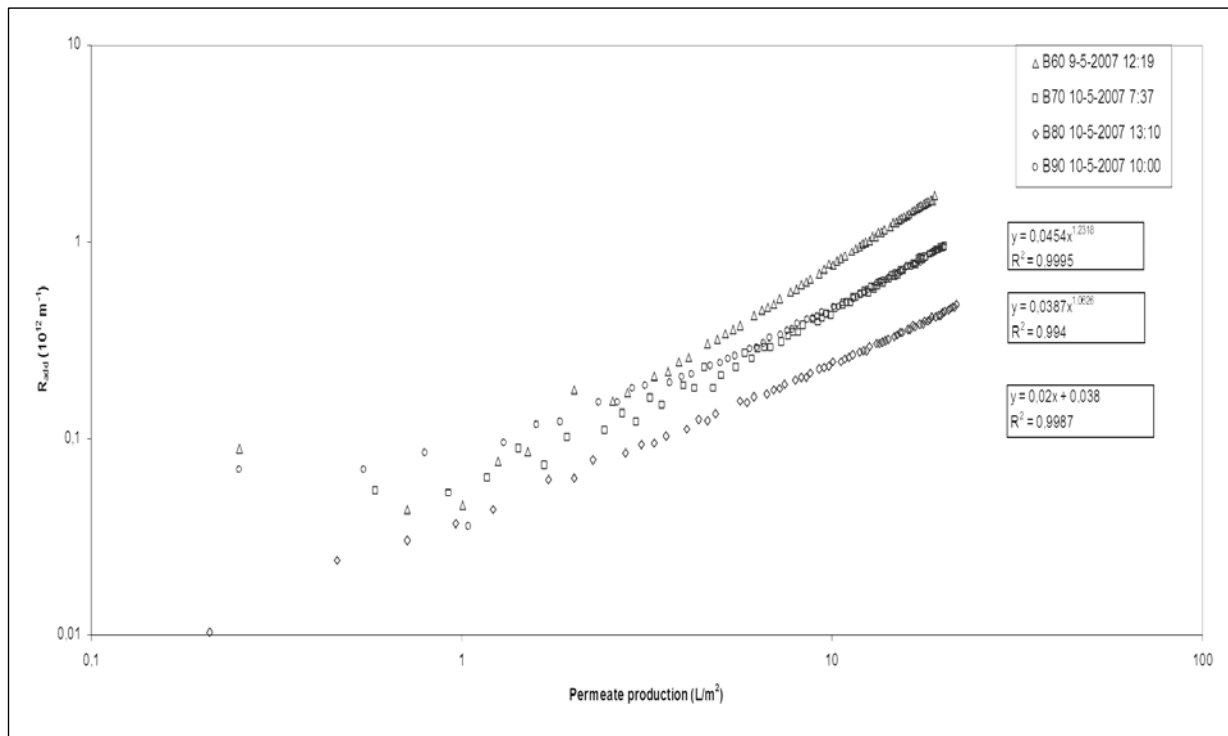
Filtration curves



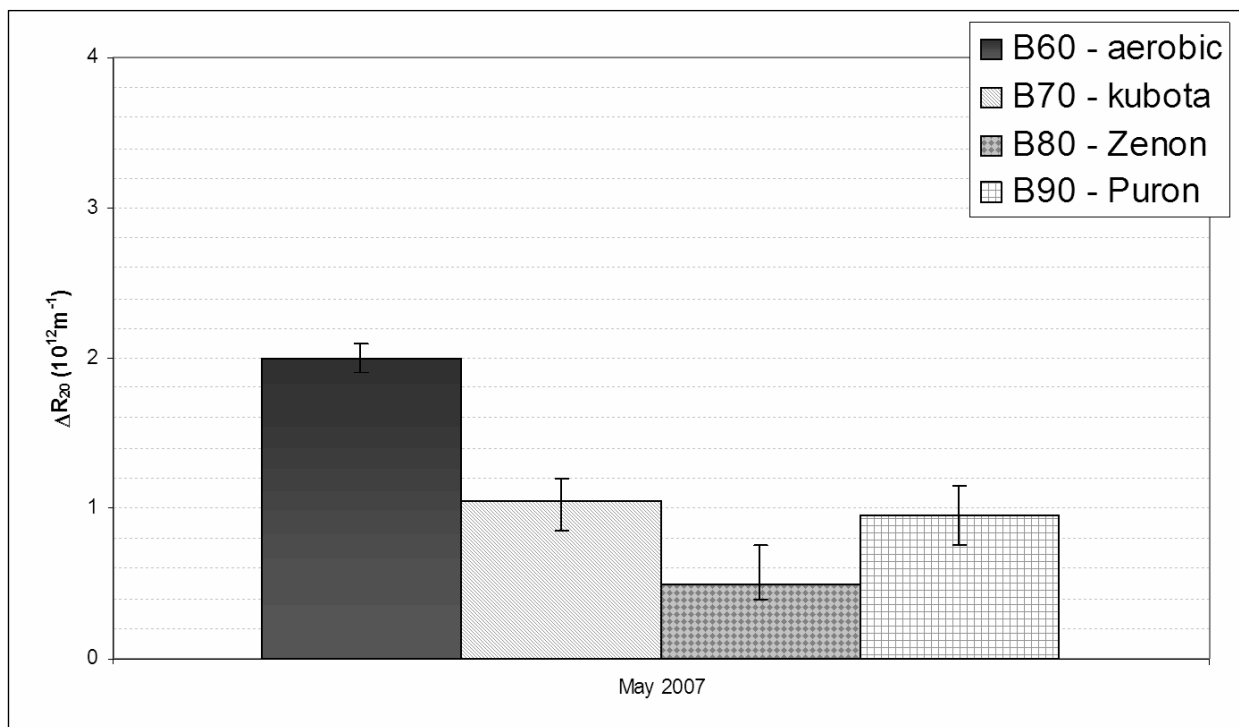
ΔR_{20} values for all the MBR sites



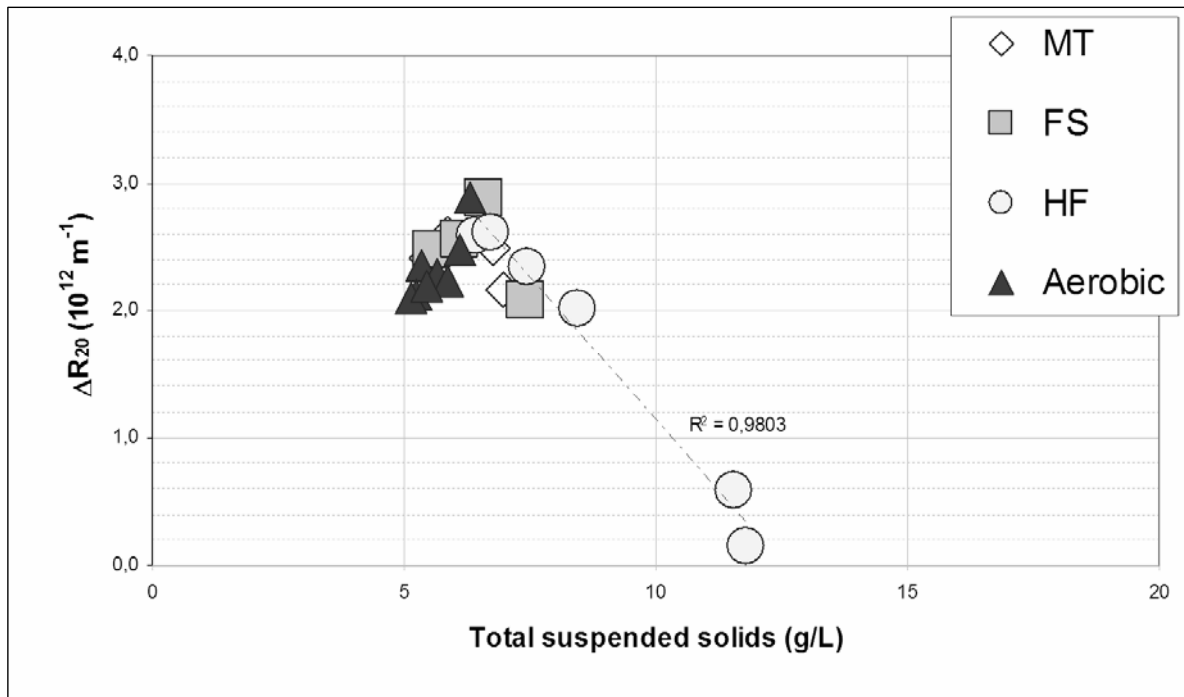
Eawag test site



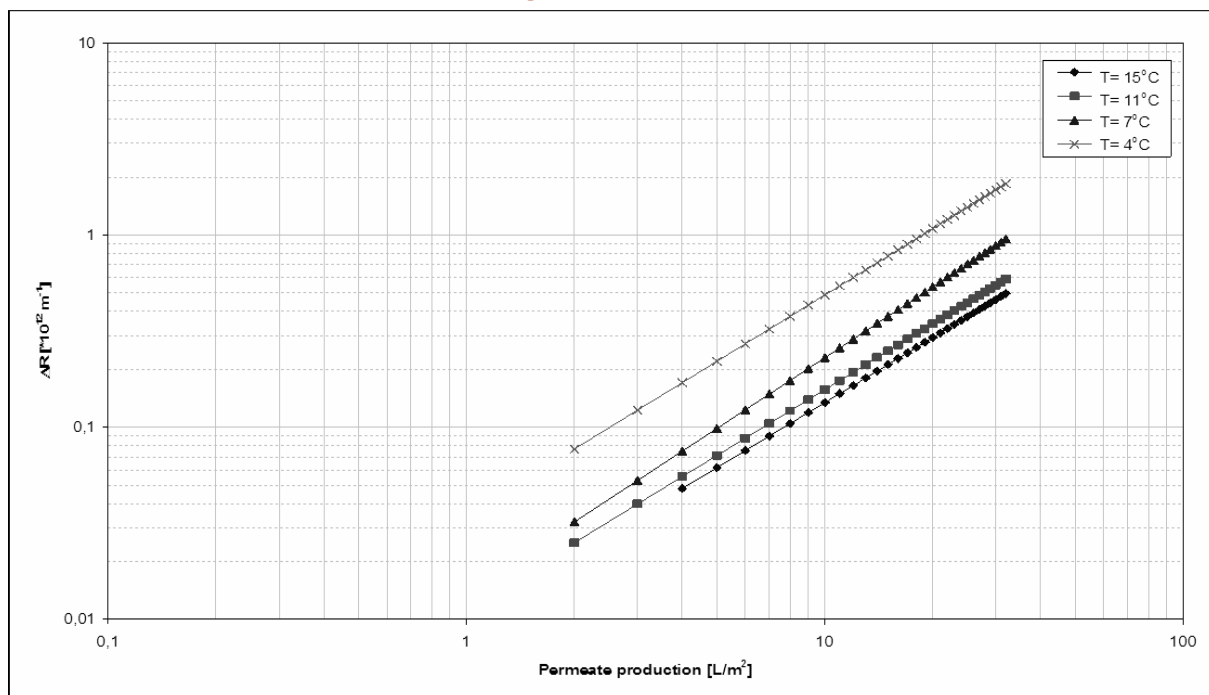
Eawag test site



Influence of the sludge concentration (Cranfield site)



Change of temperature



Filterability model

What is the reason for good or bad filtration characteristics?

- ▶ EPS?
- ▶ SMP?
- ▶ Proteins?
- ▶ Polysaccharides?
- ▶?

