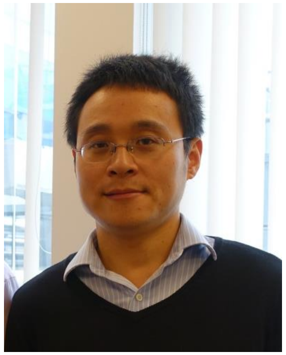
Developments in Membrane Separation for Water Treatment

Nigel Graham and Wenzheng Yu



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Twenty65 Theme 1:
Demand-based technologies for tailored treatment

Why membrane separation?

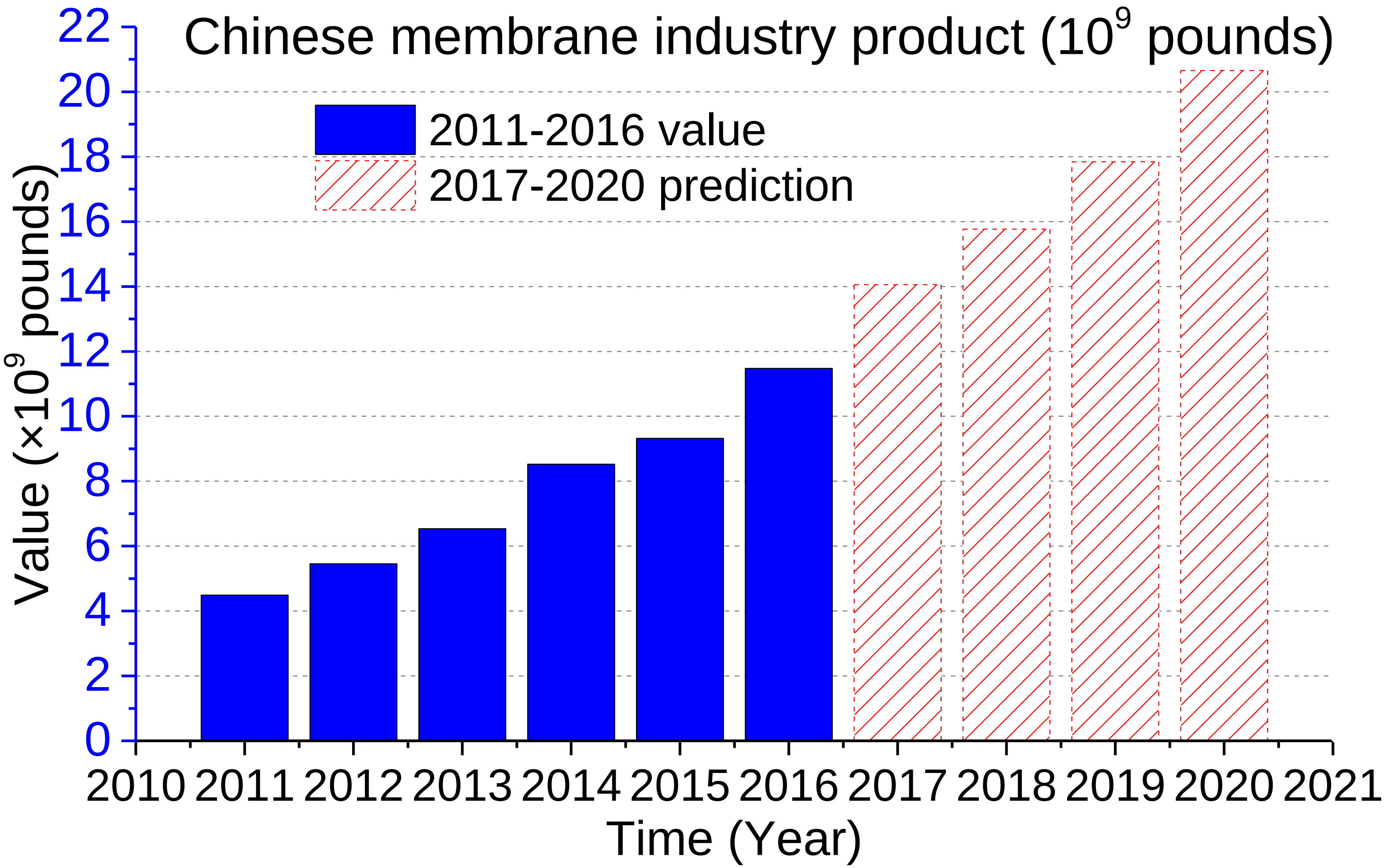
- Absolute barrier
- **Variety of applications (remove micro-organisms, dissolved organics, salts)**
- Tolerant to feed fluctuations (flow, quality)
- Compact, modular plant
- **Scalable to a wide range of applications ('tailored treatment')**
- Easy to automate

Types of membranes:

- **RO – Reverse Osmosis** (99% salt retention)
  - Ions, low MW compounds / 1 Lmh/bar / TMP 10-100bar
- **NF – Nanofiltration** (500 Da MW cut-off)
  - Medium-high MW compounds / 10 Lmh/bar / TMP 1.5 -20 bar
- **UF – Ultrafiltration** (>0.01 μm or 100 kDa MW cut-off)
  - Colloidal matter (viruses), and suspended solids / 100-400 Lmh/bar / TMP 0.1- 5 bar
- **MF – Microfiltration** (>0.1 μm)
  - Microparticles, bacteria / 1000 – 2000 Lmh/bar / TMP 0.1 – 2 bar

(Lmh – litres/m^2 h; TMP – Transmembrane pressure)

Membrane Production: China

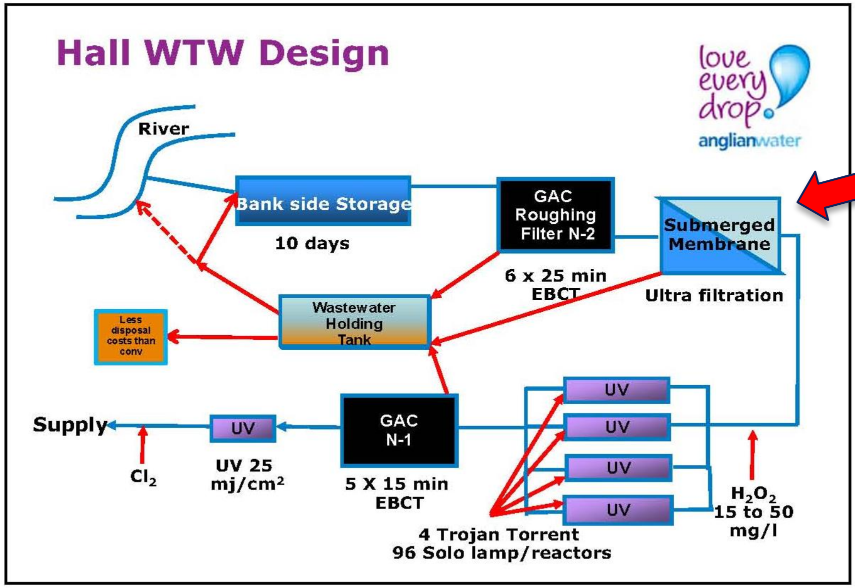


http://www.chinacitywater.org/zwdt/swyw/96949.shtml

Current UK examples
(municipal scale):

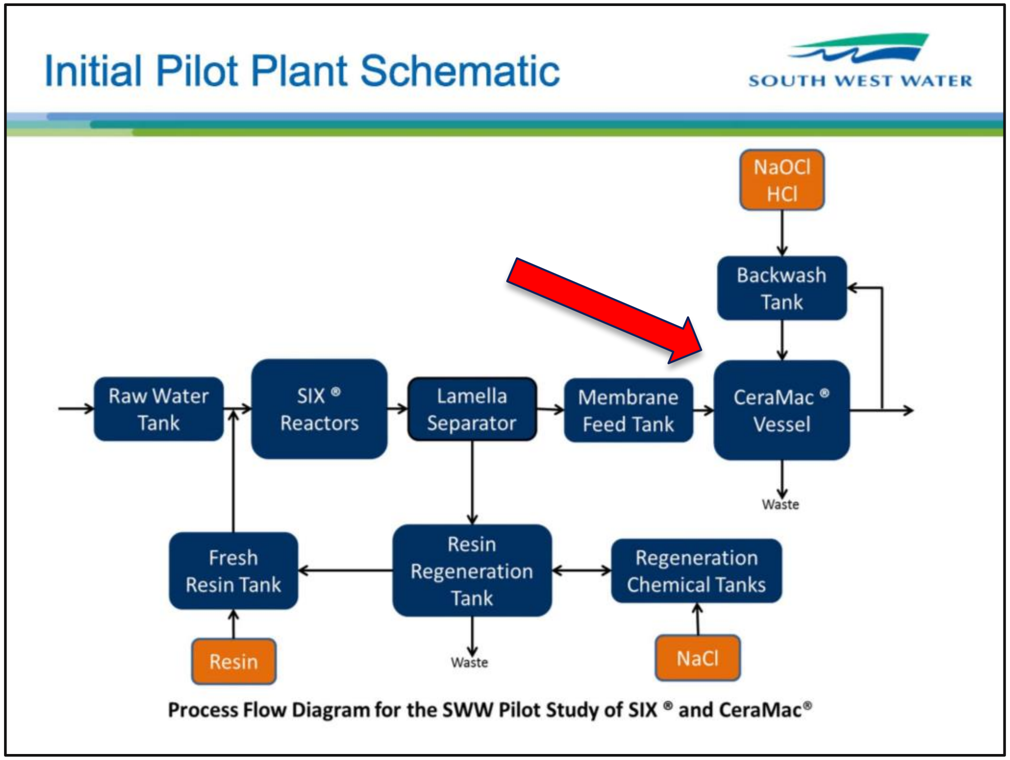
Hall WTW (Anglian Water)

- 20 ML/d, Submerged **UF** membranes

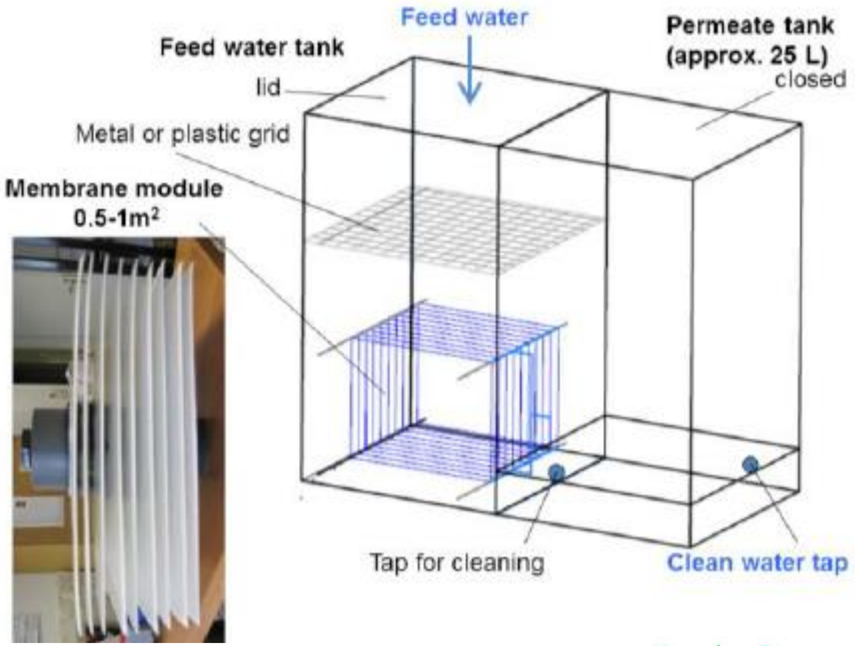


Crownhill WTW (South West Water)

- 150 m^3/d, Ion exchange / ceramic **MF** membrane (SIX/CeraMac Process, PWN Technologies)



Household (decentralised) scale:



Gravity driven UF/NF

(Protoype of the GDMD system (Biocell® membrane, Microdyn-Nadir, 150kDa cut-off), 10 L/d)

Ref: Peter-Varbanets et al, 2011 (EAWAG)

‘PAUL’ Portable Aqua Unit, 1,200 L/d (10 m^2)

