Utilizing benefits by combining micro-/ and ultrafiltration with other processes

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Combining micro-/ and ultrafiltration (MF and UF) with other processes

- Treatment Target
- Turbidity/Particles
- Multistage treatment with membranes
- Polymeric/Ceramic MF/UF Membrane
- Ceramic Membrane
- Disinfection (optional)
- Distribution Net

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- Coagulation and/or MIEX®
- Sedimentation and/or Conventional Filtration or Flotation
- Oxidation (e.g. KMnO₄, O₂)
- CO₂-Dosage, Calcite Filtration
- Powdered Activated Carbon
- Activated Carbon Filtration
- Ozonation, Activated Carbon Filtration
- Dehardening/ decarbonization/ precipitation
- Flotation
- Ozonation, Residual Ozone Destruction
- Ceramic Membrane
- Manganese Removal
- Nanofiltration/ Reverse Osmosis
- Stabilization
- Oxidation (e.g. KMnO₄, O₂)
- Manganese Removal
- MIEX
- Biofiltration
Summary

- Combined membrane processes can produce synergies
  - Combined coagulation/membrane filtration
    - increase the removal for dissolved organics
    - decreases the required dosage of coagulant (if needed for particle removal)
    - decreases fouling
  - Combined ozonation/membrane filtration
    - increases the removal of oxidizable compounds
    - decreases the required dosage of ozone (if needed for disinfection)
    - decreases fouling
  - Combined PAC/membrane filtration
    - increases the removal of adsorbable compounds
    - decreases the required dosage of PAC (as single dosage is possible)
    - decreases fouling (first single results give reason for believing in this)
- BUT: operational parameters have to be optimized and properly adjusted
Foulants in MF/UF

- Inorganic and organic colloids
Different fractions of DOC (dissolved organic carbon)

LC-OCD chromatography by DOC Labor Huber

- Building Blocks
- Humics
- Acids
- Low molecular weight amphiphilics & neutrals
- Polysaccharides

Time ~ decreasing molecular weight

OCD-Signal ~ DOC concentration
Foulants in MF/UF

- Inorganic and organic colloids
- High molecular weight organics e.g.
  - Biopolymers,
    - polysaccharides,
    - proteins,
    - polyhydroxyaromatics,
    - amino sugars
  - TEP = transparent exopolymeric particles
    - negatively charged biopolymers usually colonised by bacteria
- Low molecular weight organics either charged or neutral
Foulants in MF/UF
- sticks on membrane surfaces or on/in membrane pores
Foulants

- Foulants in MF/UF
  - sticks on membrane surfaces or on/in membrane pores
  - crosslinks particles and particles and membrane
Foulants

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- cannot be removed by backwashing (irreversible fouling)
Foulants

Foulants in MF/UF

- sticks on membrane surfaces or on/in membrane pores
- crosslinks particles and particles and membrane
- cannot be removed by backwashing (irreversible fouling)
- cannot be removed by chemical cleaning (chemically irreversible fouling)
How to reduce irreversible fouling

**Pre-treatment**

- **Coagulation**
  - to remove high molecular weight organics
  - to remove colloids
  - to enhance backwash efficiency
- **Anionic resins (MIEX ®, SIX ®)**
  - to remove charged organics (either of low or high molecular weight)
- **Powdered activated carbon (PAC)**
  - effect unclear (may be deep bed filtration effect)
- **Combined coagulation and PAC dosage**
  - PAC improves the cake behavior of the flocs → more permeable layers, further enhanced backwash efficiency
- **Ozonation**
  - residual ozone on the membrane surface increases membrane permeability
Principle of the Coagulation / UF combination

**UF, flow direction**

**Solid Substances**
- particles, colloids, e. g.
  - bacteria
  - parasites
  - algae
  - clay particles
  - viruses

**Dissolved Substances**
- organic subst., high-molecular
- organic subst., middle-sized
- organic subst., low-molecular

Inorganic subst.:
- ions, polyvalent
- ions, monovalent

Floc
Effect of coagulation prior to UF

Results of pilot experiments in Addur (Persian gulf)