Filterability model

Strong relation between filterability and

- ▶ submicron particles (0.1 - 1.0 μm) in the free-water phase
- ▶ total number => total volume / mass
- ▶ species => compressibility

- ▶ after negative temperature shock => increase SP
- ▶ higher temperatures => lower SP
- ▶ with high sludge conc (>10g/L) => decrease of SP
- ▶ sludge under stress => increase of SP

=====> flocculation and deflocculation

Acknowledgement

EUROMBRA and MBR-TRAIN are research projects supported by the European Commission under the Sixth Framework Programme (Priority “Global Change and Ecosystems”)



Contract No. 018480 - EUROMBRA

Duration: 01/10/05 – 31/05/09

EUROMBRA is part of the MBR-NETWORK Cluster



MARIE CURIE ACTIONS

More info: www.mbr-network.eu

www.mbr-network.eu

8. THE QUEST FOR INDICATORS OF MEMBRANE FOULING IN MEMBRANE BIOREACTOR SYSTEMS

*T. de la Torre, J. Stueber, V. Iversen, A. Drews, B.
Lesjean*

The Quest for Indicators of Membrane Fouling in Membrane Bioreactor Systems

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A. Drews**,***, B. Lesjean*, M. Kraume**,
F. Meng**

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Objective

- ▶ To find a universal indicator of fouling propensity of MBR sludge for plant operators
 - Easy
 - Quick
 - Cheap

How to find the fouling indicator?

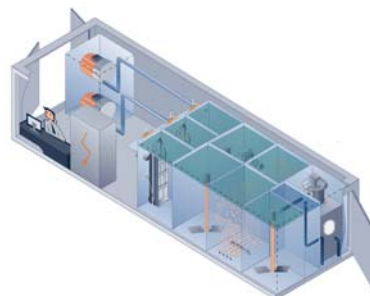
Long-term monitoring campaign of several pilot to full scale MBR

- ▶ Measure filterability
- ▶ Measure parameters in activated sludge

→ Find correlations

MBR units

| INVESTIGATED MBR UNITS | | SRT (d) | MLSS (approx.) | Wastewater influent | Membrane | Reactor |
|---------------------------|------|------------|-------------------|------------------------|--------------------------|----------------|
| | | | (g/L) | | | m ³ |
| Pilot plant | MBR1 | 12 | 9-10 | Municipal | 22 m ² A3 | 1.5 |
| | MBR2 | 12 | 7-13 | Municipal | 22 m ² A3 | 1.5 |
| Demonstration plant | MBR3 | 25 | 10-23 | Domestic | 31 m ² A3 | 10 |
| | MBR4 | 35 | 9-11 | Domestic | 20 m ² Kubota | 5 |



Monitoring program

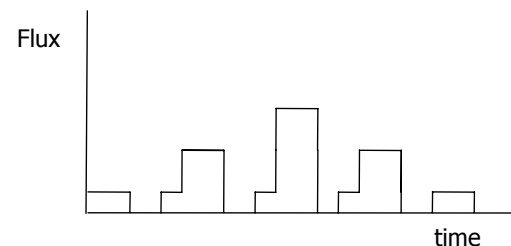
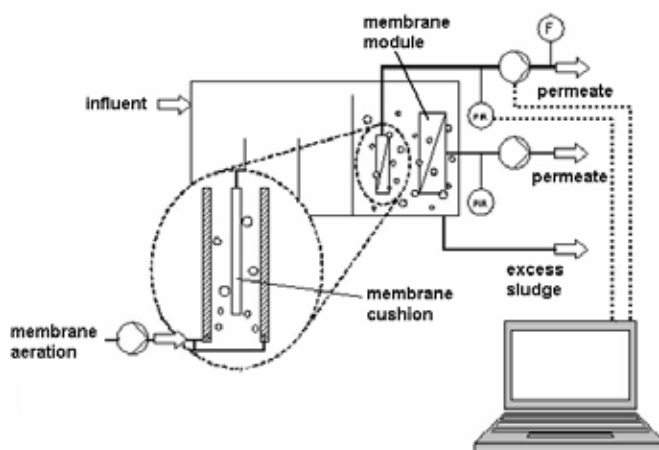
Monitored Parameters

- Quick-Filterability assessment:
 - Time to filter (TTF)
 - Capillary suction time (CST)
 - Sludge Volume Index (SVI)
- Bound and soluble EPS (SMP)
 - Polysaccharides
 - Proteins
 - Transparent exopolymer particles
- Temperature
- pH
- Nitrate
- Total solids
- Organic total solids
- COD....

On all 4 MBR units
2-4 samples / month
10 months campaign
Some parameters in fractions

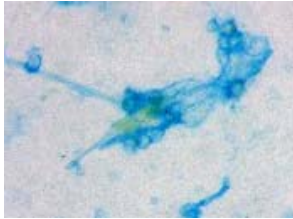
- 10 μm
- 2 μm
- 0.2 μm

in-situ test cell BFM (Berlin Filtration Method)



- Critical flux measurements with standard protocol
- TMP Temperature corrected using $TMP_{corrected} = TMP * \eta_{20^{\circ}\text{C}} / \eta_{act}$

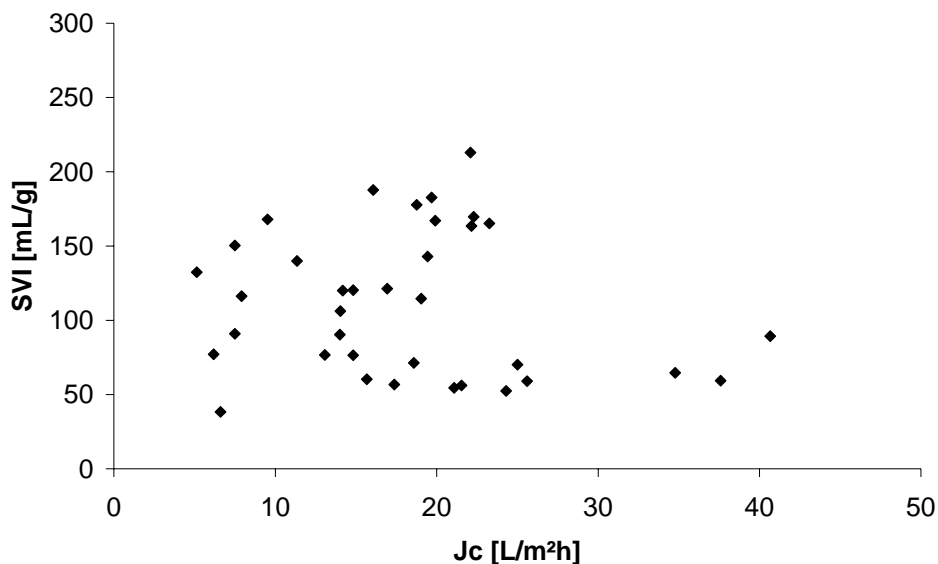
Transparent Exopolymer Particles (TEP)



- Mostly acid mucopolysaccharides = sticky polysaccharides (e.g. xanthan gum, alginate,..)
- Relationship with biofouling in RO (Berman and Hoenberg, 2005)
- No study of TEP in wastewater treatment to date
- Easy to measure

Results – Correlations against J_c Univariable Analysis

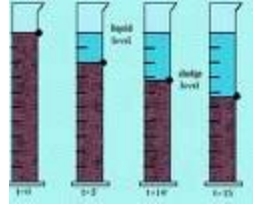
Example Sludge Volume Index (SVI): no correlation at all



Results – Correlations against J_c Univariable Analysis

▶ Other typical parameters...

- TTF
- CST
- TS



→ Only TTF was relevant for MBR3 (high TS and COD)

- ▶ No distinction between fractions (10 μm , 2 μm , 0.2 μm)

Results – Correlations against J_c Univariable Analysis

- ▶ Best correlations against J_c :

| | |
|--------------------|----------------------------|
| bTEP/TEP | $r=0.84$ |
| PS 2 μm | $r=0.69$ |
| TEP rejection | $r=0.68$ |

- ▶ bTEP/TEP associated to flocculation-deflocculation processes
- ▶ The filterability of the activated sludge cannot be explained with one variable (no universal indicator)

Results – Correlations against Jc Multivariable Analysis

Best fit for all units against Jc in situ

$$R^2 = 0.95$$

↑ bTEP ↑ T ↓ TEP ↑ NO₃ → ↑ Jc

| Parameter | Beta coefficient |
|-----------------|------------------|
| NO ₃ | 0.488 |
| TEP | -0.596 |
| T | 0.566 |
| bTEP | 0.812 |

(relative influence
of the parameter on Jc)

- NO₃ → important beyond its influence on SMP
- TEP → more importance than PS
- T → relevant even with T corrected Jc
- bTEP → favoures flocculation

Conclusions

- ▶ 95% of the variability of the Jc could be explained by the variation in 4 parameters in 4 MBR units for 10 months

| | |
|-----------------|-----|
| bTEP | TEP |
| NO ₃ | T |

Easy to monitor MBR plant operation

- ▶ TEP --> New important parameter introduced in wastewater investigations (fouling, flocculation,..)
- ▶ TTF and other "classical" parameters not so relevant

The filterability of activated sludge cannot be explained with one variable (no universal indicator)

.....But with 4!

Acknowledgement

MBR-TRAIN is a Marie Curie Host Fellowship for Early Stage Research Training supported by the European Commission under the 6th Framework Programme (Structuring the European Research Area - Marie Curie Actions)



Microdyn-Nadir - membrane supply

Berliner Wasser Betriebe – ENREM unit

Moritz, Guillem, Dhijan, Björn, Andrew, ... for their work

Hauke and Bernardo for their help



MARIE CURIE ACTIONS

Contract No. MEST-CT-2005-021050

Duration: 01/01/06 - 31/12/09

MBR-TRAIN is part of the MBR-NETWORK Cluster

More info: www.mbr-network.eu and www.mbr-train.org

9. NEW DEVELOPMENTS IN MEMBRANE BIOREACTORS CHARACTERISATION AND MONITORING

*C. F. Galinha, G. Carvalho, C. Portugal, R.
Oliveira, M. T. B. Crespo, M. A. M. Reis, J. G.
Crespo*

NEW DEVELOPMENTS IN MEMBRANE BIOREACTORS CHARACTERISATION AND MONITORING

Claudia F. Galinha, Gilda Carvalho, Ana F. Silva, Carla Portugal, Rui Oliveira, Maria T. B. Crespo, Maria A. M. Reis, João G. Crespo

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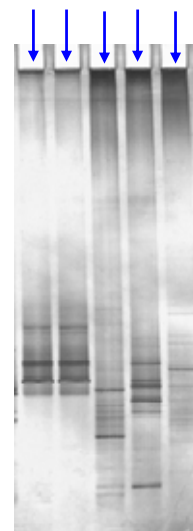
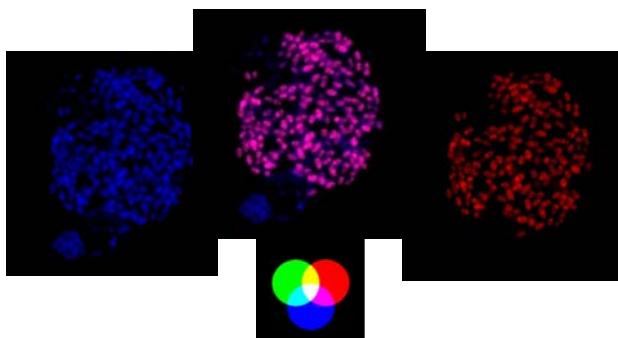


Membrane Bioreactor Characterisation and Monitoring

- ▶ Microbial Population Analysis
- ▶ 2D Fluorescence Monitoring
- ▶ Multivariate Statistical Analysis using Fluorescence Monitoring
- ▶ Hybrid Modelling Approaches

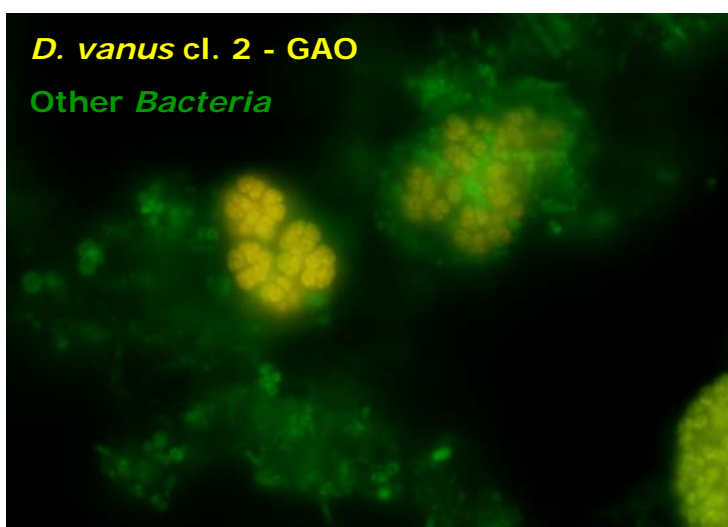
Microbial Population Analysis

- ▶ FISH (Fluorescence *in situ* hybridisation)
 - Analysis (quantification) of specific microbial groups