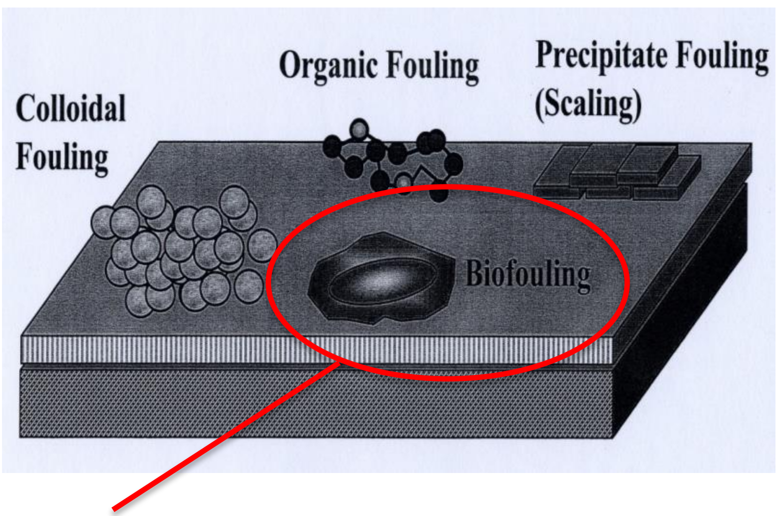
UF membrane

www.uni-kassel.de/fb14/slwawl

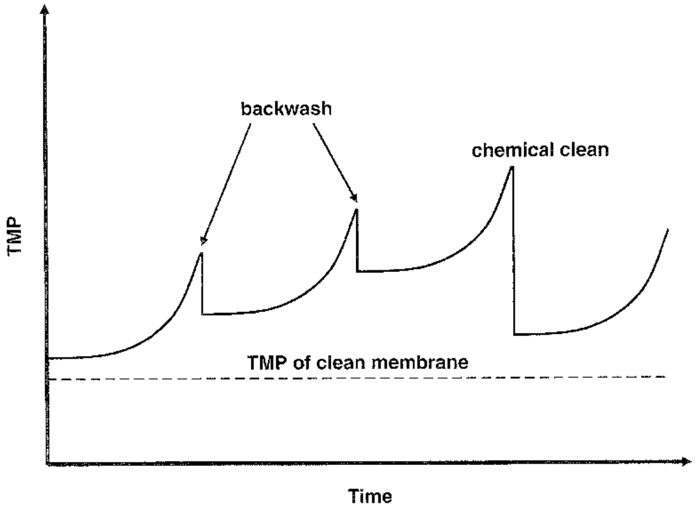
But, present limitations → research motivation

- Fouling / cost of operation
- Treatment performance -vs- flux

Causes of fouling?



Biofouling – micro-organisms, extracellular polymeric substances (EPS), etc

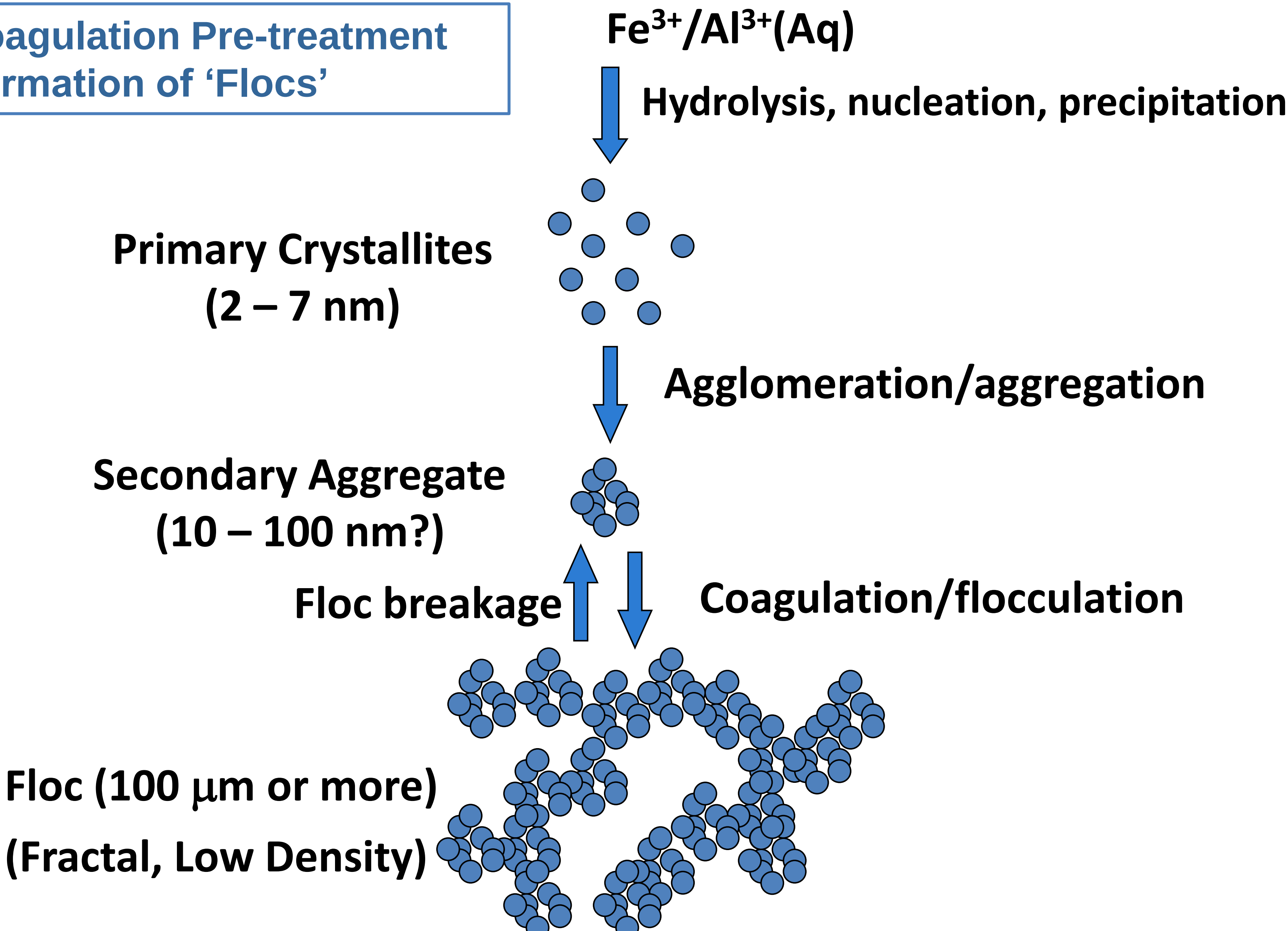


Reversible – backwashing
Irreversible – chemical clean

Project objectives

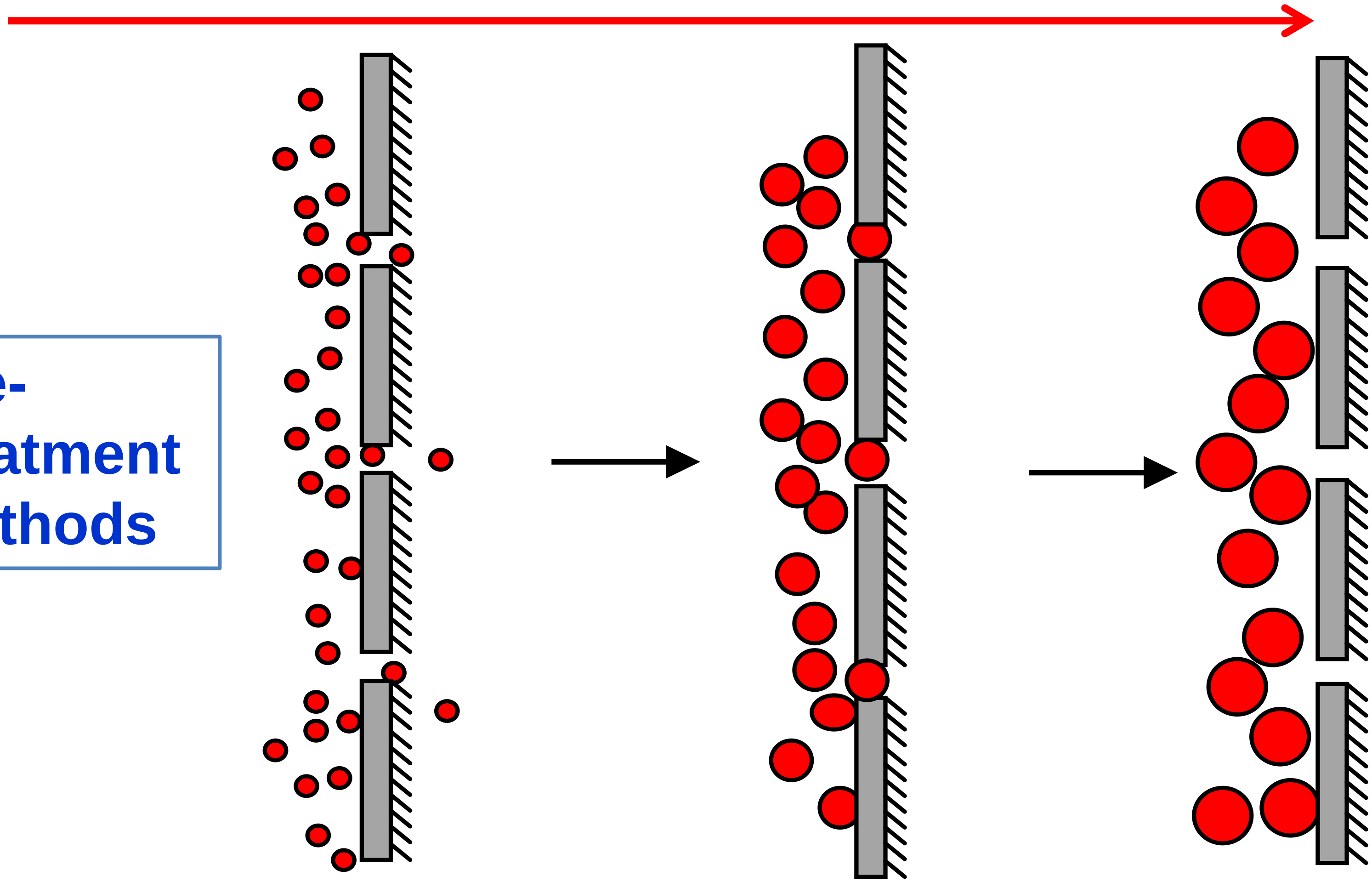
- Focus on Ultrafiltration (UF) and Nanofiltration (NF) for drinking water from non-saline surface waters
- Process modifications to reduce UF fouling
- Application of Graphene Oxide (GO) as novel UF/NF intermediate material (higher flux, more hydrophilic, etc.)
- Bench-scale testing
  Both short term, flat sheet (< 30 mins), and long term, hollow fibre (~ 60 days)

Coagulation Pre-treatment Formation of ‘Flocs’