Without FeCl₃

With FeCl₃
Effect of coagulation on membrane performance

Switching off of dosage pump

Switching on of dosage pump
Combined Coagulation-UF

Options of dosage of coagulant

Feed-Pump

Membrane Modul

Source Water

Filtrate Tank
Combined Coagulation-UF

Options of dosage of coagulant

Feed-Pump

Coagulant

Source Water

Membrane Modul

Filtrate Tank

$t_{Retention} = 5 - 10 \text{ s}$

$G > 1,000 \text{ s}^{-1}$  $G \sim 100 \text{ s}^{-1}$

$t_{Retention} = 5 - 10 \text{ min}$
Combined Coagulation-UF

Options of dosage of coagulant

Source Water

Coagulant

Feed Pump

G ~300 s⁻¹

t_{Retention} > 45 s

Membrane Modul

Filtrate Tank

Options of dosage of coagulant
Combined Coagulation-UF

Influence of retention time

Kinetics-Experiment
FeCl₃-dosage: 1 mg/l Fe

<table>
<thead>
<tr>
<th>Time [s]</th>
<th>Concentration Fe₅olved [mg/l]</th>
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<tbody>
<tr>
<td>0</td>
<td>n.d.</td>
</tr>
<tr>
<td>20</td>
<td>n.d.</td>
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<tr>
<td>40</td>
<td>n.d.</td>
</tr>
<tr>
<td>60</td>
<td>n.d.</td>
</tr>
<tr>
<td>80</td>
<td>n.d.</td>
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<tr>
<td>100</td>
<td>n.d.</td>
</tr>
<tr>
<td>120</td>
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specific dosage
Combined Coagulation-UF

- By coagulation ...
  - ... smaller colloids are embedded in larger floc-aggregates and are thus not able to contribute to a pore blocking
  - ... adsorbable molecules are hold off from the membrane

- It is to avoid ...
  - ... forming layers made of smallest, compact flocs
  - ... residual concentration of the coagulant on the membrane

- Important factors are ...
  - pH-value (in dependency on kind of coagulant)
    - pH 6.2 - 6.5 with Al-Sulfate, up to pH 7 with Poly-Al-Chloride
  - G-value in between 300 und 500 s⁻¹ with inline-coagulation
  - retention time > 45 s
  - periodic CEB (e.g. alternate alkaline-acidic)

- Further on ...
  - the mass load has to be adapted to the capillary geometry (flux and filtration time, concentration of coagulant)
Advanced drinking water treatment technology in Roetgen/Aachen/Germany (6,000 m³/h)

Pre-filtration

PAC (optional)

NaOH / CO₂

Al₂(SO₄)₃

Coagulation (in-line)

Re-feed

UF 1. Stage

UF 2. Stage

sludge containing water

CO₂

Neutralisation

NaOH (optional)

Desinfection

Storage Tank

Discharge

Reservoir
Pilot investigations on combined
- ozonation, coagulation, and ceramic membrane filtration (microfiltration)

Source water: spring water in Lucerne/Switzerland
- serious quality changes after heavy rains
- high content of organic and inorganic colloids with high affinity to plug membrane pores
What we wanted to know

- Long term performance of process chain depending on
  - dosage of ozone,
  - dosage of coagulant,
  - combined dosage of both

- Design data for the technical process
Ceramic membranes from Metawater

- **3rd generation**
  - $L = 1.500\text{mm}$
  - $25\text{m}^2$

- **2nd generation**
  - $L = 1.000\text{mm}$
  - $15\text{m}^2$

- **Small membrane element (1st generation; 0.4 m}^2)
Design of the monolith

Feed Channel
Ø 2.5 mm

Plugged passageways which isolate filtrate conduits from feed flow channels. Opposite end has exactly same appearance.

Filtrate flows in conduits to end of module

Open slots for filtrate removal from successive layers of conduits. Slots pass across monolith piercing skin and coincide completely with conduit layers.
Ceramic membranes from Metawater

- Ceramic Microfiltration (MF): $\alpha$-$\text{Al}_2\text{O}_3$
  nominal pore size 0,1µm
Speciality of Ceramic MF: Backflush process

**Filtration**
- Feed
- Filtrate

**Backflush**
- Backflush Water
- Waste Water

**Air Flush**
- Pressurized Air

**Dead-End Filtration**
- In-Out

**Backflush Pressure:** 5 bar
- **Duration:** 2 - 20 sec

**Air Pressure:** 2 bar
- **Duration:** 2 - 3 sec
Moduls and Systems

Source: Metawater
Pilot results

- Treatment of spring water highly affected by surface water with 3 (4) independant lines operating with ceramic MF

- Turbidity 0.5 – 50 NTU
- DOC 0.6 – 2.4 mg/l
- $\text{UV}_{254}$ 1.6 – 8.2 m$^{-1}$
- Temp. 6 – 10°C
Pilot results line 1

- Coagulation (Polyaluchlorid) → Ceramic MF, 0.8 m²
- Filtration time 30 min, 3-6 mg/l Al, acidic CEB each 3rd BW

(CEB = Chemical enhanced backwash)
Pilot results line 2

- **Ozone → Ceramic MF, 0.8 m²**
- **Filtration time 210 min, no CEB, 0.4 mg/l residual ozone at outlet reactor**
Pilot results line 3