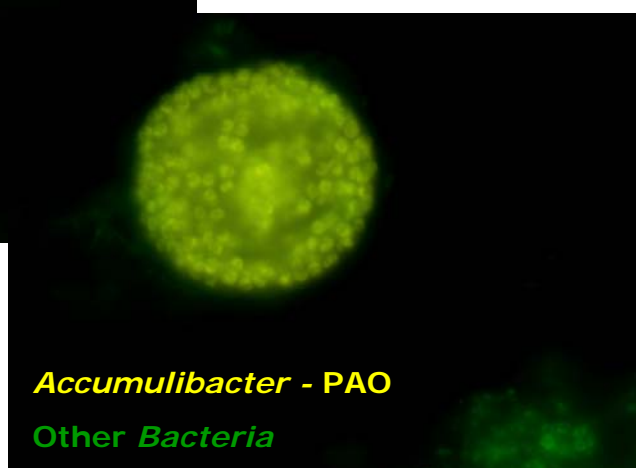


- ▶ DGGE (Denaturing gradient gel electrophoresis)
 - Profiling of microbial population structure
 - Diversity

FISH Results

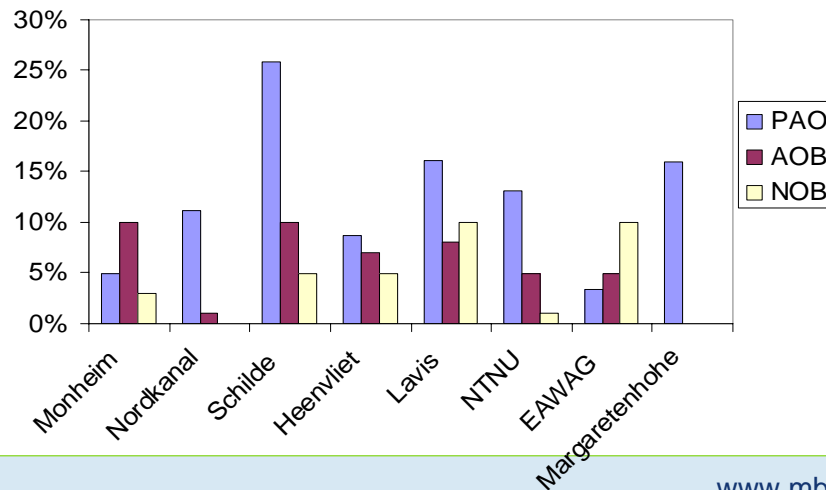


P-removal related
bacteria in Lavis MBR
pilot-plant, Trento



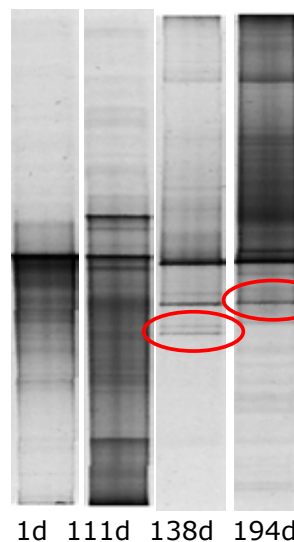
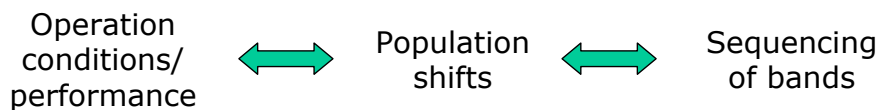
FISH Results

- ▶ Microbial community composition
 - General phylogenetic groups (*Alpha-, Beta-, Gamma-Proteobacteria*, etc.): **dominant phyla**
 - Specific bacterial populations (ammonia oxidising bacteria - AOB, polyphosphate accumulating organisms - PAO, etc.): **correlation with plant performance**



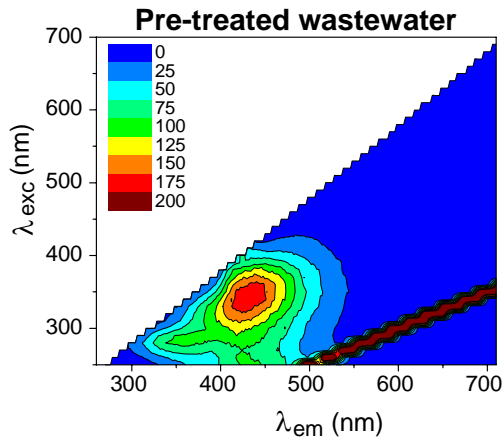
DGGE Results

- ▶ Identification of changes occurring in a community



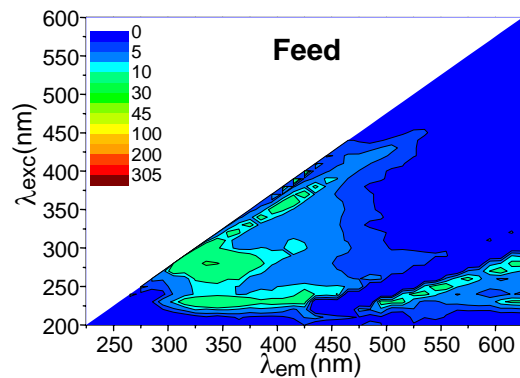
From band excising and sequencing it is possible to identify the corresponding bacteria

2D-Fluorescence Spectroscopy

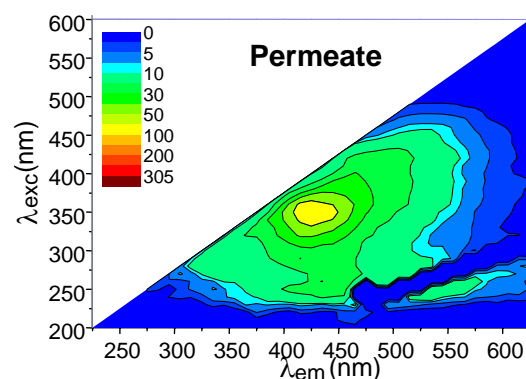
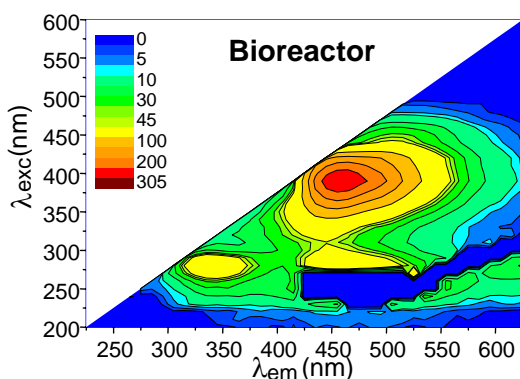


- ▶ Steady-state fluorescence
- ▶ Excitation wavelength, emission wavelength, intensity of emission
- ▶ Natural fluorophores: **proteins; some vitamins and cofactors**; substances with delocalised electrons such as **humic compounds**
- ▶ Quenching effects makes difficult a direct interpretation of fluorescence maps

2D-Fluorometry Monitoring of Membrane Bioreactors

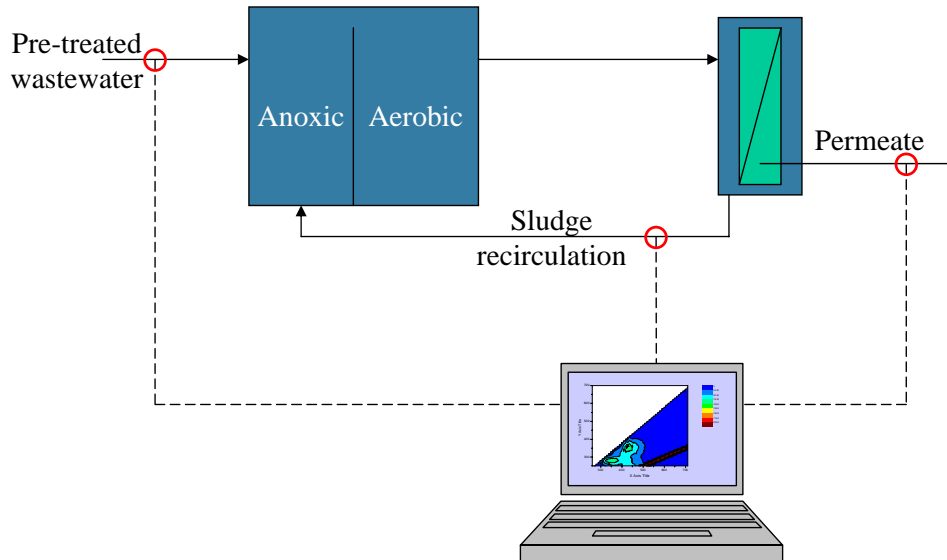


Fluorescence fingerprints reflect different compositions of feed stream, bioreactor media and permeate

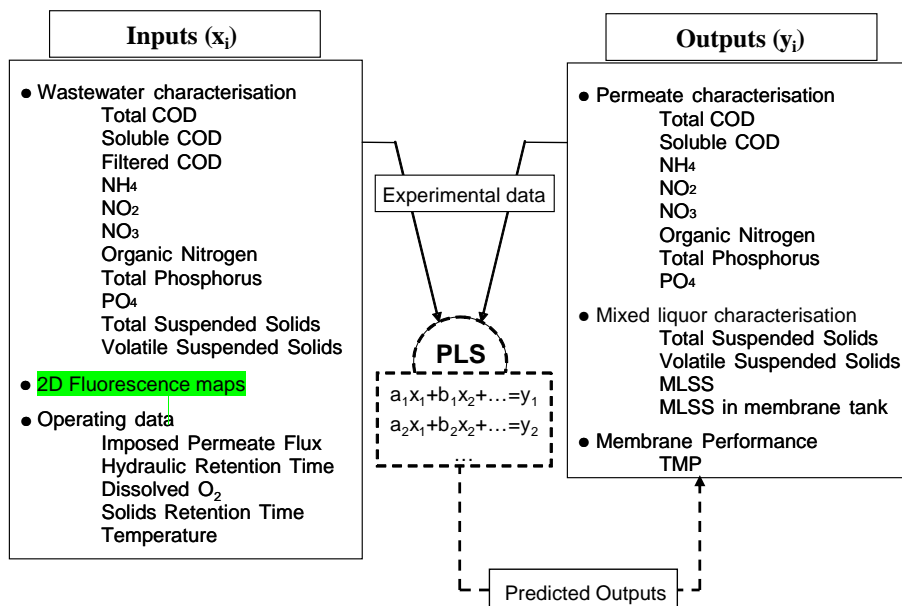


Experimental Setup

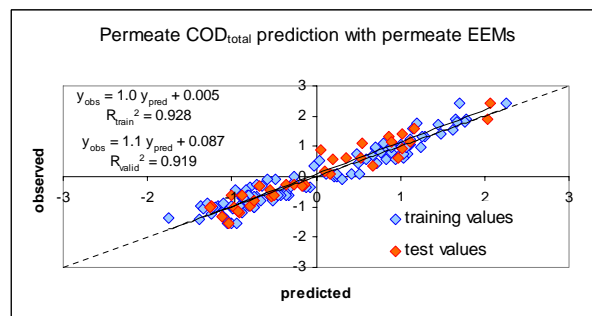
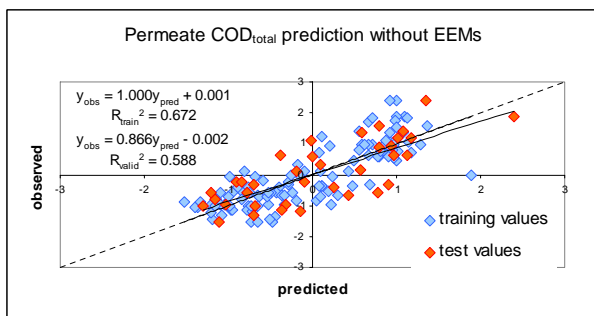
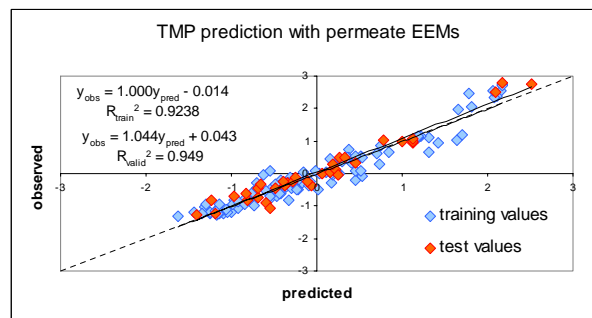
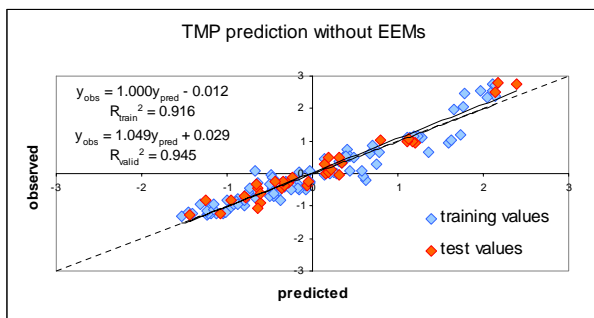
- ▶ Pilot MBR located in the Wastewater Treatment Plant of Lavis, Trento, Italy