J. Gregory et al (2004)

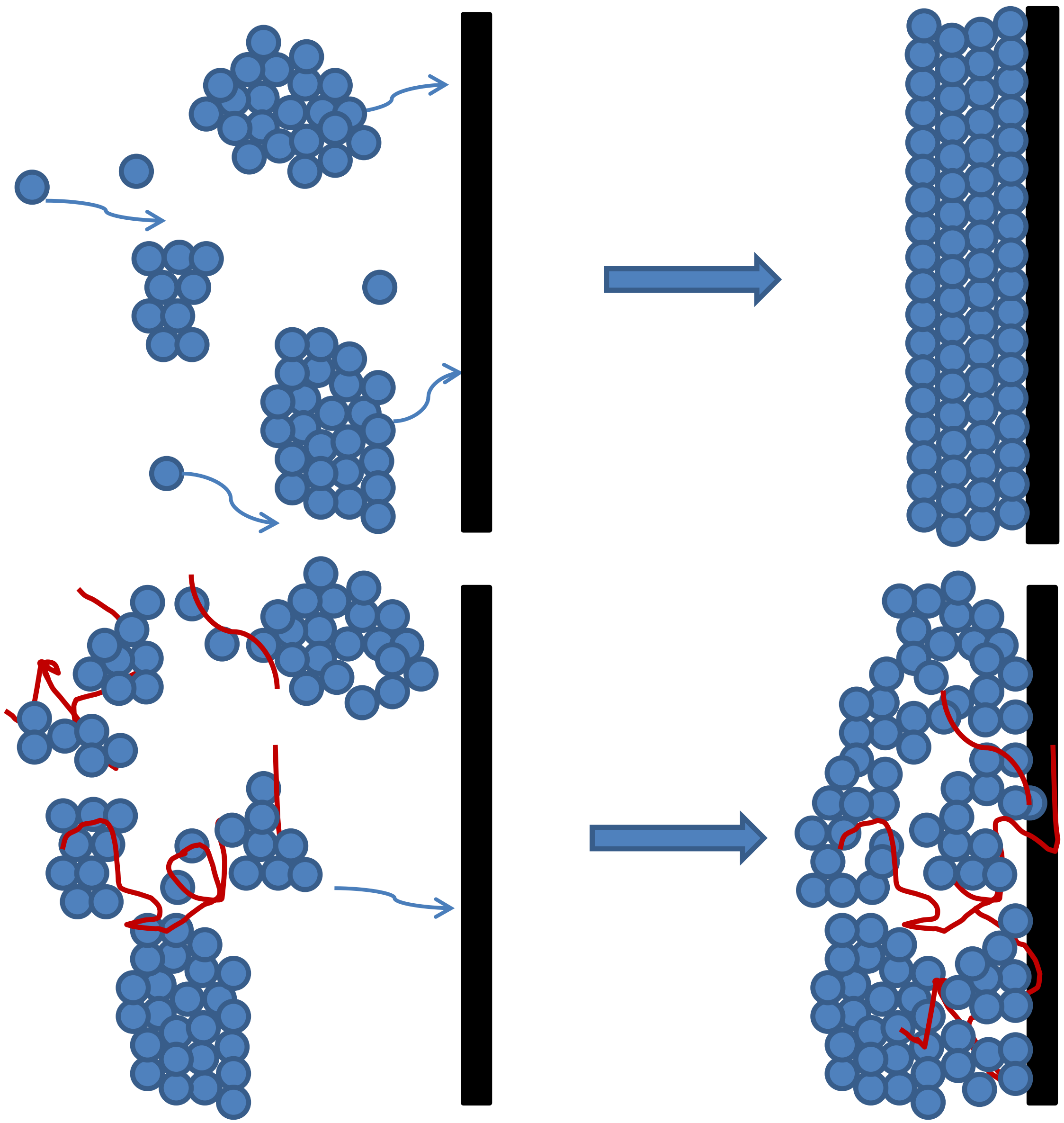
Pretreatment affects the size of nano-scale particles



Pre-treatment methods

Pretreatment controls the structure of cake layer

Pre-treatment methods



Process modifications to reduce UF fouling

Coagulation

- Type of coagulant (Fe, Al), coagulant aid (polyacrylamide)
- Combined oxidant/coagulant (permanganate, manganate + Fe, ferrate)

Disinfection / Oxidation

- Chlorine, pulsed UV irradiation
- Ozone, ozone + catalyst (MnO_2 membrane coating)

Adsorption

- Powdered activated carbon
- Ion exchange (MIEX) with ozone, MIEX with sand

Other

- Sand layer membrane protection
- Ultrasound

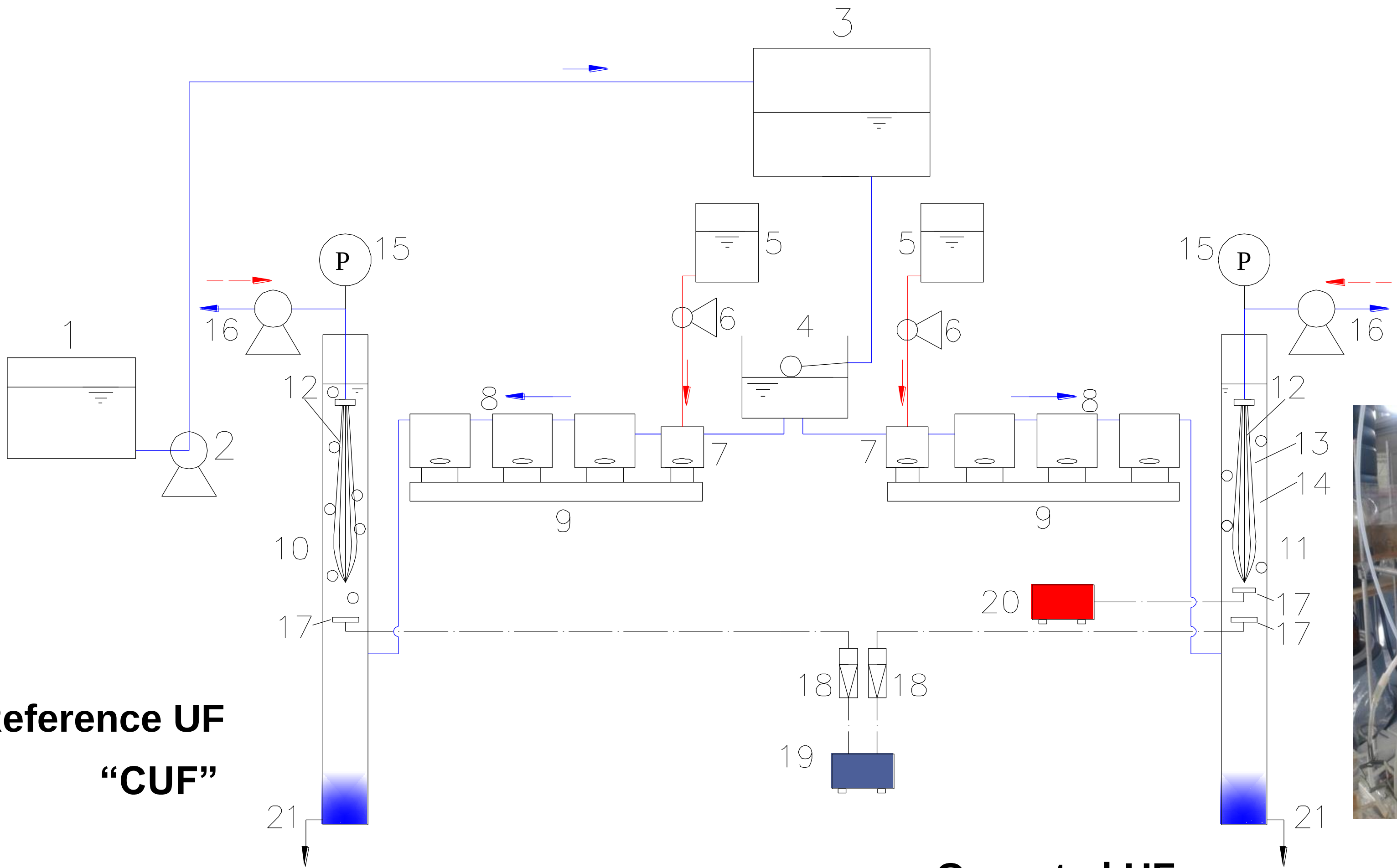
Controlling membrane fouling in drinking water treatment: Effect of *low dose of ozone* in submerged membrane tank

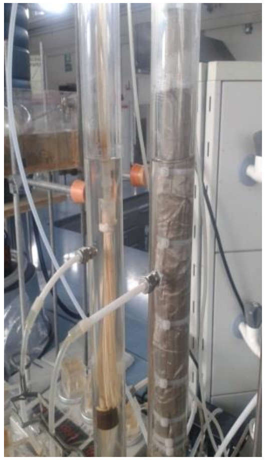
Refs:

Yu, W., Graham, N.J.D. and Fowler, G.D. (2016). 'Coagulation and Oxidation for Controlling Ultrafiltration Membrane Fouling in Drinking Water Treatment: Application of Ozone at Low Dose in Submerged Membrane Tank'. *Water Research*. 95, 1-10.

Yu, W., Brown, M. and Graham, N. (2016). 'Prevention of PVDF Ultrafiltration Membrane Fouling by Coating MnO_2 Nanoparticles with Ozonation'. *Scientific Reports*. 6, 30144.

Schematic diagram of the experimental set-up





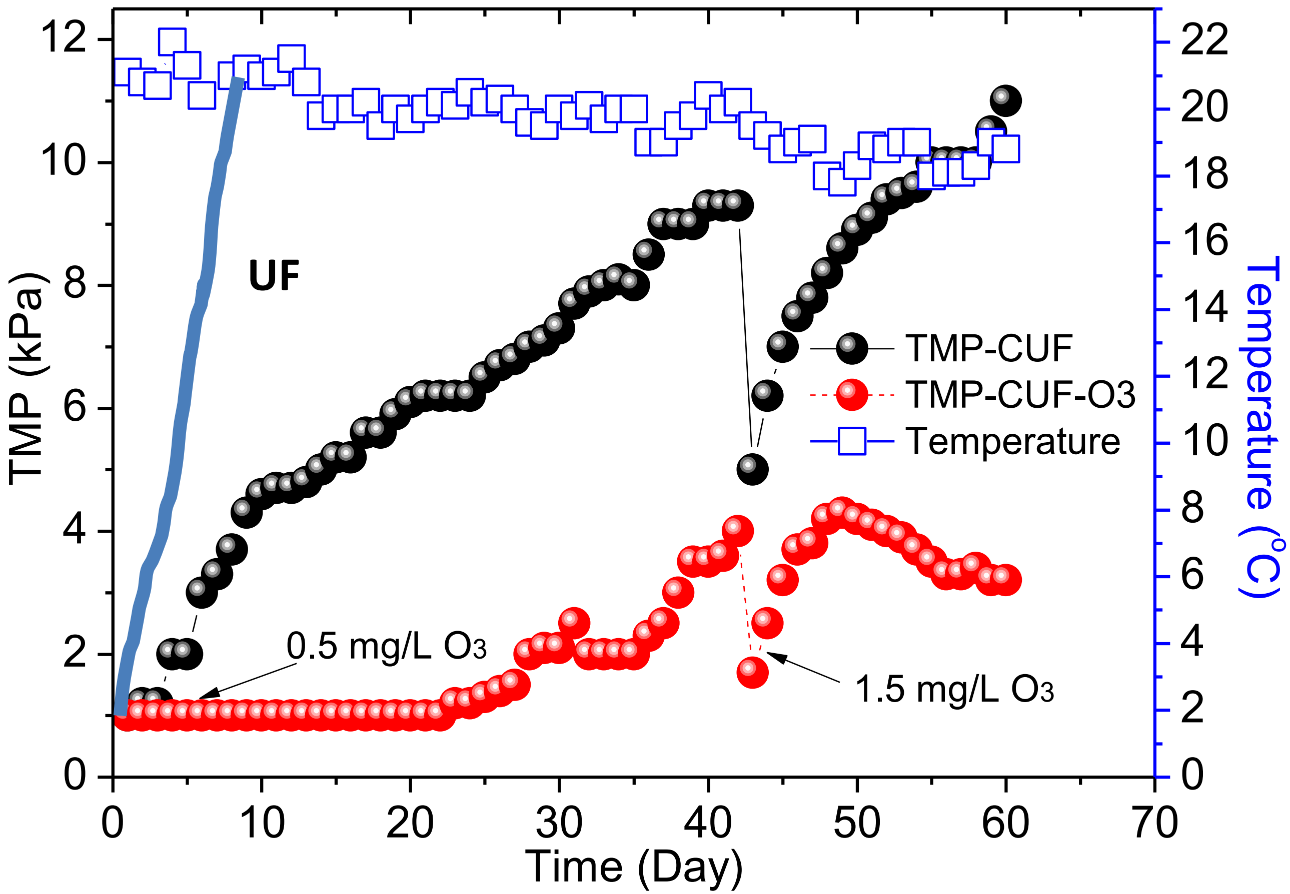
Reference UF
"CUF"

Ozonated UF
"CUF-O_3"

UF Membrane:
PVDF hollow-fibre (pore 0.03 µm)
30 min filtration (20 L/m^2 h), 1 min backwash and air scour