- Ozone → Coagulation (Polyaluchlorid) → Ceramic MF, 0.8 m²
- Filtration time 210 min, 0.5 mg/l Al, no CEB, 0.4 mg/l residual ozone at outlet reactor
Ozone $\rightarrow$ Coagulation (Polyaluchlorid) $\rightarrow$ Ceramic MF, 25 m²

Filtration time 30 min, 0.5-2 mg/l Al, acidic CEB each 16th BW, 0.25 mg/l residual ozone at outlet reactor
Pilot results line 1

- Coagulation (Polyaluchlorid) → Ceramic MF, 0.8 m²
- Filtration time 60 min, 0.5-5 mg/l Al, acidic CEB each 5th BW

![Graph showing permeability, TMP, and flux over time](chart.png)

- Permeability 20°C
- TMP
- Flux l/m²h

*completely fouled membrane*
Pilot results line 1: cleaning effect

- Ozone → Coagulation (Polyaluchlorid) → Ceramic MF, 0.8 m²
- Filtration time 60 min, 0.5-5 mg/l Al, acidic CEB each 5th BW, 0.25 mg/l residual ozone at outlet reactor
Effect of residual ozone

- Enhancement of BW efficiency by oxidation organic foulants
- Effect depends on concentration of residual ozone on the membranes surface
- Assumptions:
  - Ozone is concentrated on the membrane surface and in the membrane pores (e.g. by adsorption) and meets foulants concentrated there as well
    - → highly enhanced mass transfer, short distances between foulants and ozone, effective and specific oxidation of foulants
  - Catalytic effect with metallooxide surface
    - → formation of OH-radicals → NO!
  - ???
Investigation of the hybrid process using Powdered Activated Carbon Adsorption and Microfiltration

- high removal of organic substances
- optimal usage of activated carbon adsorption capacity
Principle of the PAC / UF combination

**UF, flow direction**

**Solid Substances**
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  - parasites
  - algae
  - clay particles
  - viruses

**Dissolved Substances**
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- organic subst., low-molecular

**Inorganic subst.:**
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- ions, monovalent
Material and methods

- **Powdered activated carbon**: Jacobi Aquasorb 5000, PAC-MG (average diameter = 5 µm)

- **Raw water**
  - Synthetic model water, SMW

- **Organic test substance**
  - Diclofenac - DFC (5 mg/L)
    (measured by UV spectroscopy)

- **Lab membrane module**
  - PALL Microza MF (PVDF) (~ 0.1 µm)
  - Membrane surface: 0.26 m²

- **Contact time**: 30 sec
Material and methods

Operation
Out/In filtration
Flux: 140 L/m²h
60 min filtration time

Raw water

Organic Substance

PAC

30 sec contact time
Material and methods

Backwash
Simultaneous Air Scrubb with Reverse Filtration

Flux: 208 L/m²h
Air assistance: 2 bar
Experimental Overview

- **Part 1: Influence of activated carbon dosage mode**
  - Step by step from continuous to single pulse dosage mode

- **Part 2: Influence of activated carbon slurry preparation**
  - Formation of carbon agglomerates and their influence on the process when single pulse dosage mode is used
Results PART 1
Influence of activated carbon dosage time

Carbon dosage time (Average Removal)
- 60 min (28.5 %) (= cont. dosage)
- 40 min (36.2 %)
- 20 min (39.3 %)
- 10 min (43.8 %)
- 1 min (48.0 %) (= single pulse dosage)

Feed: 5 mg/L DFC in SMW
PAC conc.: 5 mg/L
Discussion PART 1
Influence of activated carbon dosage time

Single pulse → higher average removal → higher loading of the carbon → “Filter effect”
Discussion PART 1
Influence of activated carbon dosage time

Single pulse → higher average removal → higher loading of the carbon → “Filter effect”
Results PART 2
Influence of activated carbon slurry preparation

- PAC slurry $\rightarrow$ high concentrations (several g/L)
- carbon particles $\rightarrow$ agglomeration tendency $\rightarrow$ up to more than 100 $\mu$m in size

1 $\rightarrow$ slowed adsorption kinetics
Results PART 2
Influence of activated carbon slurry preparation

2. → changed carbon distribution on the membrane

Carbon layer on the membrane surface for different PAC slurry concentrations
Results PART 2
Influence of activated carbon slurry preparation

Feed: 5 mg/L DFC in SMW
PAC conc.: 5 mg/L

Filtration time [min]

PAC slurry [g/L] | Removal [%]
--- | ---
3.6 | 33
1.8 | 41
0.9 | 47
0.2 | 54
0.05 | 55
0.005 | 54
Agglomerates negatively influence the process

→ slower adsorption kinetics

→ incomplete covering of membrane surface

→ further investigations – fully covered membrane – still negative effect

→ main reason - the reduced adsorption kinetics
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