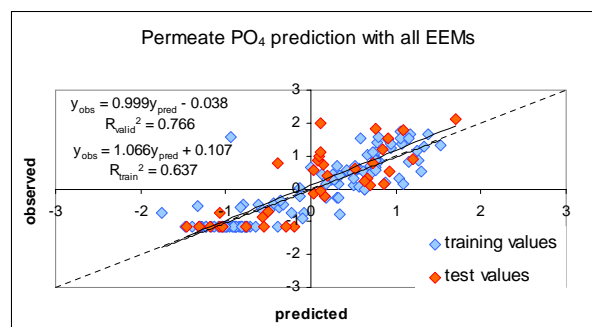
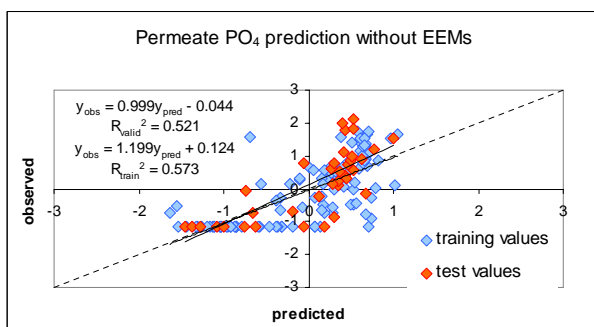
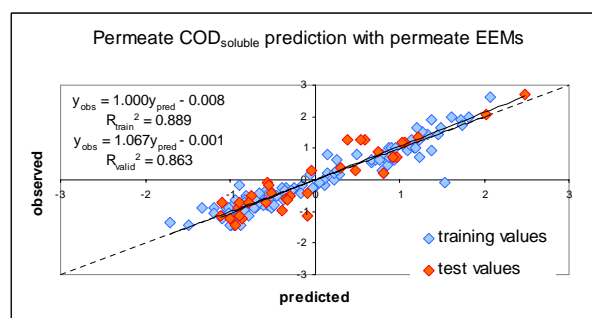
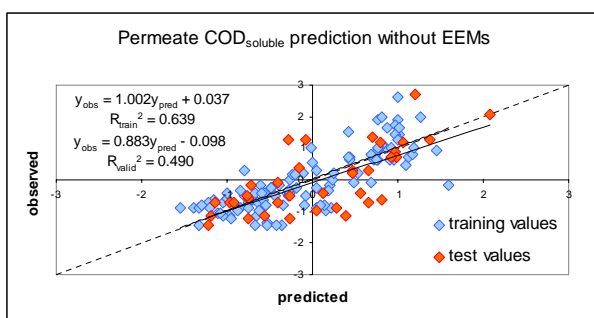
Development of Multivariate Statistical Models



Modelling Results



Modelling Results



Integration of Information in Hybrid Models

Mechanistic knowledge

Other sources of knowledge...

Bioreactor characterisation data:

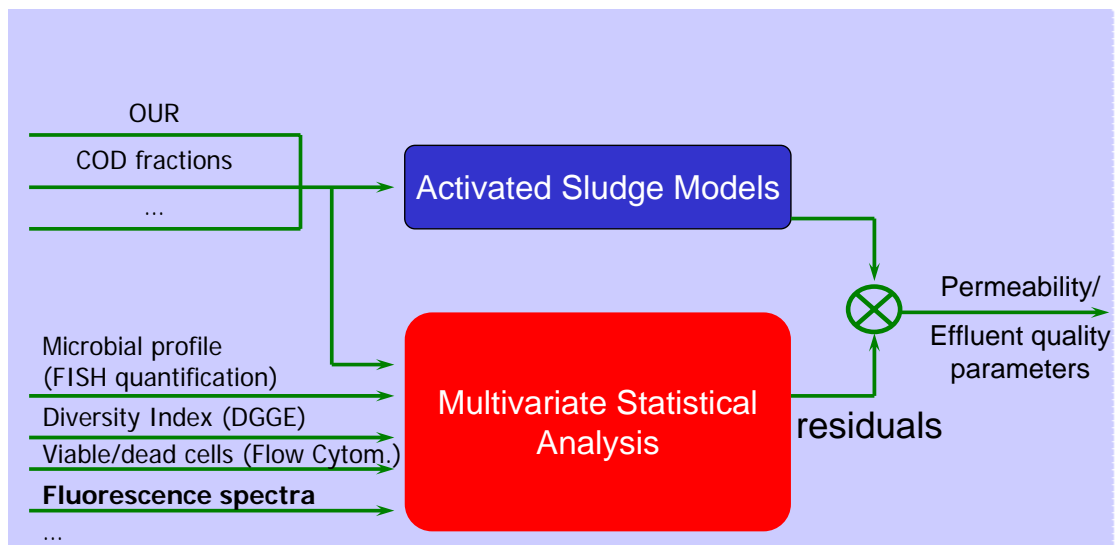
Spectra analysis
Image analysis

Modelling Challenges

1. Effective data mining

2. How to integrate different sources of knowledge in a model?

Hybrid Modelling Applied to MBRs





Acknowledgement

EUROMBRA is a research project supported by the European Commission under the Sixth Framework Programme (Priority "Global Change and Ecosystems")



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EUROMBRA is part of the MBR-NETWORK Cluster



More info: www.mbr-network.eu

10. FOULANT DYNAMICS ON SUPPORTED MEDIA MEMBRANE BIOREACTOR

R. Aryal, S. Vigneswaran, J. Kandasamy, A. Grasmick

FOULANT DYNAMICS ON SUPPORTED MEDIA MEMBRANE REACTOR

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**Université Montpellier II, CC005, Place Eugène Bataillon; 34095, Montpellier Cedex 05, France



UTS



NTNU
Innovation and Creativity



EUROMBRA

Introduction

CONTROLLING FOULING DURING MBR OPERATION REMAINS A CHALLENGE

Fouling due to biological conditions

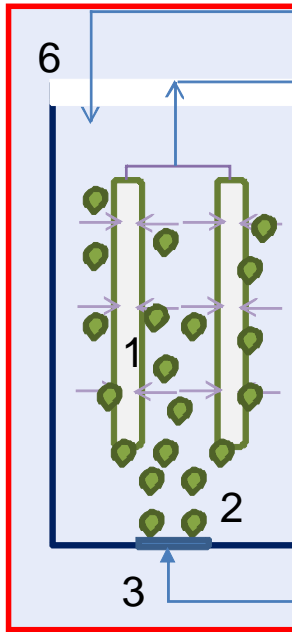
**Hydrodynamics
Membrane and
Module configuration**

Unsteady operating conditions
(flow input/HRT and organic loading)

Sludge Retention time, F/M ratio
(controls biomass characteristics)

OBJECTIVES : Identification of
(i) means to control reversible fouling and minimise energy consumption and
(ii) Irreversible foulant materials in SMBR



Study on effect of aeration and support medium in membrane fouling (with kaolin clay suspension)


Reactor volume: 12 L

Membrane: Flat sheet module (mean pore size 0.14 μm)

Aeration rate: 1-4 $\text{m}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$
Bubble size: 2-4 mm in diameter

Suspension of Kaolin :

- average particle size 4.1 μm
- $D[v, 0.1]$, $D[v, 0.5]$ and $D[v, 0.9]$ were 4.00, 4.46 and 5.10 μm , respectively
- particle concentration : 10 g/L

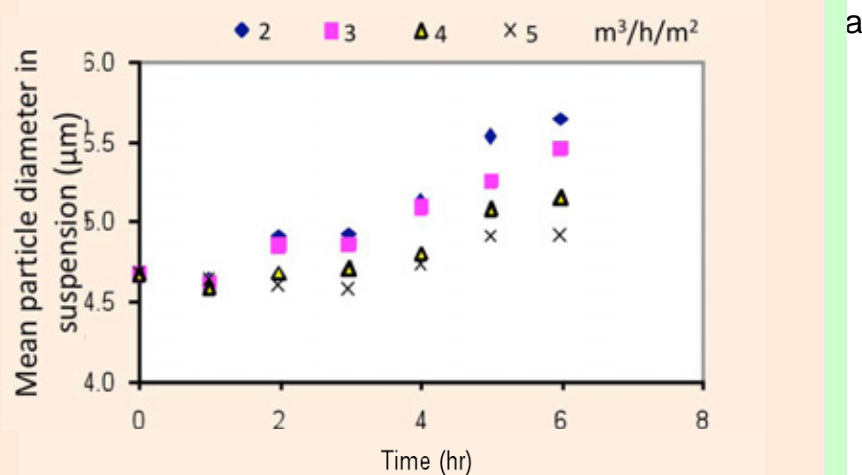
Procedure:

- No relaxation and no backwashing
- TMP measurement: Every 5 min interval (on line)

Effect of aeration on membrane fouling (TMP)

Increase of aeration decreased the fouling propensity

Reason: Aeration increases shear stress on membrane surface that helps scouring the surface

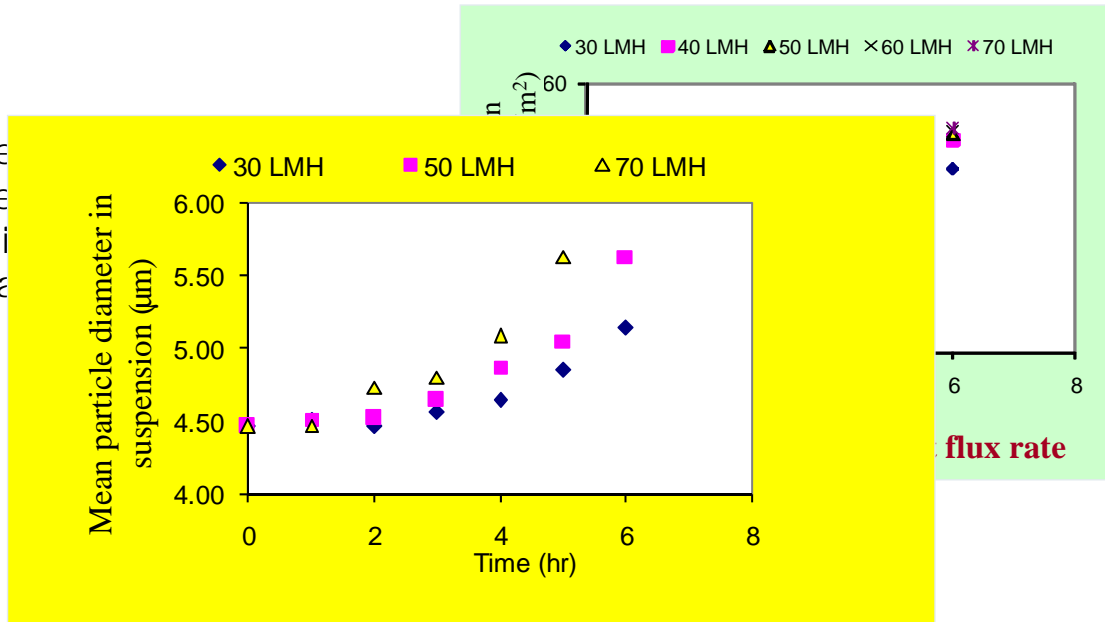


Low aeration favours fine particle deposit
 Aeration increases mixing the suspension then both finer and coarser particles reach the membrane surface and heterogeneous deposition occurs.