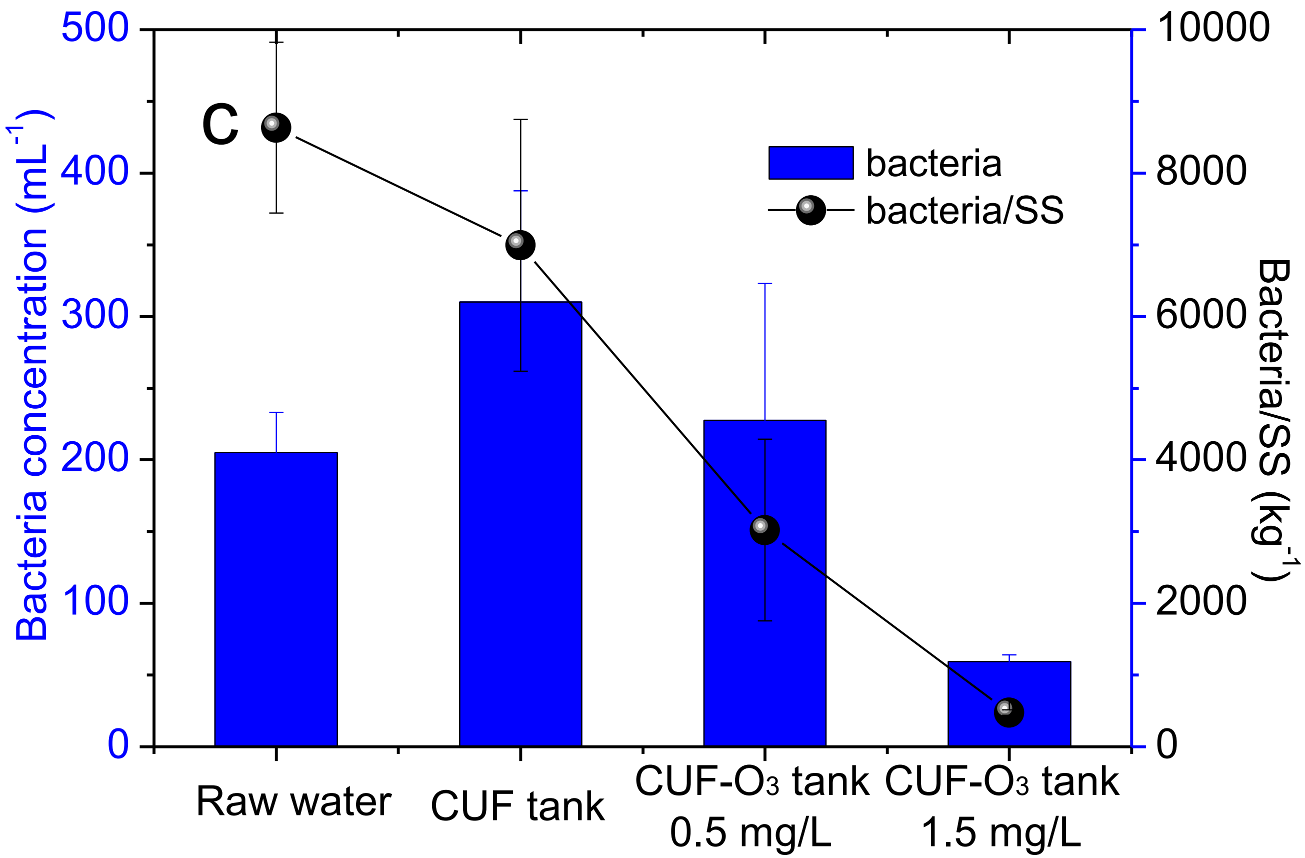
Experimental set-up

TMP Development (@ 20 Lmh)



- **Much lower TMP development with Ozone**
- **Very little irreversible fouling (after physical washing)**

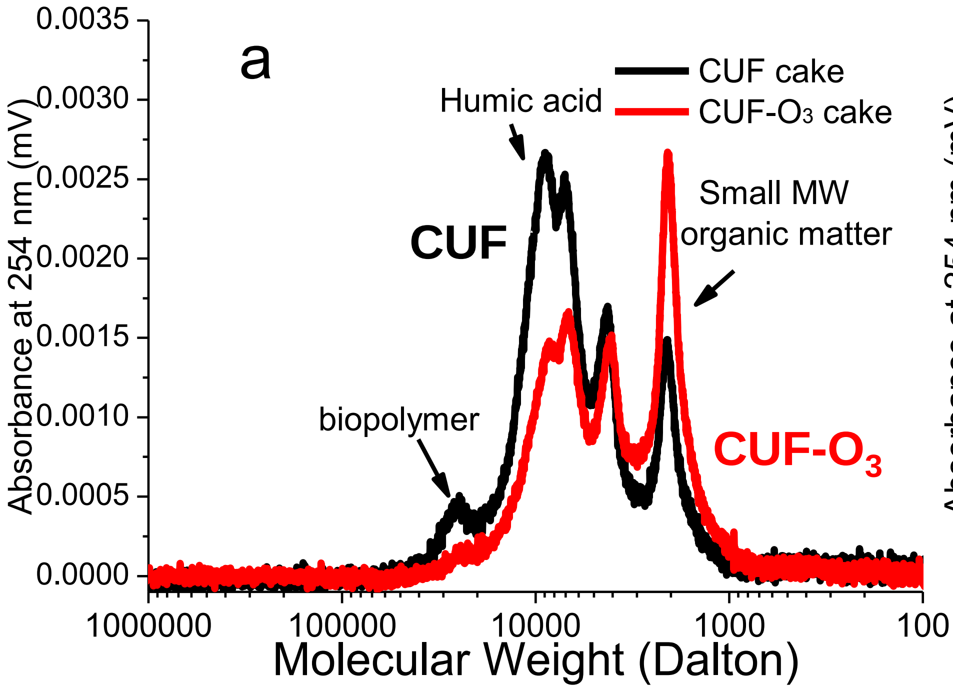
Bacteria concentration



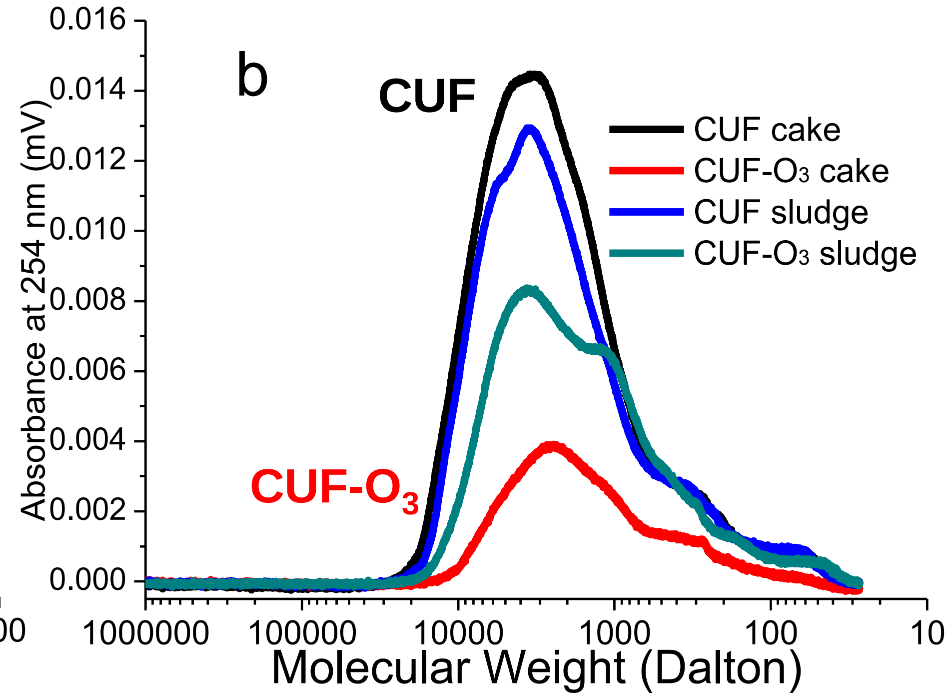
- **HPC bacteria in membrane tank – end of each phase**
- **Reduced counts with ozone (especially at 1.5 mg/l ozone)**

Presence of Extracellular Polymeric Substances (EPS)

Loosely-bound EPS



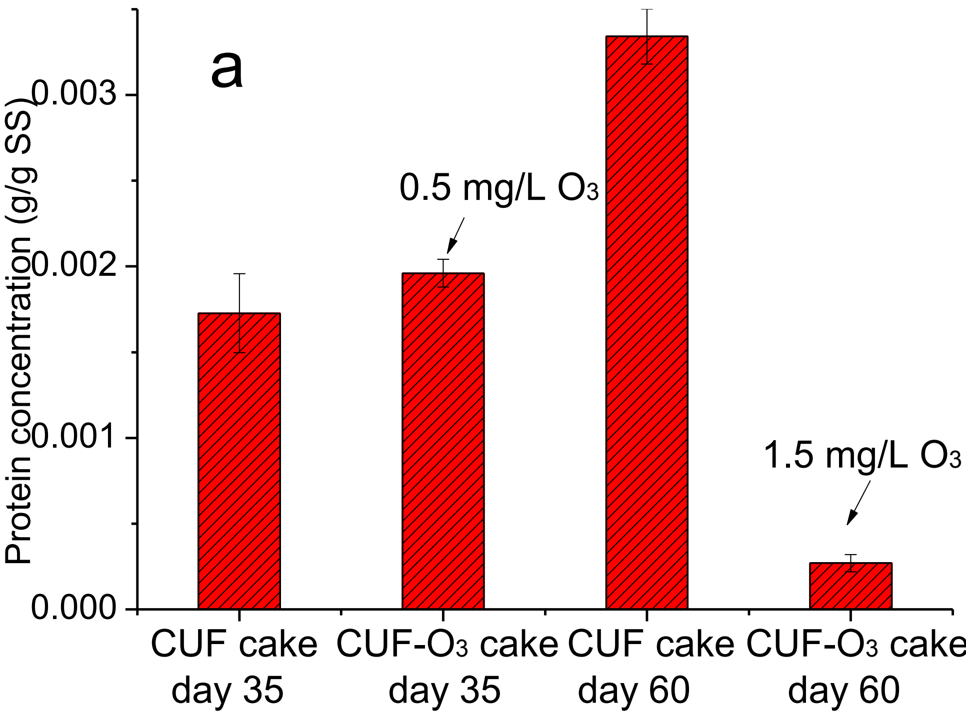
Tightly-bound (EPS)



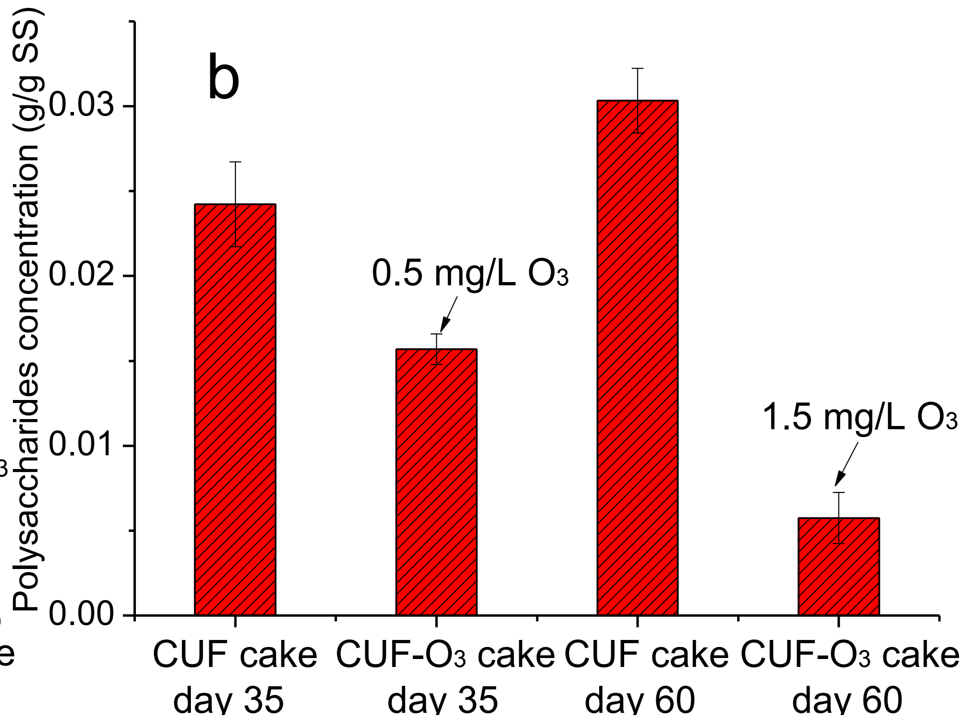
- **Much lower presence of EPS in membrane cake with Ozone**
- **Reduction in high MW fractions, especially biopolymers**