Effect of permeate flux on membrane fouling

Aeration rate of $2 \text{ m}^3\text{h}^{-1}\text{m}^{-2}$

At the
force
rapid
appea

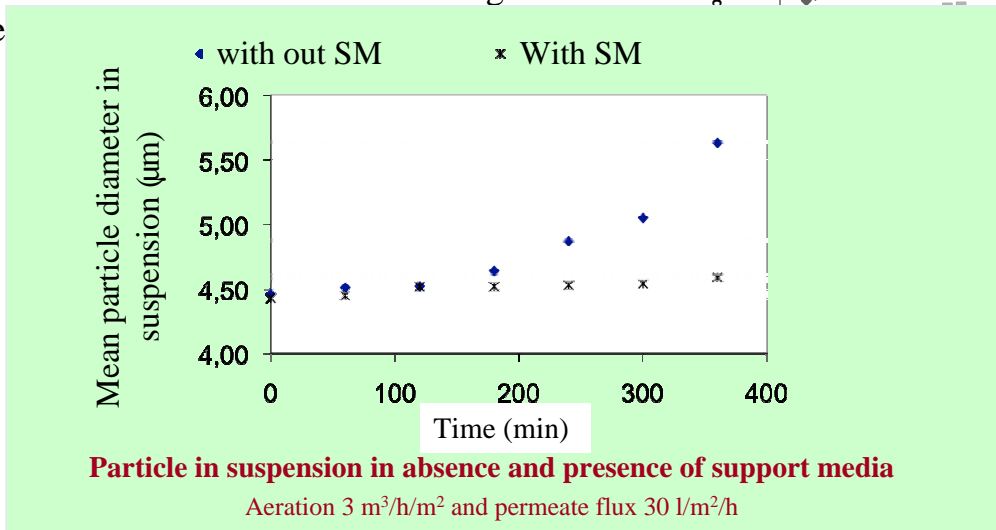
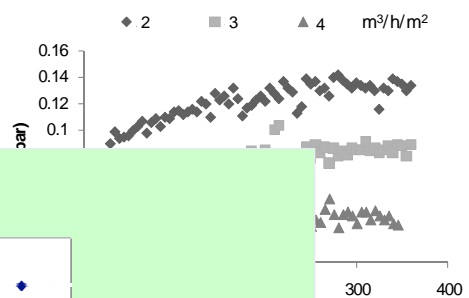


The smallest particles remain preferentially onto the membrane surface when increasing permeate flux

Effect of support media on membrane fouling (TMP)

Adding of 2 g/L Anthracite as support media (particle diameter $>640 \mu\text{m}$)

At all three different aeration rate found similar TMP rise reflecting support media has effective role in reducing cake de



Particle in suspension in absence and presence of support media

Aeration $3 \text{ m}^3\text{h}^{-1}\text{m}^{-2}$ and permeate flux $30 \text{ l/m}^2\text{h}$

Support medium plays crucial role in scouring and mixing the suspension and thus allows a significant fouling reduction

Conclusion - Part 1

Study on effect of aeration and support medium in membrane fouling control

- Influence of **shear stresses** (air flow rate and **support medium**) and filtration intensity on **deposit structuring** and **reversible fouling control**
- Theoretical aspect :
 - Modelling with clay suspension and biological suspension
- **Practical aspects :**
 - **Nature of medium** (size, density...)
 - **Long term experimentation**
 - **Membrane life time and medium properties ...**

Part 2

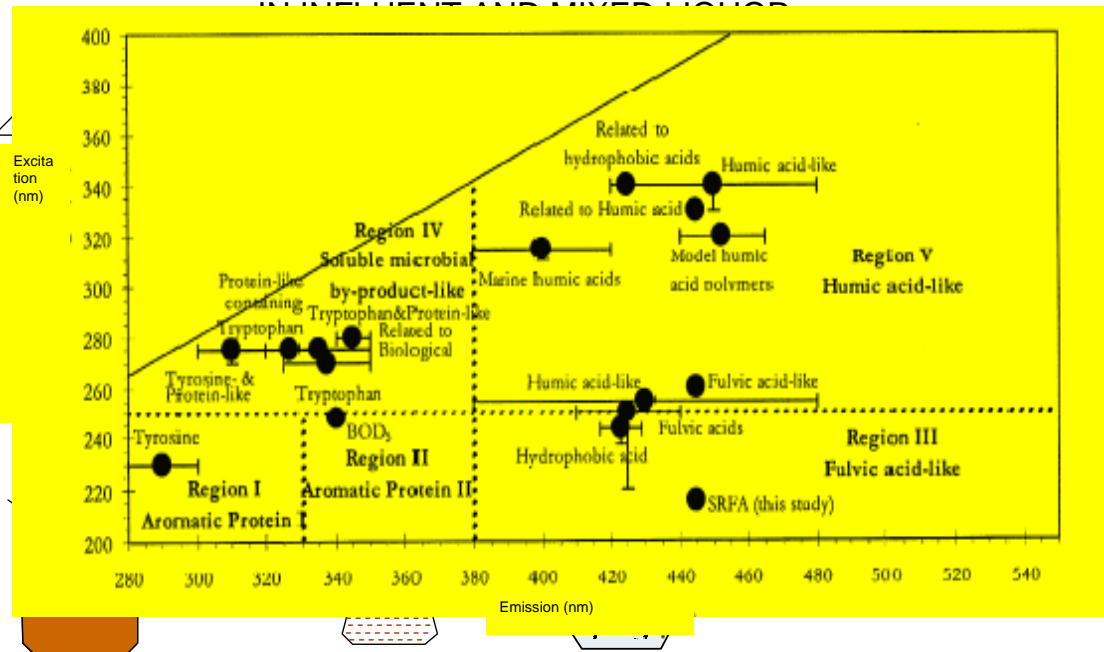
IDENTIFICATION OF IRREVERSIBLE FOULANTS IN MBR AND TEMPORAL VARIATION OF FOULANT CHARACTERISTICS

| Parameters | Units | Periods | |
|--------------------|--|---------------|-------------------------|
| | | I (days 0-22) | II (days 24-39) |
| Working volume | L | 36 | 36 |
| Organic load (Cv) | kg COD.m ⁻³ .d ⁻¹ | 0.9 to 3.0 | 1.5 to 3.0 |
| Mean permeate flux | L.m ⁻² .h ⁻¹ (LMH) | 5 to 20 | 10 |
| TSS | g/L | 1.8 to 4 | 4 - 5 |
| Dissolved oxygen | mgO ₂ .L ⁻¹ | > 2 | > 2 |
| Membrane aeration | m ³ /h.m ² (L/h) | 1.5 (300) | 0.5 to 1.5 (100 to 300) |

Membrane characteristics

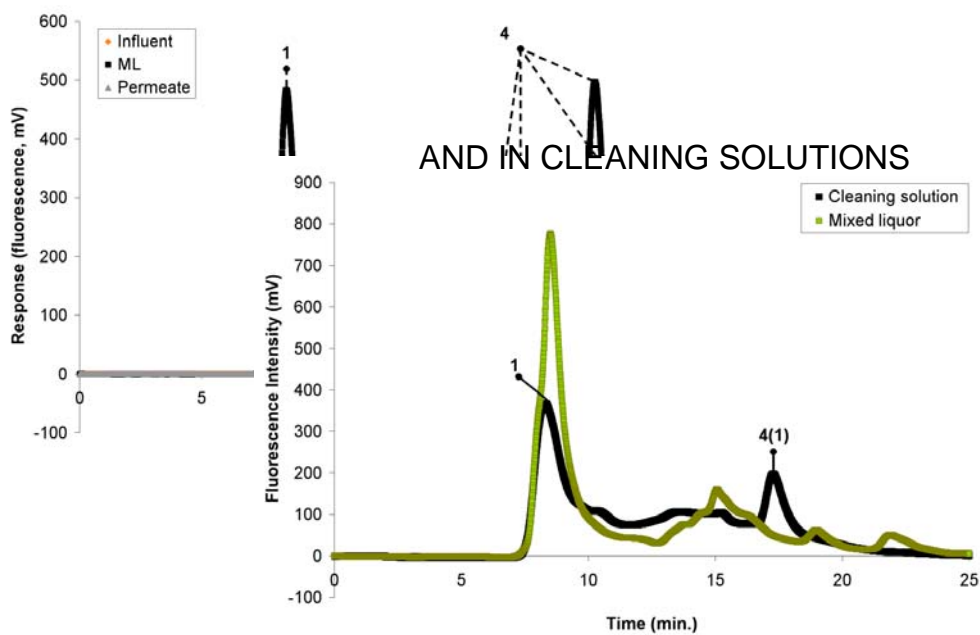
PVDF – Pore size 0.14µm – Filtration area 0.2m²
 Number of sheets 8 - Gap between sheets 12mm
 Specific surface 54m²/m³

IDENTIFICATION OF SOLUBLE COMPOUNDS BY HPSEC (High Performance Size Exclusion Chromatography) AND EEM FLUORESCENCE SPECTROSCOPY

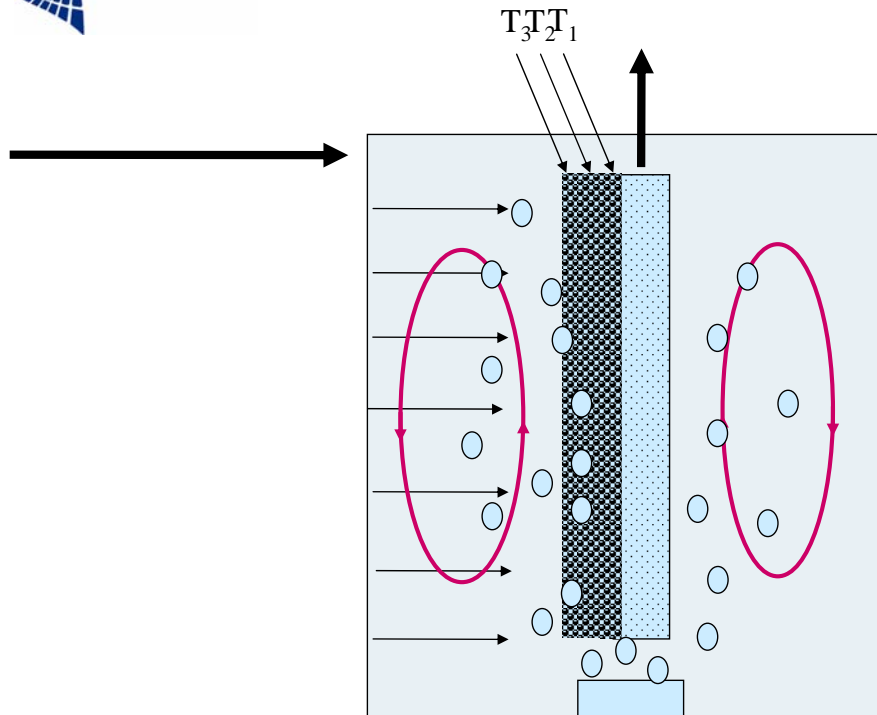
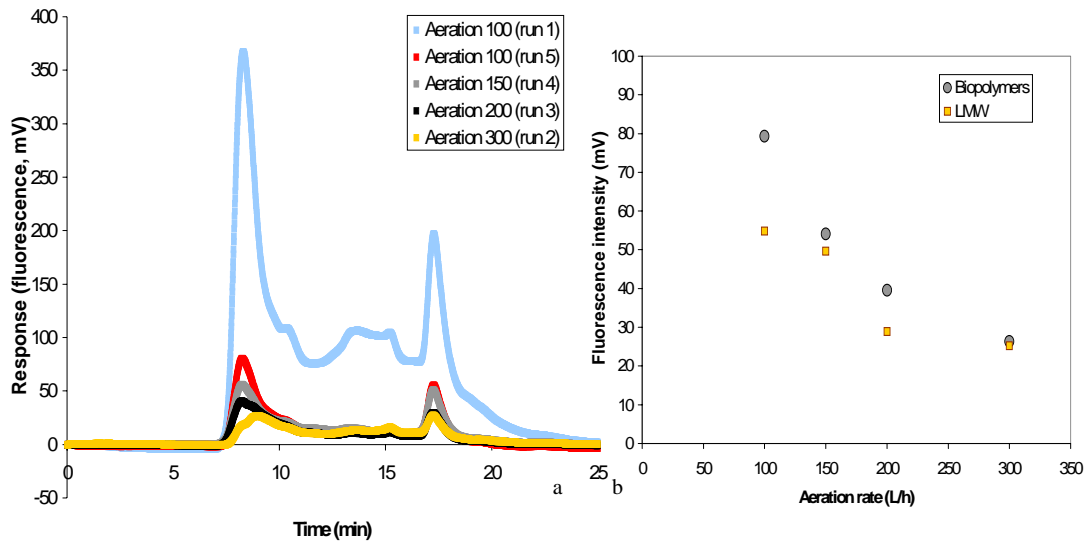


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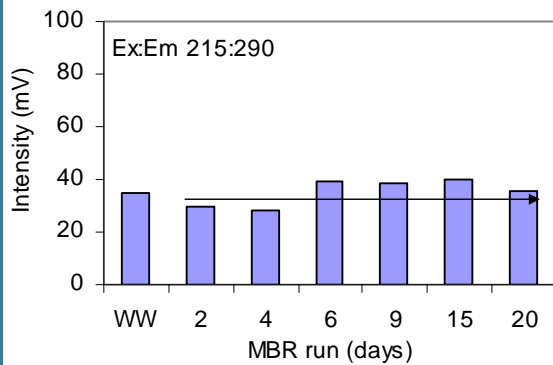
IDENTIFICATION OF SMP IN INFLUENT MIXED LIQUOR - PERMEATE AND IN CLEANING SOLUTIONS



ROLE OF AERATION TO CONTROL SMP FIXATION
ANALYSES OF CLEANING SOLUTIONS

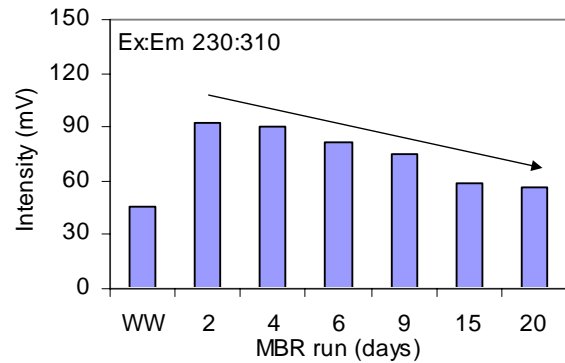


Foulant composition with time



Low molecular weight substances including amino acids

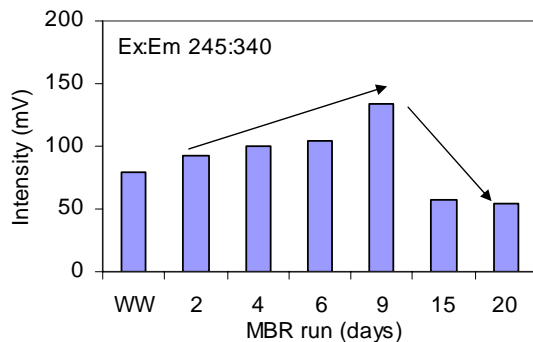
Remain unchanged in the foulant composition



Low molecular weight amino acids and aromatic proteins like substances

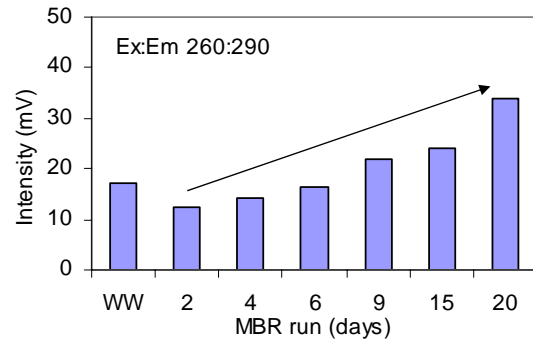
Relatively higher concentration during the early days and then decreased

Foulant composition with time



BOD5 type substances

Increase of bacterial activity in the beginning might have caused an increase of BOD5 substances in the foulant.



soluble microbial by-products

Foulant composition is more dominant with soluble microbial by-products with time.

Conclusion of part 2

➤ The organic foulants found onto the membrane surface appeared generated by the biological activity. They showed some changing of their ch

➤ Two longer p of bipo accumu

➤ The short d of oper of low

RELATION BETWEEN EVOLUTION OF BIOFILM COMPOSITION AND

-DRASTIC TMP EVOLUTION WITH TIME

-OPTIMISATION OF THE CLEANING STRATEGY

(HYDRAULIC AND CHEMICAL CLEANING)

d for a tulation sludge

with a 20 days version

Thank you for your attention and Acknowledgement

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More info: www.mbr-network.eu

11. ORGANIC MATTER IN MBR SLUDGE WATERS: FOULANT IDENTIFICATION AND CLEANING CONSIDERATIONS

*A. Fenu, O. Braimah, J.W. Mulder, M. Kennedy, G.
Amy*

Organic Matter in MBR Sludge Waters: Foulant Identification and Cleaning Considerations

Alessio Fenu*, Osi Braimah*, Jan-Willem Mulder*,
Maria Kennedy*, Gary Amy*

*UNESCO-IHE Institute for Water Education, Delft, The Netherlands

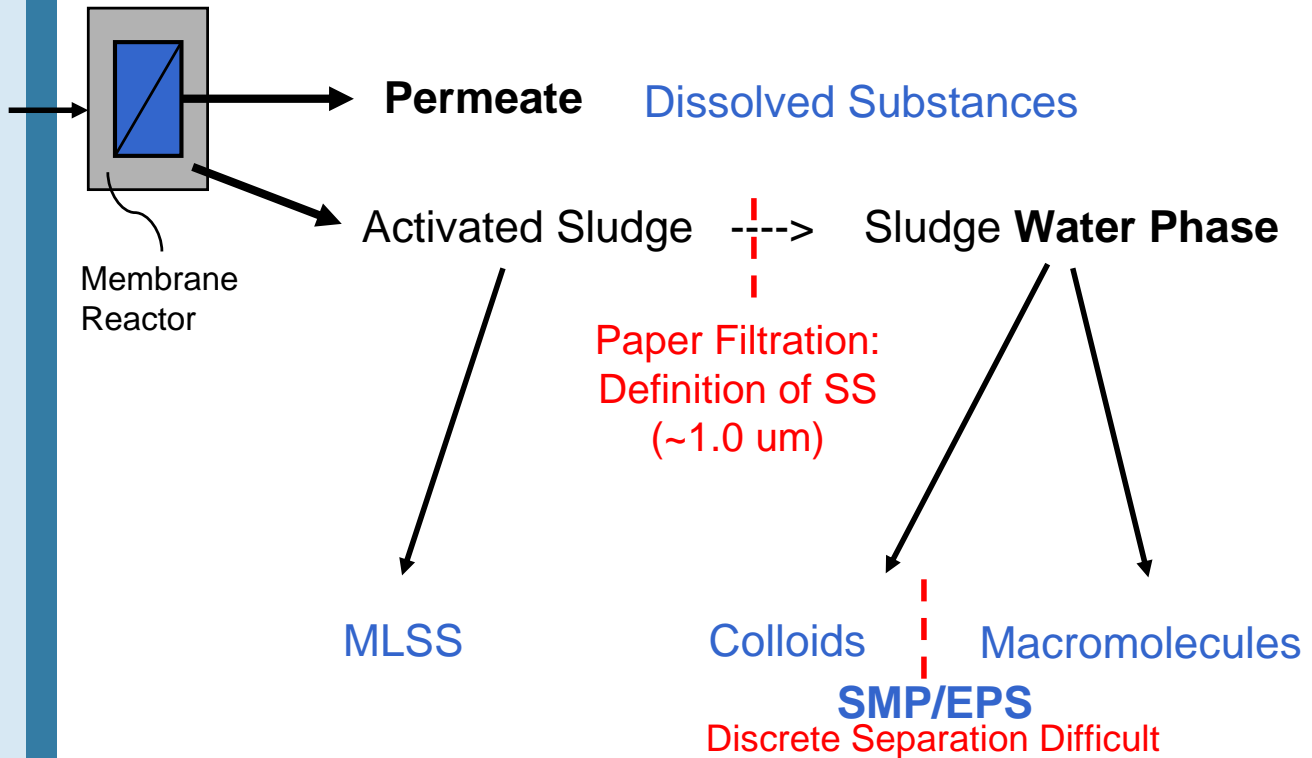
**Waterschap Hollandse Delta, Ridderkerk, The Netherlands



Background

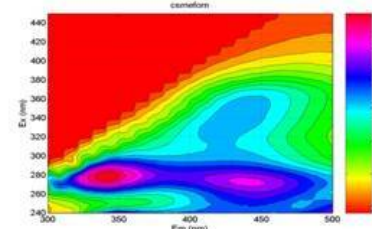
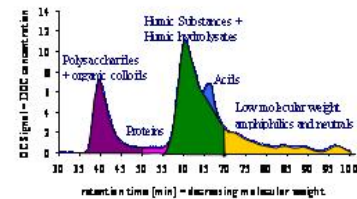
- ▶ Extracellular polymeric substances (EPS)
/Soluble microbial products (SMP)
 - Hypothesized as membrane foulants in MBRs
 - Macromolecules (Proteins, Polysaccharides) & Organic Colloids
- ▶ MBR operating conditions (e.g., sludge retention time (SRT), mixed liquor suspended solids (MLSS), flux (J)) may affect:
 - EPS and SMP production and/or
 - Membrane permeability

MBR Permeate versus Sludge Water Phase



Foulant Measurements

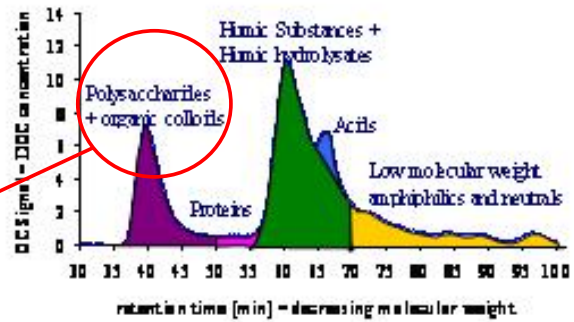
- ▶ Liquid Chromatography w/ Organic Carbon Detection (LC-OCD)
 - Separation According to Biopolymers (BP), Humic Substances (HS), and Low MW Acids (LMA)
 - ≈ LC-OCD (also, LC-OND, LC-UVD)
- ▶ 3-D Fluorescence Spectra
 - Excitation-Emission Matrices (F-EEMs)
 - Differentiate Protein- vs. Humic-Lake Materials
 - *Differential Spectra* (e.g., feed – permeate)
- ▶ Dissolved Organic Nitrogen (DON)
 - Separate Dissolved Inorganic Nitrogen (DIN) by Dialysis
 - *Direct* Measurement of DON by TN