Presence of proteins and polysaccharides in cake layer

Proteins

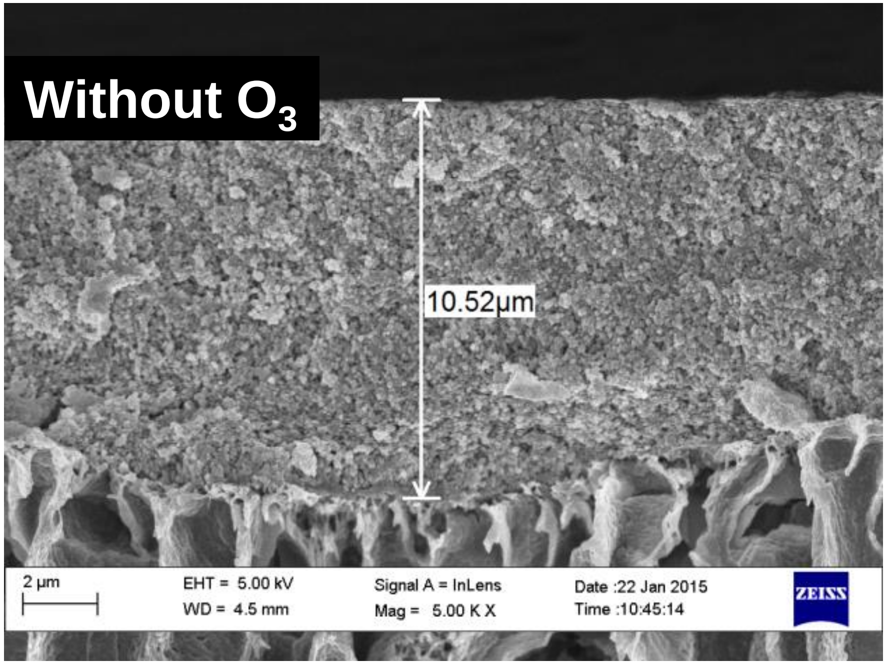


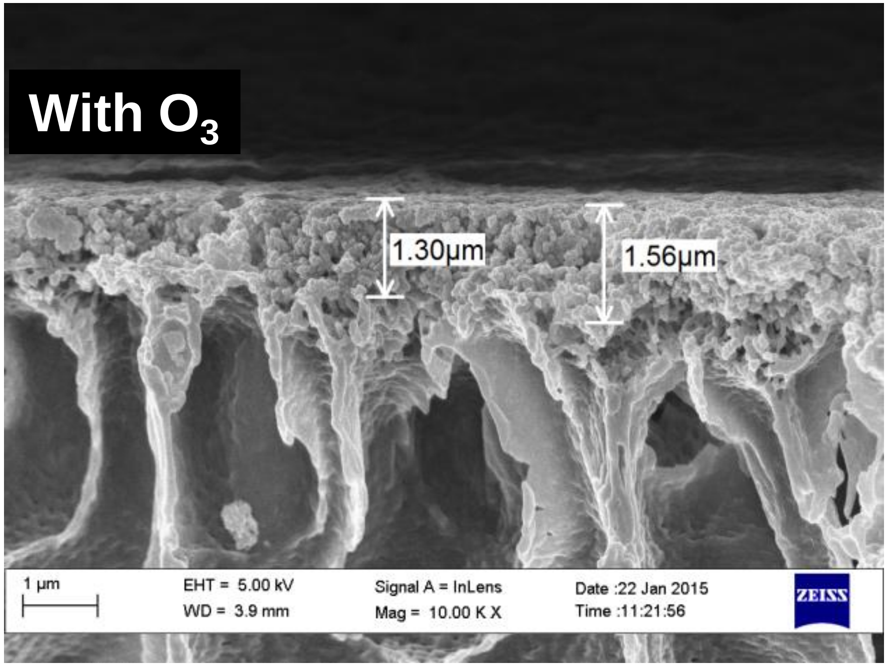
Polysaccharides



- **Much lower presence of proteins/polysaccharides in membrane cake with Ozone (esp. at 1.5 mg/L O_3)**
- **Reduction linked to lower bacteria numbers (generally less EPS)**

SEM images of fouled membranes (cake layer)

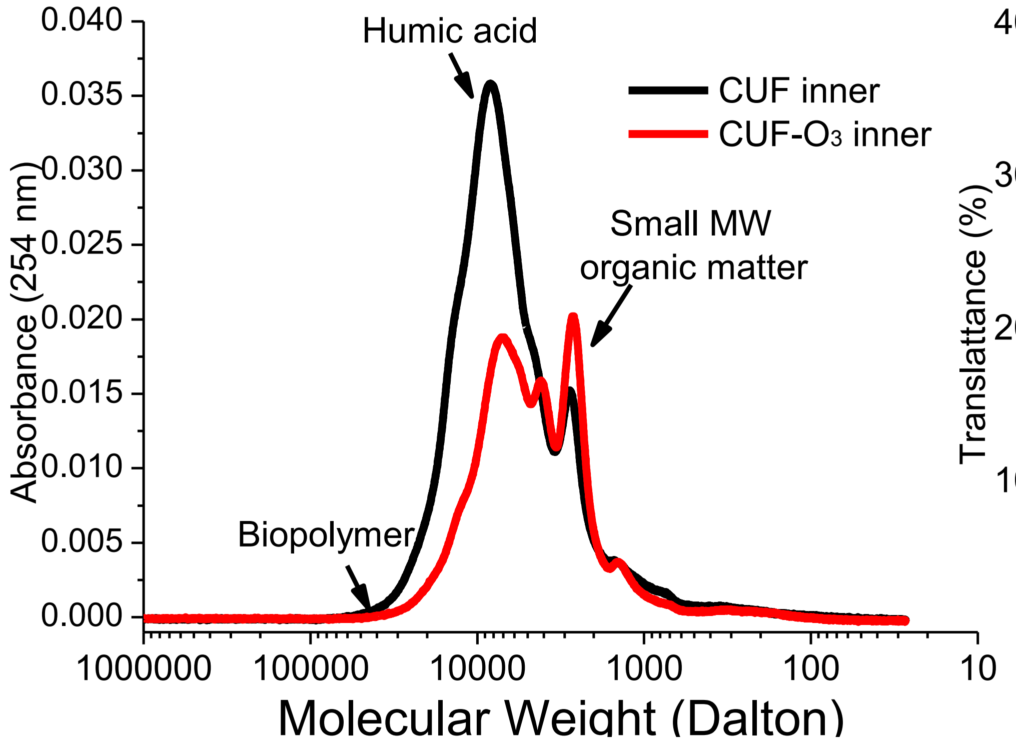




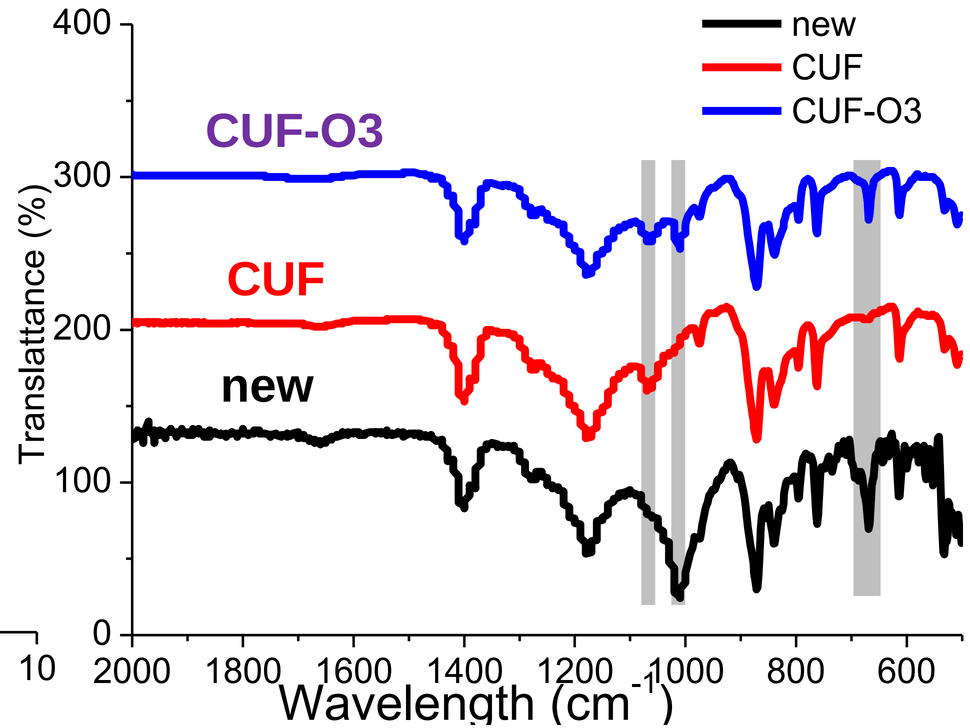
- **Much reduced cake thickness with Ozone**
- **Greater cake thickness without ozone consistent with greater quantities of EPS and EPS-bound material**

Evidence of inner membrane fouling

Organics extracted



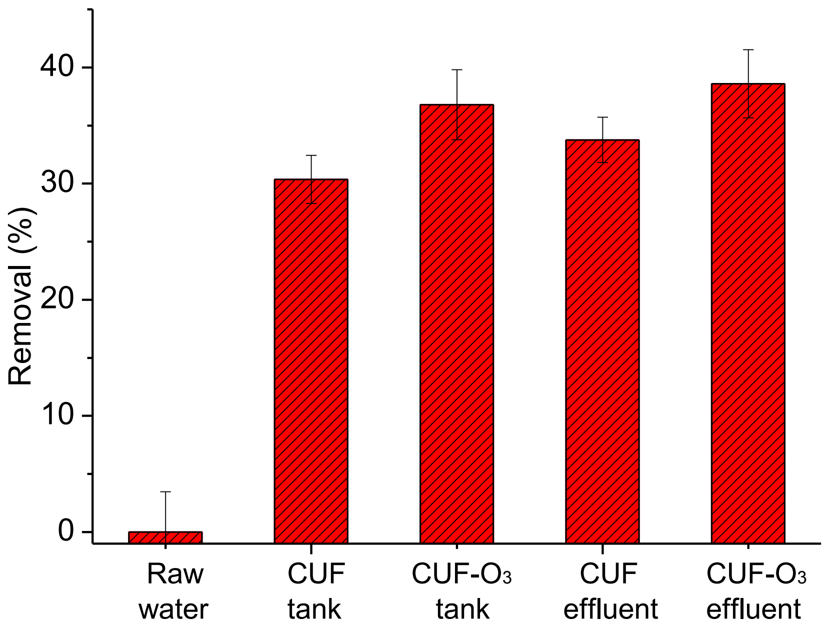
FTIR spectra of fouled membranes



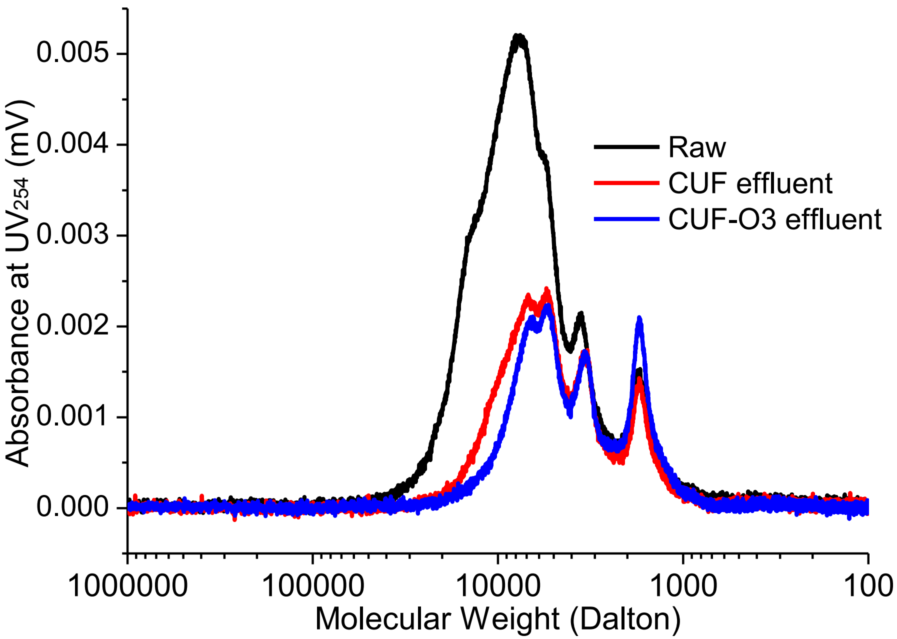
- **Much less high MW organic matter, but more of low MW, with Ozone**
- **FTIR results indicated less adsorption of organic matter in pores with ozone (less reduction in specific spectral peaks)**