DON determination using dialysis



Foulant Measurements



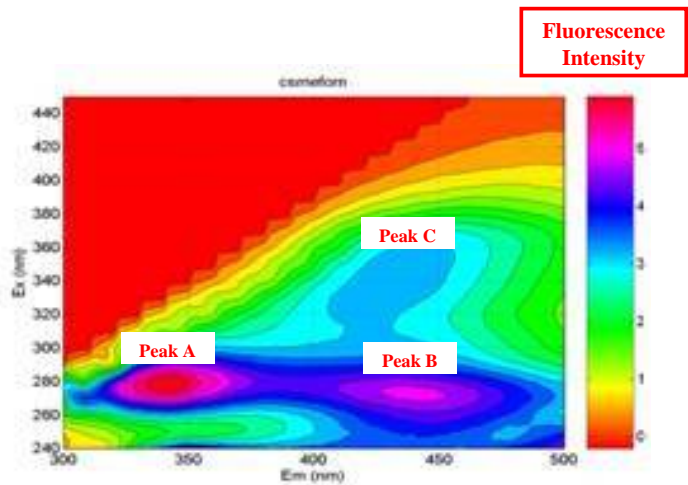
**Biopolymers
(proteins, polysaccharides)**

Foulant Measurements

Peak A:
Protein-like peak ✓

Peak B:
(Primary) Humic-Like Peak

Peak C:
(Secondary) Humic-Like Peak



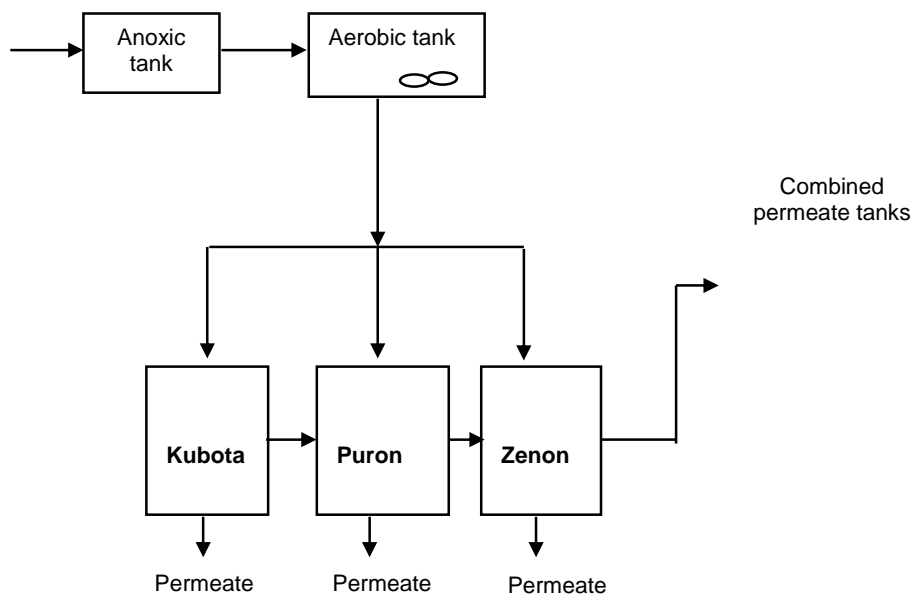
Foulant Measurements

Proteins
(+ amino acids, amino sugars)

DON determination using dialysis



EAWAG Pilot MBRs (Joss, 2008)

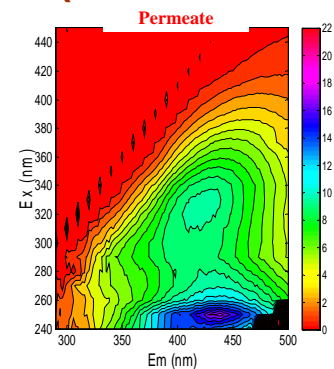
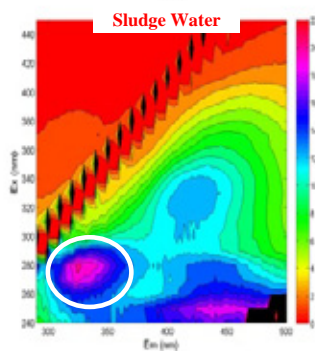


EAWAG Pilot MBRs (Joss, 2008)

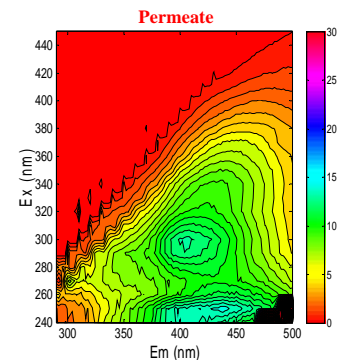
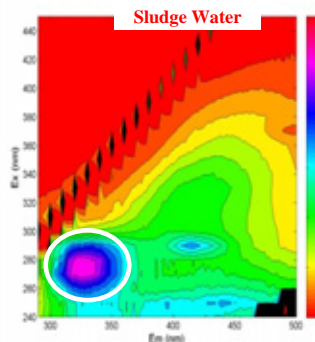
| MBR | EAWAG Switzerland | | |
|-----------------------------|-------------------|--------|----------|
| | Kubota | Puron | Zenon |
| Membrane type | FS | HF | HF |
| Design capacity [p.e.] | 100 | 100 | 100 |
| Pore size [μm] | 0.4 | 0.03 | 0.04 |
| MLSS [g/L] | 7.7-8.0 | 8-10 | 6-11 |
| SRT [d] | 10-14 | 7-8 | 8-10 |
| Flux [LMH] | 6.8-7.0 | 9-15 | 8.6-14.5 |
| TMP [mbar] | 502 | 336 | 110 |
| Permeability [LMH/bar] | 80-135 | 90-106 | 180-215 |

F-EEM Spectra: EAWAG Pilot MBRs (Puron, Zenon)

Puron membranes



Zenon membranes



Retentions of Protein-Like and, to a lesser degree, Humic-Like: Fouling?

Fluorescence Intensities of Protein-Like Peak: EAWAG Pilot MBRs (Puron, Zenon)

| Membrane | Fluorescence Intensity | |
|----------|------------------------|----------|
| | Feed | Permeate |
| Kubota | 30 | 25 |
| Zenon | 26 | 12 |

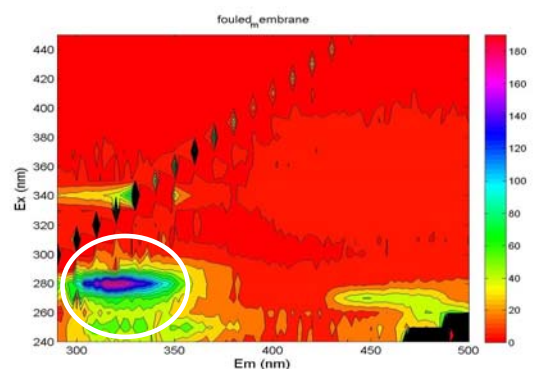
Pore Size: Kubota > Zenon

MBR Autopsy: Kubota Membrane

**Fouled Kubota membrane:
24 hrs post chemical cleaning**



**F-EEM spectrum:
Extract from fouled Kubota membrane**



Application of Protocols to Samples from Operating MBRs

► MBRs

- Arapahoe MBR
 - SRT = 19 days; HRT = 6 hours; MLSS = 11,100 mg/L
 - *Immersed Zenon 0.02 um UF; Anoxic/Oxic*
- Georgia MBR
 - SRT = ? Days; HRT = 10 hours; MLSS = 3,360 mg/L
 - *Sidestream Memcor 0.1 um MF; Aerobic*

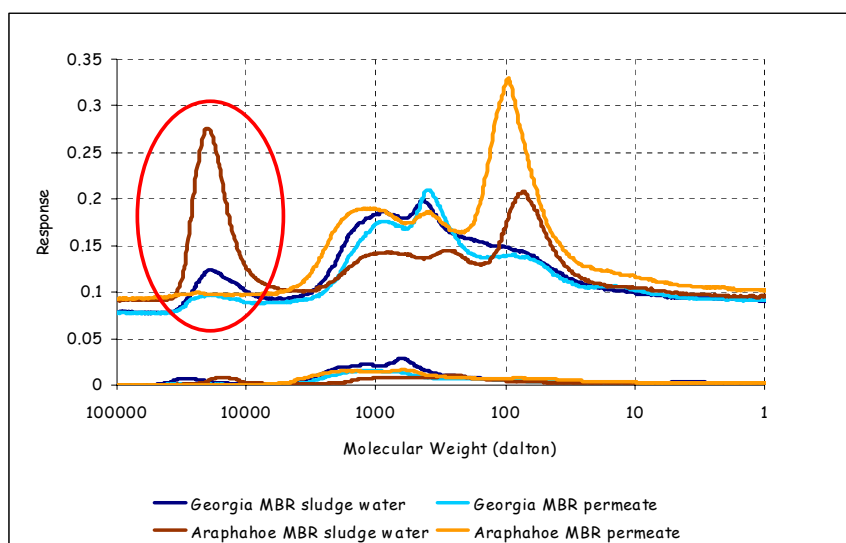
► Samples

- Sludge Water
- Permeate

► Testing

- LC-OCD, F-EEM, and DON
- Stirred Cell Simulations

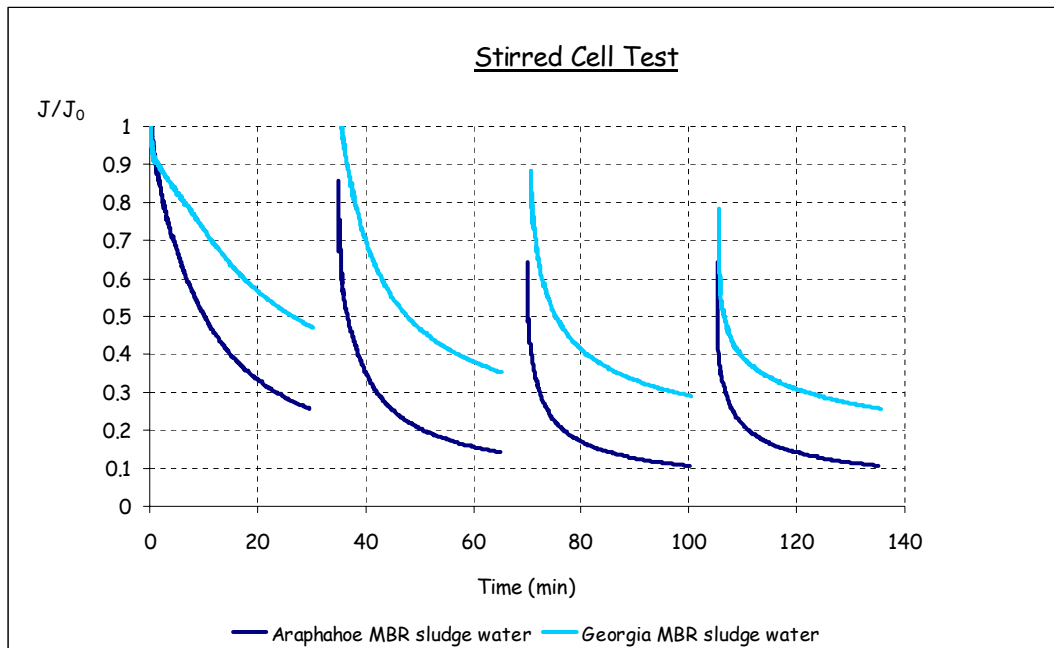
LC-OCD and DON: Sludge Water and Permeate



Biopolymer Peak:
 ARM-MB = 4.5 mg/L
 GEL-MB: 0.8 mg/L

| Sample/ Parameter | Arapahoe MBR Sludge Water | Arapahoe MBR Permeate | Georgia MBR Sludge Water | Georgia MBR Permeate |
|----------------------|------------------------------|--------------------------|-----------------------------|-------------------------|
| DON (mg/L) | 1.33 | 0.66 | 0.59 | 0.41 |

Stirred Cell Tests Results with Sludge Waters: Normalized Flux vs. Time (min) + Simulated Backwashing



Hydraulically Irreversible Fouling: Arapahoe Sludge Water > Georgia Sludge Water

Heenfliet MBR (Netherlands)

- ▶ Immersed Membrane
- ▶ Toray Flat Sheet Modules
 - 0.08 μ m PVDF
 - No hydraulic backwash
 - No maintenance cleaning
 - Low cleaning frequency (at time of study)
- ▶ Advised Toray Cleaning Protocol
 - Citric acid (max 3 %)
 - NaOCl (max 0.6 %)
 - Dosage by permeate pipes
 - Sludge remains in membrane tank

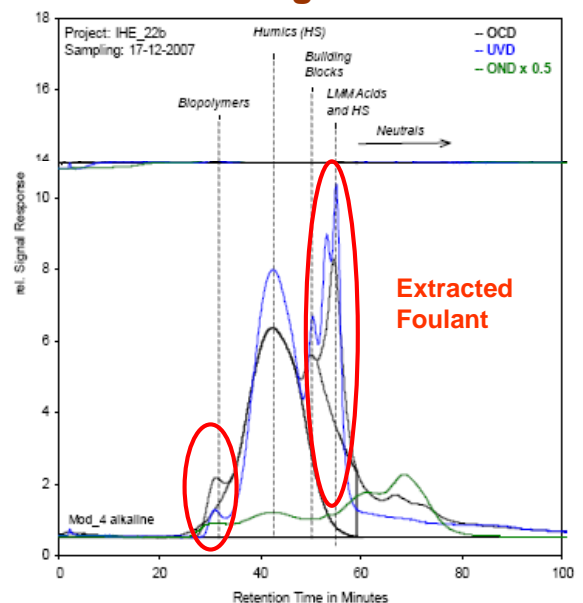
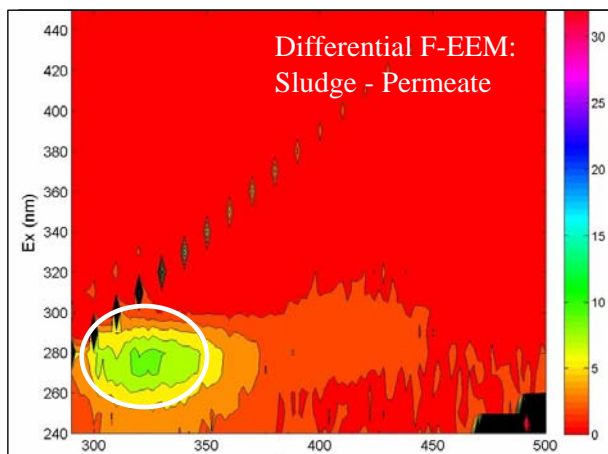


Heenfliet MBR (Netherlands)

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 - 0.08 um PVDF
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 - No maintenance cleaning
 - Low cleaning frequency (at time of study)
- ▶ Advised Toray Cleaning Protocol
 - Citric acid (max 3 %)
 - NaOCl (max 0.6 %)
 - Dosage by permeate pipes
 - Sludge remains in membrane tank
 - High pH Hypochlorite (NaOH + NaOCl)?

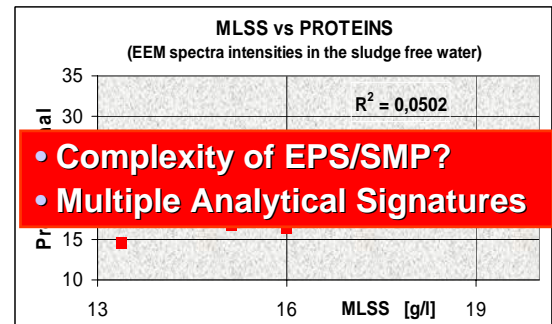
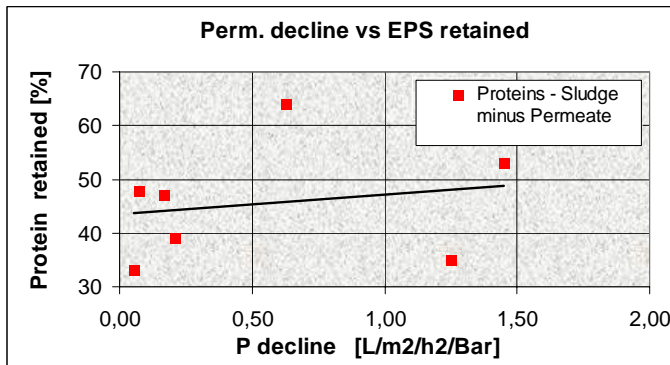
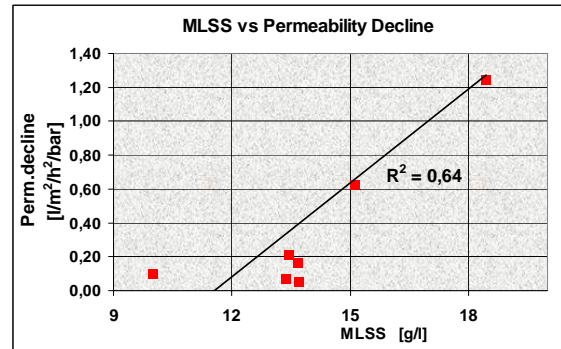
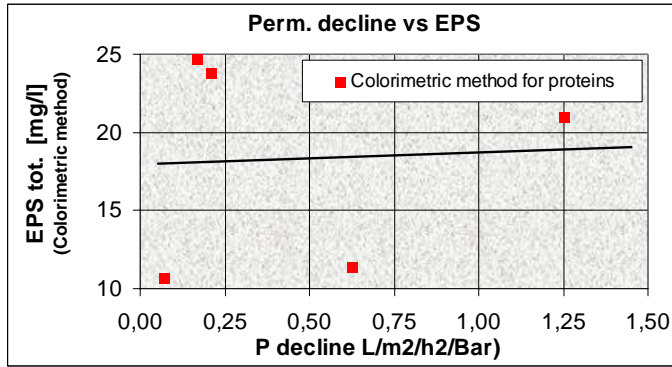


Characterization of Sludge Water and Extracted Organic Fouls

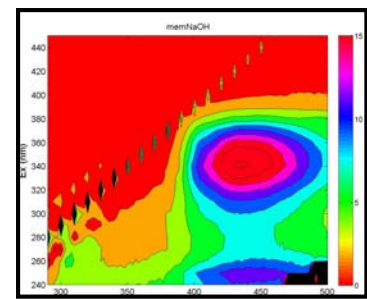
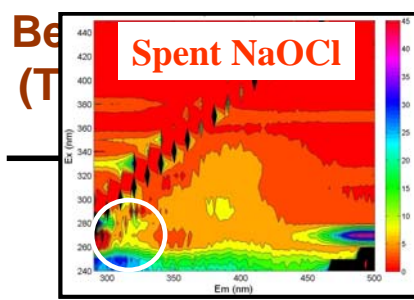
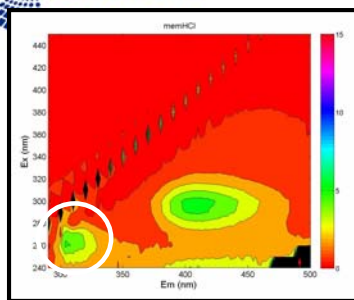


- Ratio of proteins to polysaccharides = 2:1 in biopolymer peak of sludge water (LC-OND and SUVA from LC-UVD)
- Protein and polysaccharide retention = 43% and 68%, respectively (colorimetric)
- Average retention of 5% for humics (F-EEM)

- Extracted by NaOH (pH 12) with sonication
- Protein hydrolysis?



• Complexity of EPS/SMP?
 • Multiple Analytical Signatures



Acid cleaning (HCl)

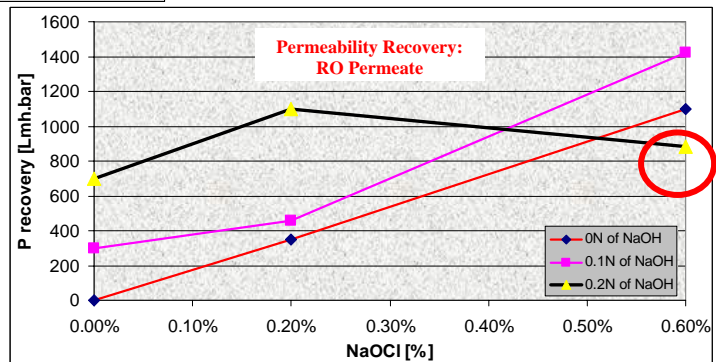
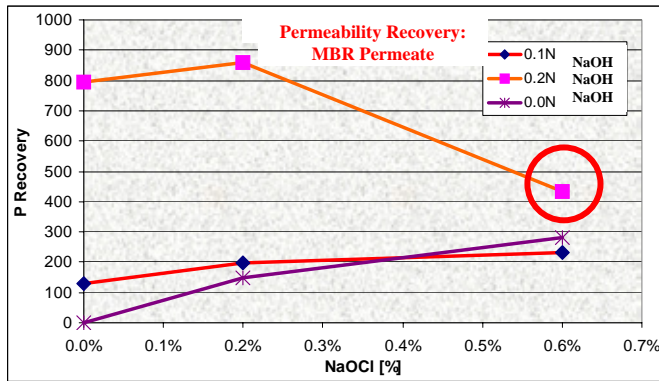
Basic cleaning (NaOH)

ext:
feed
side

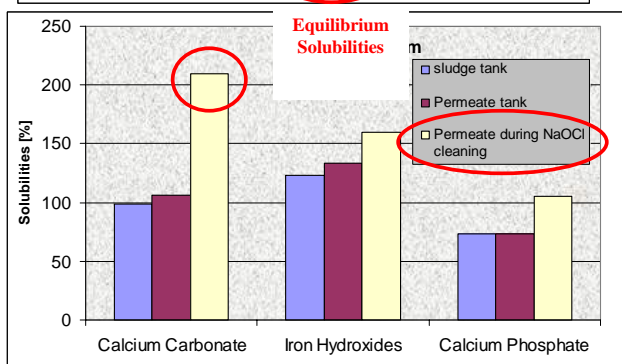
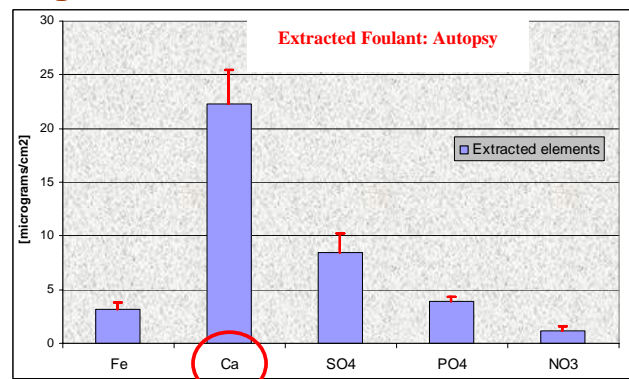
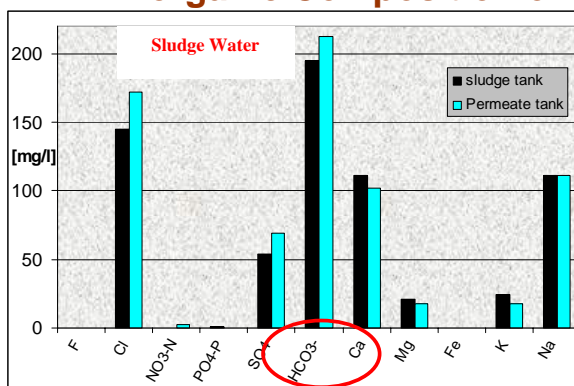


int:
permeate
side

Bench-Scale MBR (Toray): Simultaneous Cleaning with NaOCl + NaOH from permeate side



Bench-Scale MBR (Toray): Inorganic Composition of Sludge Water and Extracted Foulants



- ▶ SEM-EDX EDS measurements show that metals are mostly precipitated on the permeate side
- ▶ CaCO₃ represents 10% of foulants on the permeate side
- ▶ Separate NaOH and NaOCl steps

Summary

- ▶ MBR membrane fouling is a complex phenomenon
- ▶ Analytical resolution of EPS/SMP (in sludge water, permeate, and extracted foulant) is possible but multiple techniques are necessary to fully reveal identity ⇒ LC-OCD + F-EEM
- ▶ EPS/SMP plays a role in MBR membrane fouling, with varying degrees of hydraulic reversibility/irreversibility
- ▶ Cleaning agents should be selected based on foulant identity; complexity of foulant generally necessitates multiple agents

Acknowledgement

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