Treatment of organic substances (1.5 mg/l O_3)

TOC removal



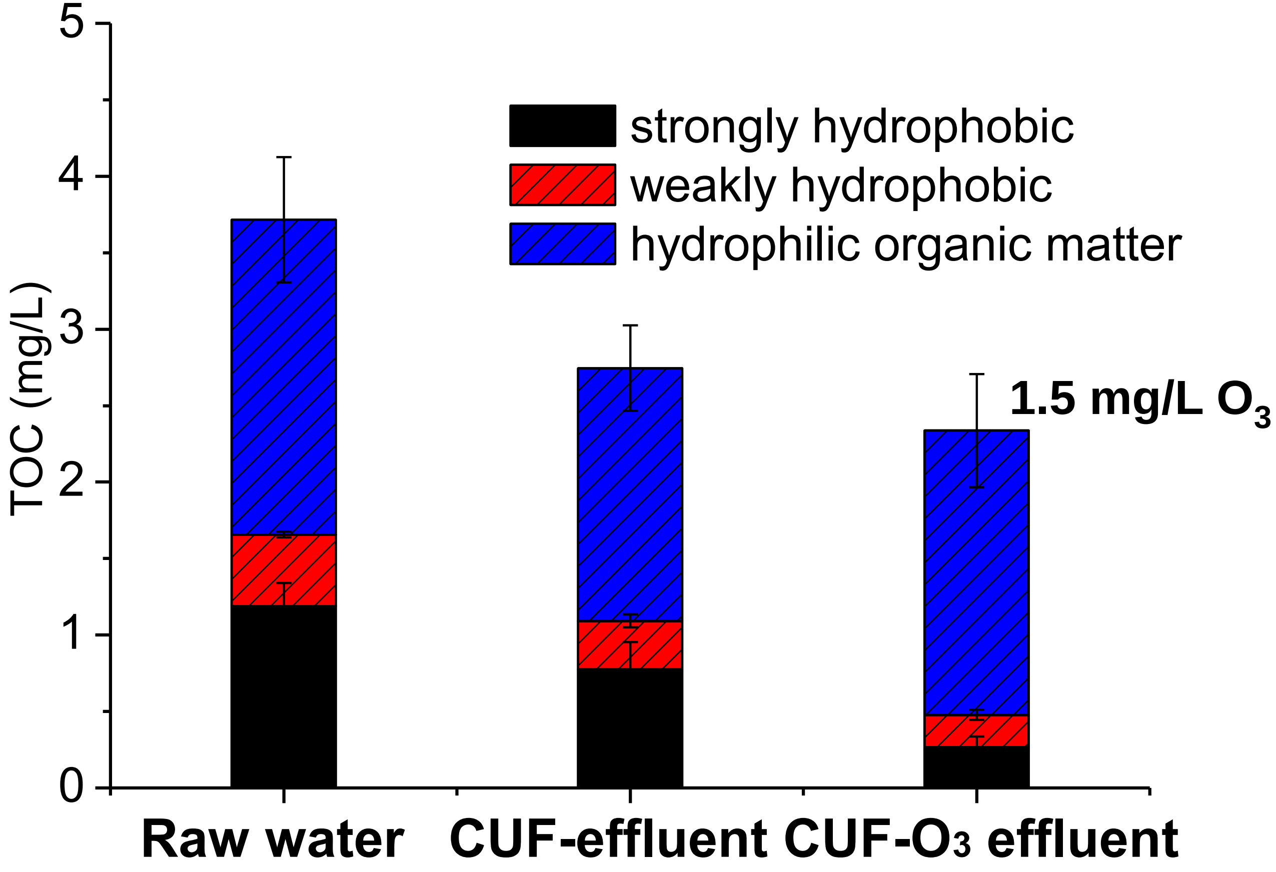
MW Distribution



- **Ozone reduces TOC level within membrane tank, and overall process**
- **Ozone reduces MW of UV adsorbing organic fractions**

Treated (permeate) waters

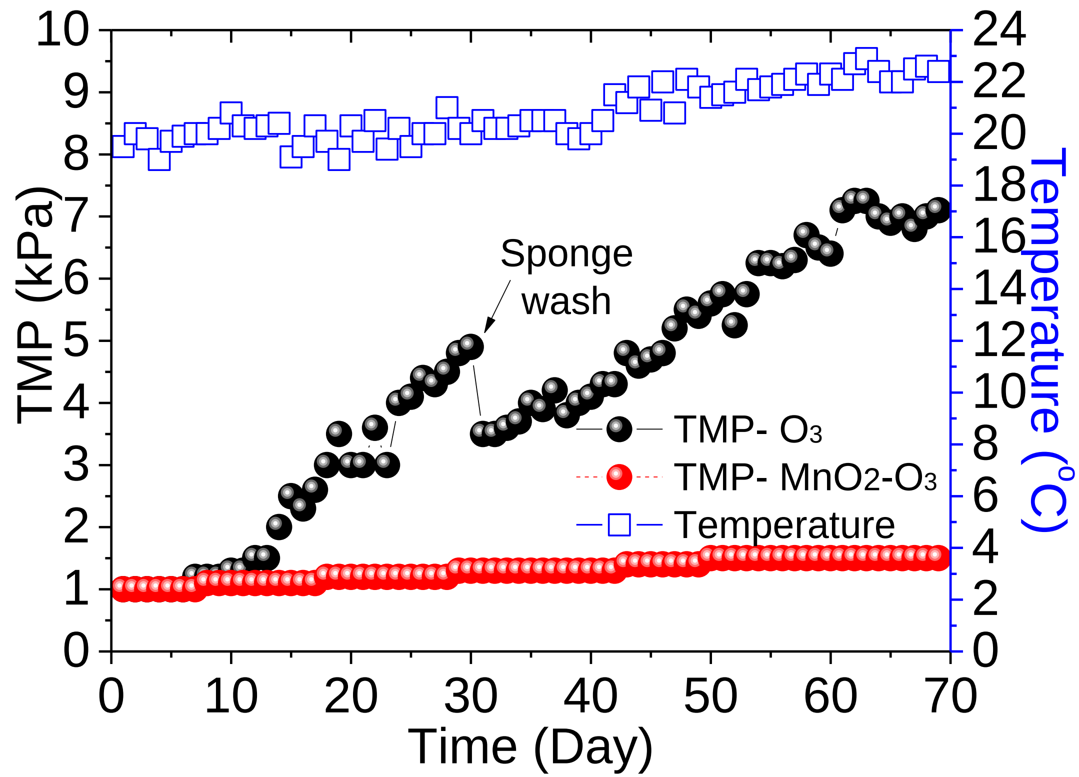
Hydrophilic and hydrophobic components



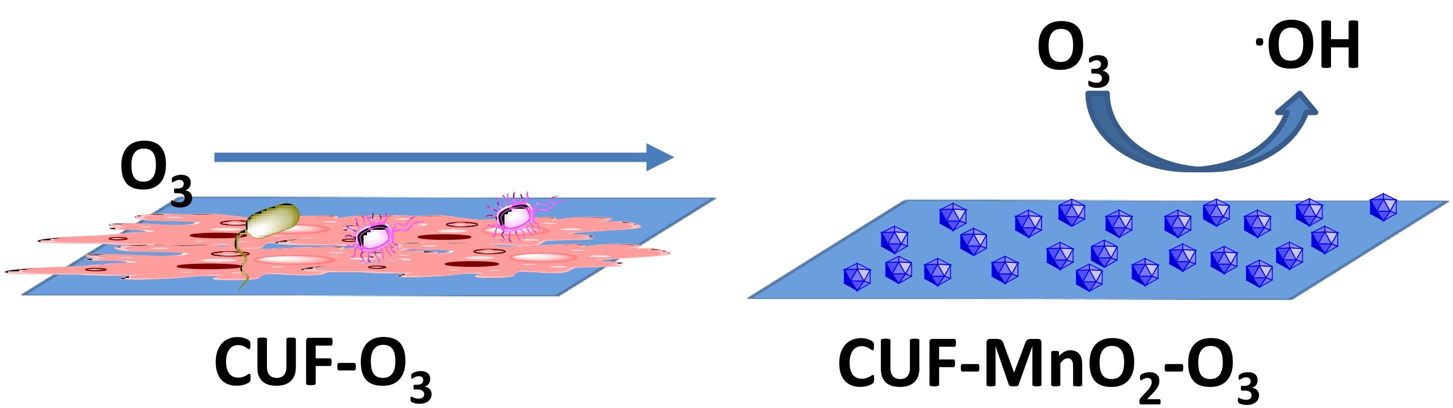
- **Ozone substantially reduces hydrophobic organic fractions**
- **Potential beneficial impact of disinfection byproduct formation**

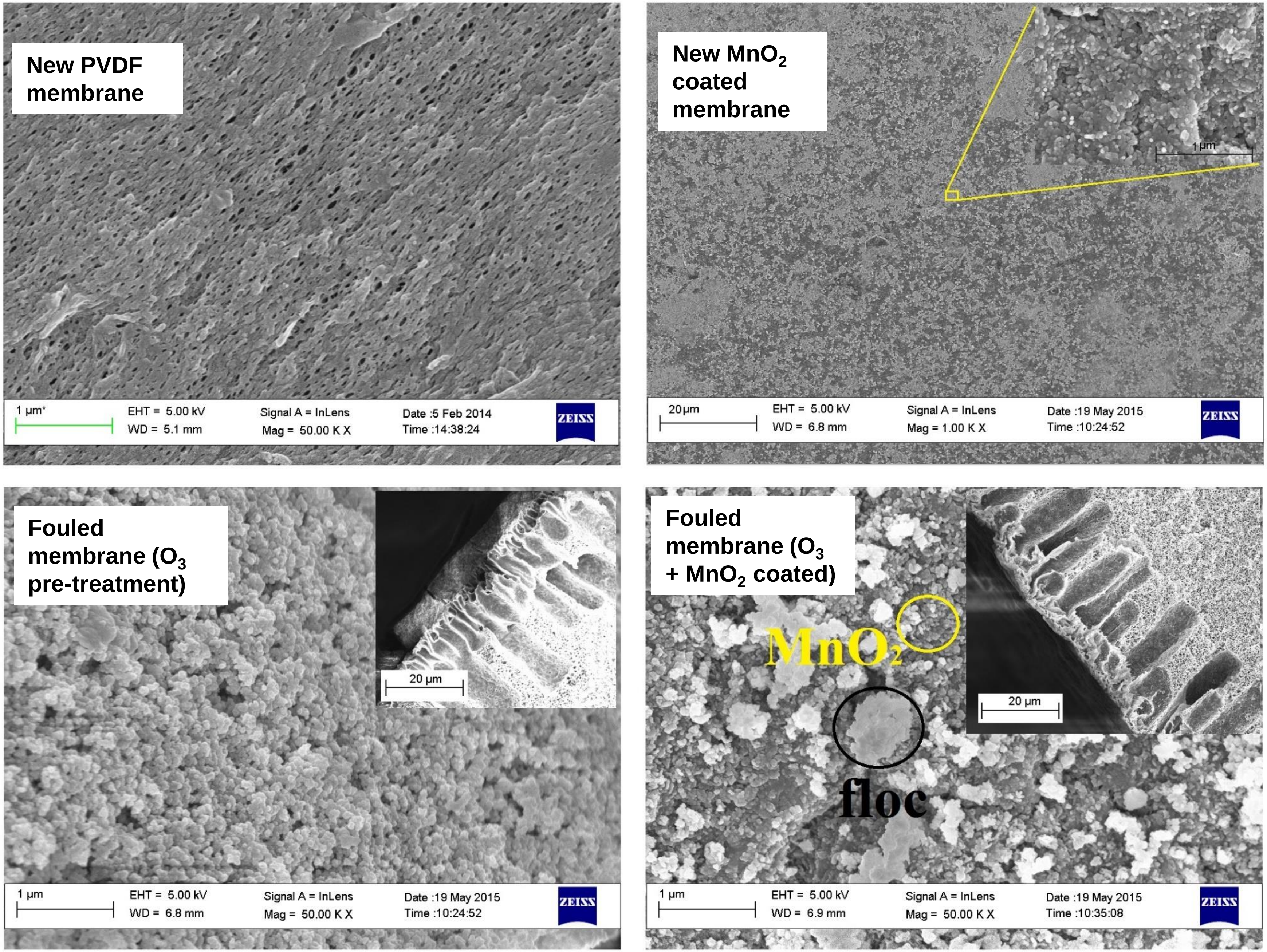
Membrane Coating with MnO_2 nanoparticles

- **MnO_2 coating of UF membrane surface**
- **Addition of 1 mg/L ozone**
- **MnO_2 catalyzes O_3 decomposition to OH° radicals**
- **Surface, and near-surface, conditions highly oxidative**

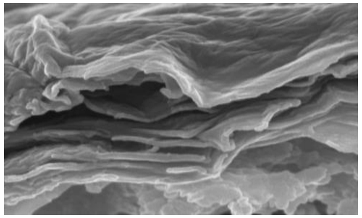


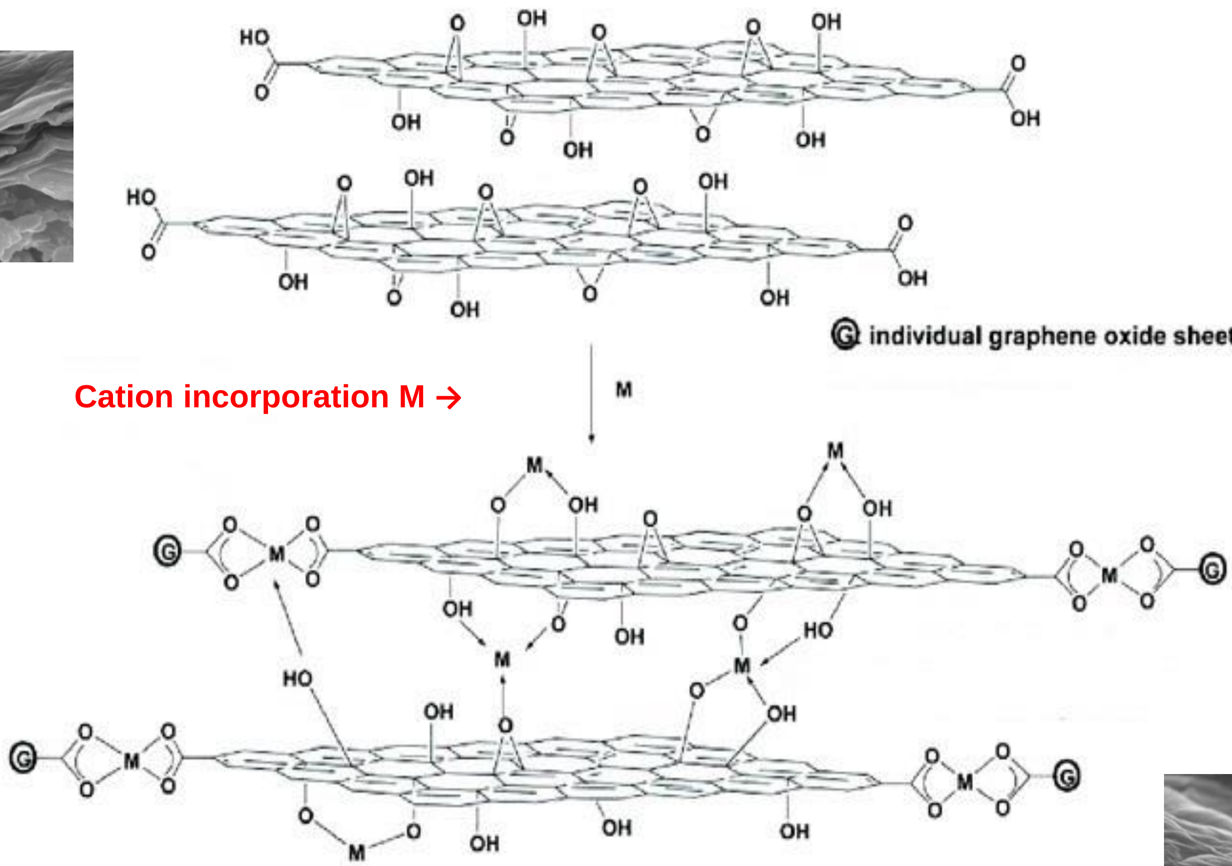
- **Minimal increase in TMP – indicates absence of fouling**
- **No significant cake development over 70 days**

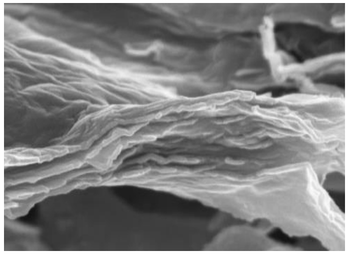



New PVDF membrane
1 µm
EHT = 5.00 kV
WD = 5.1 mm
Signal A = InLens
Mag = 50.00 K X
Date :5 Feb 2014
Time :14:38:24
ZEISS
New MnO_2 coated membrane
1 µm
20µm
EHT = 5.00 kV
WD = 6.8 mm
Signal A = InLens
Mag = 1.00 K X
Date :19 May 2015
Time :10:24:52
ZEISS
Fouled membrane (O_3 pre-treatment)
20 µm
1 µm
EHT = 5.00 kV
WD = 6.8 mm
Signal A = InLens
Mag = 50.00 K X
Date :19 May 2015
Time :10:24:52
ZEISS
Fouled membrane (O_3 + MnO_2 coated)
MnO_2
floc
20 µm
1 µm
EHT = 5.00 kV
WD = 6.9 mm
Signal A = InLens
Mag = 50.00 K X
Date :19 May 2015
Time :10:35:08
ZEISS

Novel Graphene Oxide Membrane Technology



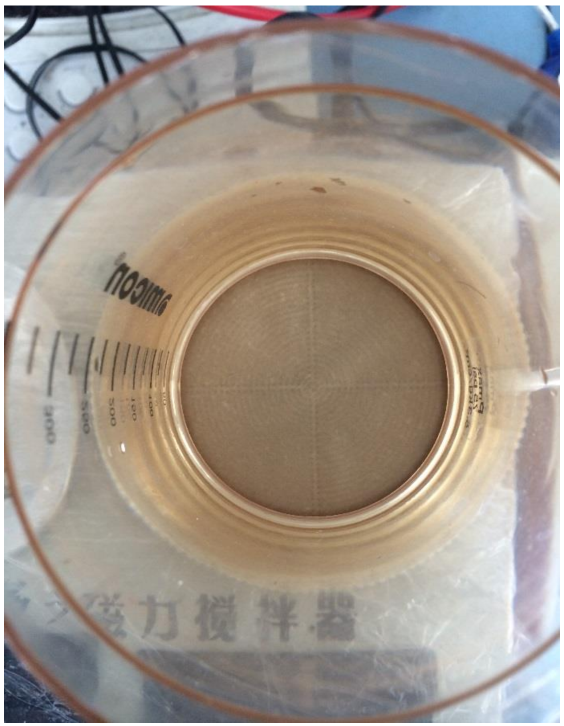




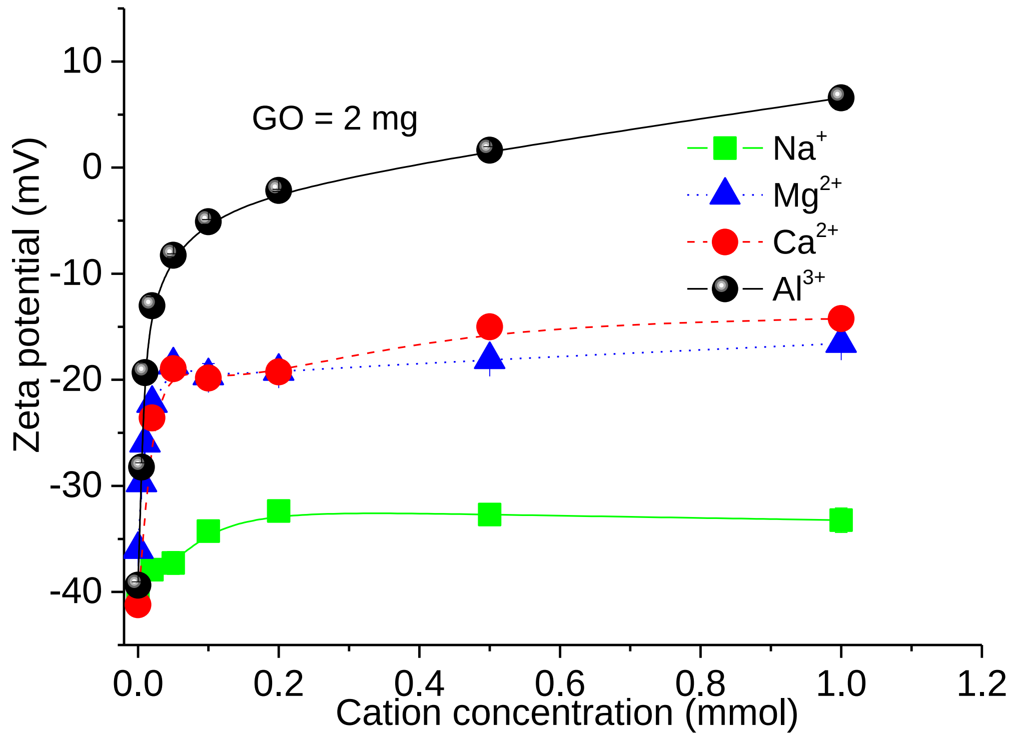
M = Mg^{2+}, Ca^{2+} and Al^{3+}

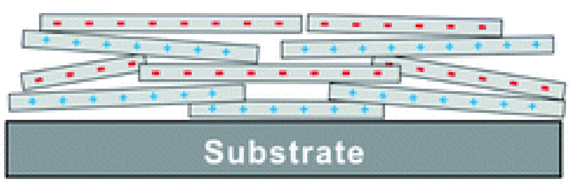
Development of a stable cation-modified GO Membrane for Water Treatment

Preparation of 2 mg GO membranes on CE or PVDF support



GO Surface Charge

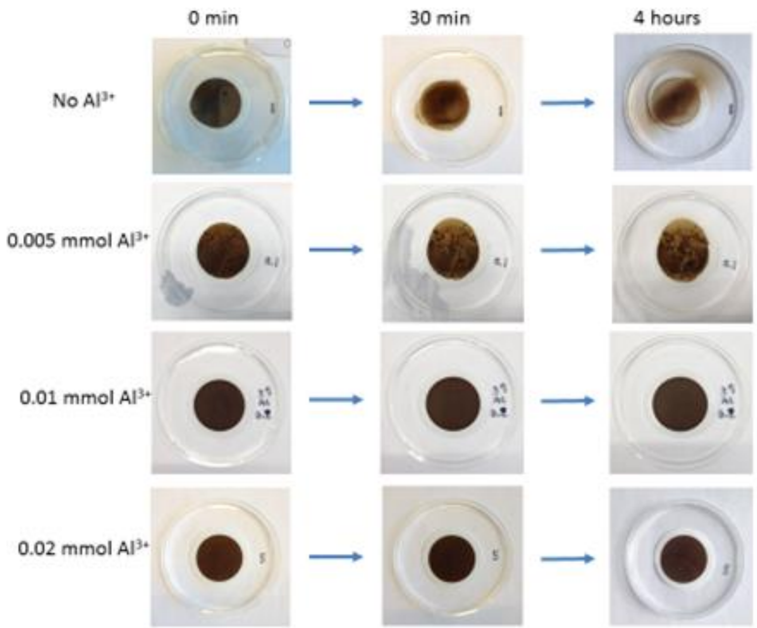




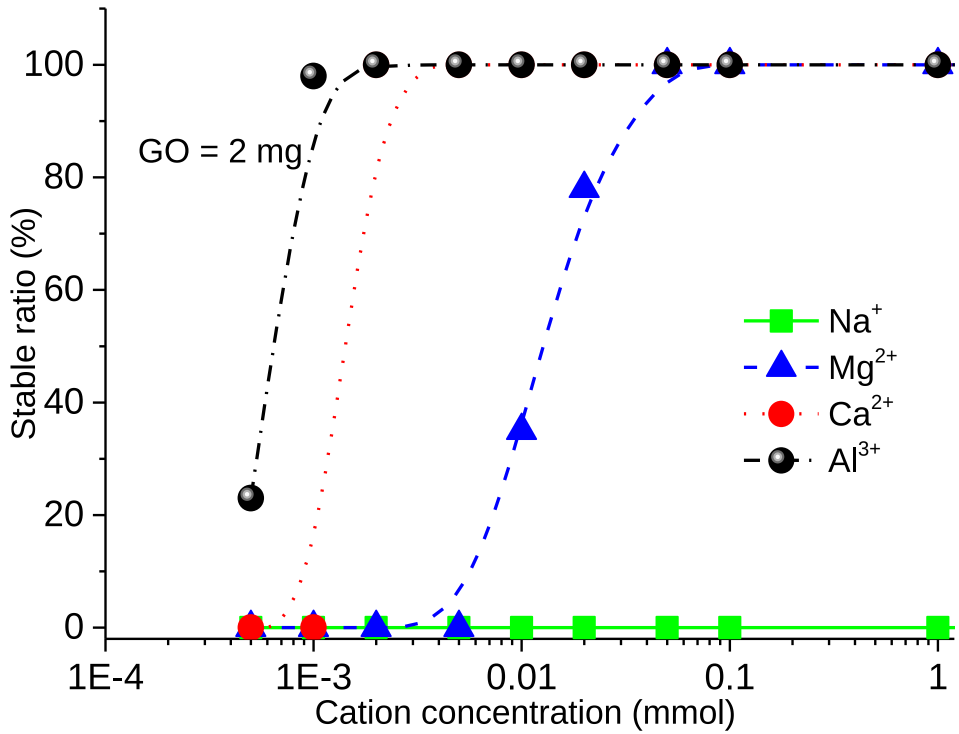
Laminates of GO flakes

Ref: RSC Publishing

Stability of GO Membranes

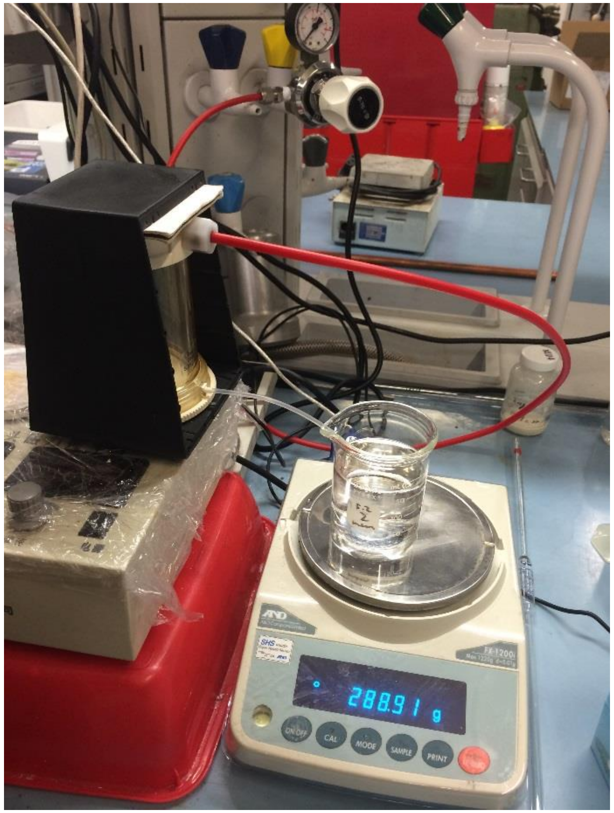


Membrane stability in Water

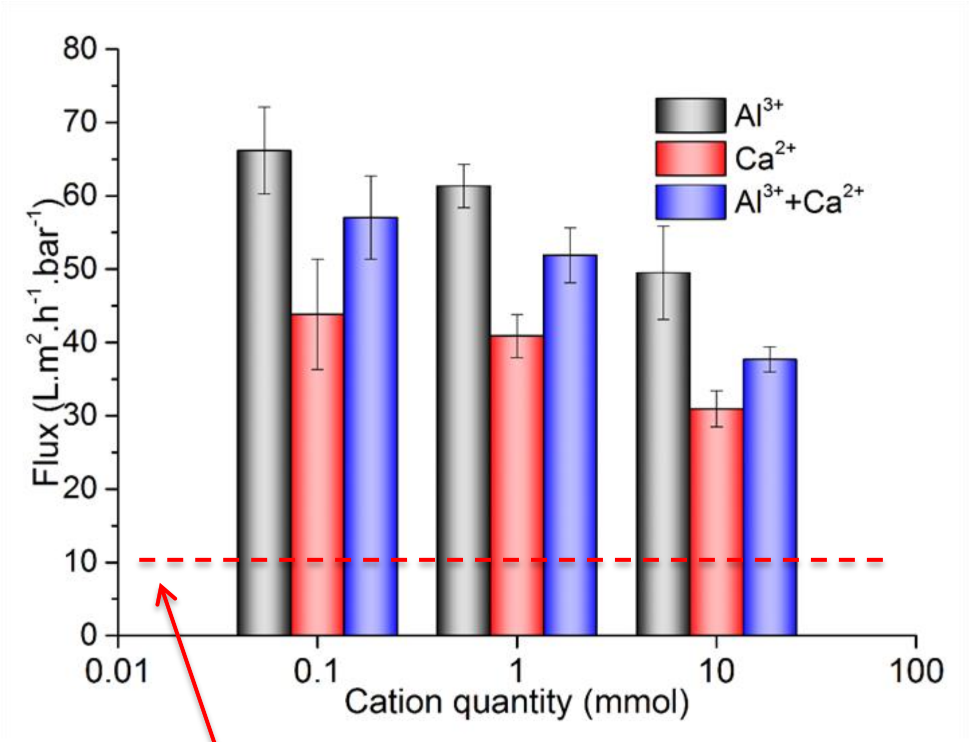


- Stability influenced by surface charge on GO, type (valence) of cation, quantity of incorporated cation
- Stability affected by strength of cation-GO bonds, influent water quality, etc.

Development of a stable cation-modified GO Membrane for Water Treatment



Stability and treatment performance (dead end flow arrangement, 1-5 bar)

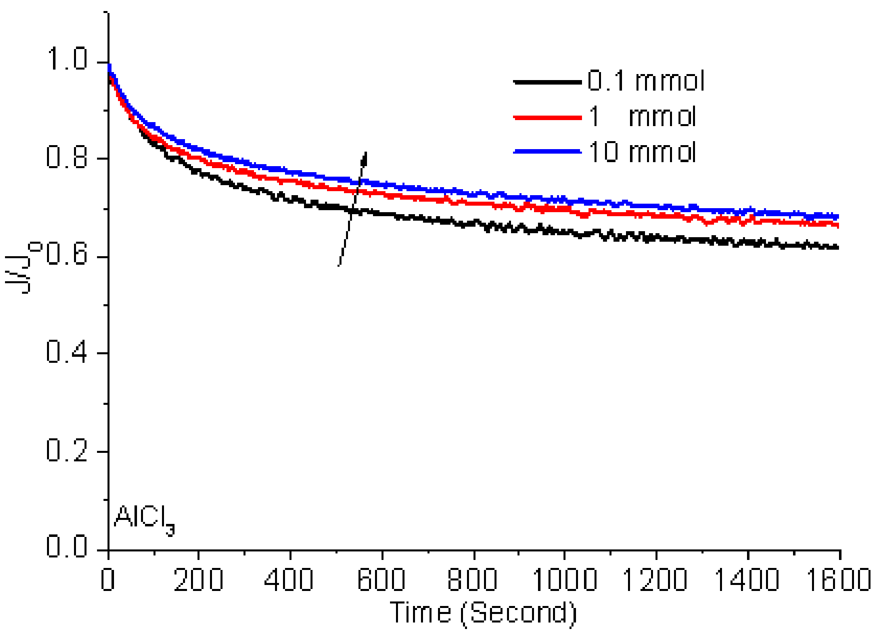


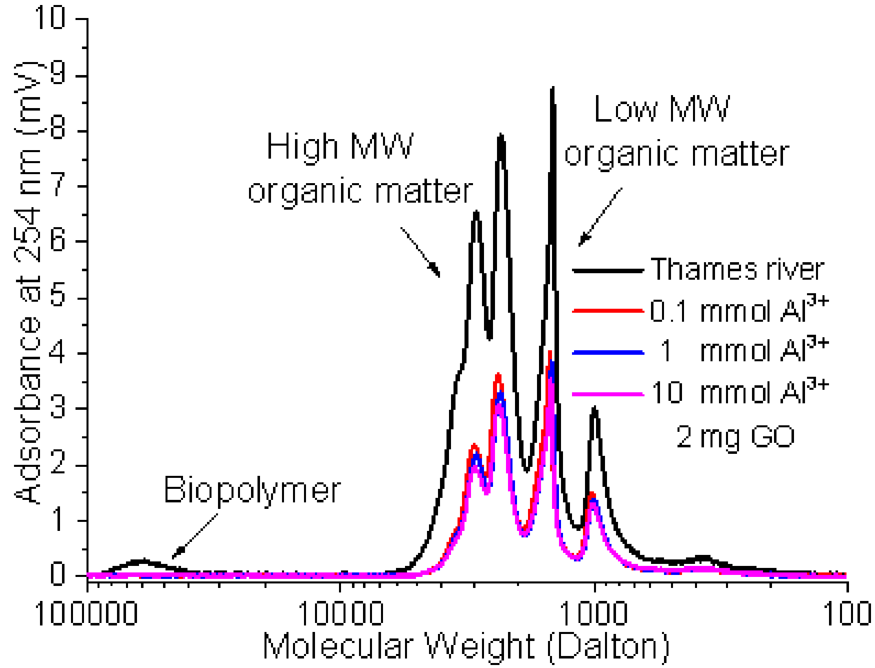
Typical NF flux ~ 10 L m^2 / h. bar

- **Flux declines with greater cation content**
- **Flux much greater than typical NF (> 5x for Al-GO/UF)**

GO Membrane Performance

Flux and treatment of samples of River Thames – influence of Al content





- **Flux decline less with greater Al content**
- **Substantial removal of broad range of organic matter**
- **Slight increase in organic separation with Al content**

Summary & Future Work

- Control of microbial activities is a key objective to minimizing membrane fouling.

- All methods studied so far have improved performance, but to different degrees.

- Non-chemical methods (e.g. pulsed UV, ultrasound) warrant further research, and potentially anti-microbial surface coatings

- Further investigation of GO-based membranes (e.g. stability and long-term performance)

Acknowledgements

- EPSRC (Twenty65), EU 'Marie Curie' Fellowship, colleagues and PG/UG students

Imperial College London

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