Technologies for the Removal of Organic Micropollutants in Drinking Water Treatment

Waterworkshop
Chemistry Department of the Faculty of Sciences
University of Novi Sad
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Institute for Energy and Environmental Process Engineering / Water Technology

IWW Rhenish-Westphalian Institute for Water Research
Where we are?
Institute for Energy and Environmental Process Engineering
Water Technology

Chair: Professor Dr.-Ing. Rolf Gimbel

Research areas
- Membrane Technology
  Dr.-Ing. Stefan Panglisch / Dr.-Ing. Ralph Hobby
  M. Sc. Mathis Keller
  M. Sc. Grit Hoffmann
  M. Sc. Anik Deutmarg
- Fixed Bed Processes, Sorption Processes
  Dr.-Ing. Ralph Hobby
  Dipl.-Ing. Carsten Bäcker
  M. Sc. Grit Hoffmann
- Artificial Neural Networks (ANN)
  Dipl.-Ing. Silke Strugholtz
  M. Sc. Mathis Keller
- Computational Fluid Dynamics (CFD)
  M. Sc. Wei Ding
- Bioprocess Technology
  N. N.
- Xenobiotics, Nanoparticles in the Environment
  Dr.-Ing. Ralph Hobby
  Prof. Dr. Ivana Ivancev-Tumbas (Universität Novi Sad)

Cooperation with IWW in the Fields of
- Water Technology (Drinking Water, Industrial Water)
- Process Analysis and Analysis of Micropollutants
- Applied Microbiology (Hygiene, Biofouling)
Main Topics

- Actual problems and challenges of drinking water treatment

- Some modern conventional processes

- Non-conventional processes
  - Oxidation / AOP
  - Membrane filtration

- Conclusions
World Population Growth Between 1750 and 2050 (Source Data of the UN 1998)
Trouble Spot of the Global Water Use

- Increasing demand on water with an appropriate quality for irrigation and for supply of industry and communities (drinking water)

- Increasing demand on water supply and waste water discharge in conurbations (megacities, megalopolis)

- Increasing pollution of water resources with anthropogenic compounds
  ⇒ xenobiotics, organic micropollutants

- Climatic change
  (especially increasing of extreme dry spells and extreme rain falls)

⇒ The World‘s Water Crisis ⇐
Water Technology as Support for the Solution of the World‘s Water Crisis

- Waste water treatment for sustainable water protection
- Waste water treatment for closing water cycles in industry and trade
- Waste water treatment for waste water reuse (e. g. irrigation)
- Treatment of ground water and surface water to produce clean drinking water
- Water treatment for special use (e. g. process water)
- Desalination of brackish water and sea water
- ...

...
Variety of Substances in Water

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 substances:
  - ions, polyvalent
  - ions, monovalent
  - gases

Some actual „groups of interfering substances“:
- too high salt concentration........................................................................................................~ kg / m³
- nutrients........................................................................................................................................~ g / m³
- micropollutants
  (e. g. EDCs, PPCPs, Pesticides, several metabolites,
  industrial chemical products like MTBE, PFT, EDTA).............. ~ µg till mg / m³
- persistent pathogens......................................................... ~ 1 Particle / m³ or 10⁻³ ng / m³

- in the future nanoparticles?
## Some Organic Micropollutants...

<table>
<thead>
<tr>
<th>Groups of Substances</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hormones, EDCs</td>
<td>17α-ethinylestradiol, 17β-estradiol, estrone</td>
</tr>
<tr>
<td>Pharmaceuticals (contrast agents)</td>
<td>Diclofenac, Ibuprofen (both antiphlogistics), Bezafibrate (lipid regulator), Diazepam (tranquilizer), Carbamazepine (anti-epileptic), Iopromide, Iopamidol, Diatrizoic acid</td>
</tr>
<tr>
<td>Personal care products</td>
<td>Tonalide (AHTN), Galaxolide (HHCB) (musk fragrances)</td>
</tr>
<tr>
<td>Disinfectants</td>
<td>Triclosan</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Fluorosurfactants, (Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA))</td>
</tr>
<tr>
<td>Flame retardants</td>
<td>Organophosphates</td>
</tr>
<tr>
<td>Gasoline additives</td>
<td>Methyl tertiary butyl ether (MTBE),</td>
</tr>
</tbody>
</table>
Characteristics of “waterworks relevant” and “drinking water relevant” Micropollutants

e. g. some EDCs, PPCPs, Pesticides, several metabolites, industrial chemical products like MTBE, PFT, EDTA

- Low or none biodegradability
- Chemical stability
- High polarity respectively high water solubility
- Low tendency to adsorb

→ Low or no removal efficiency in soil passage

→ Characteristics of micropollutants are very important for the efficiency of treatment steps
  - e. g.
    - water solubility
    - octanol-water partition coefficient (log $K_{OW}$)
Main Topics

- Actual problems and challenges of drinking water treatment
- Some modern conventional processes
- Non-conventional processes
  - Oxidation / AOP
  - Membrane filtration
- Conclusions
Processes for Drinking Water Treatment

- Bank Filtration
- Aeration
- Flocculation
- Sedimentation
- Rapid Filtration
- Adsorption (GAC)
- Oxidation (Ozonation)
- Advanced Oxidation Processes (AOP)
- Nanofiltration, Low Pressure RO
- Adsorption onto PAC / Micro-, Ultrafiltration
Bank Filtration

Infiltration via river or lake

Removal of org. and inorg. compounds by microbiological processes

Oxygen reduction

Denitrification, Reduction of Mn and Fe

Reduction of sulfate, CH₄ formation

Groundwater Flow – Change of Hydrochemical Conditions

Konzentrationserhöhung: Physikalische / geochemische / mikrobielle Mobilisierung oder Produktion

Konzentrationsverminderung: Physikalische / geochemische / mikrobielle Eliminierungsprozesse

Schulte-Ebbert, 2004, modified
Modern Treatment of River Water with Conventional Technologies (Example)

River Ruhr  Pre-ozonation  Flocculation  Main-ozonation  DM-Filtration  GAC-Filtration

The „Mülheim Process“

⇒ Multibarrier System ⇐
Adsorption on Activated Carbon

- usual for the removal of organic micropollutants
- high removal efficiency for non-polar substances
- log $K_{OW}$ suitable indicator for
  - non-polar substances
  - substances without heterocyclic or aromatic bound nitrogen
    - log $K_{OW} > 3$ (→ removal efficiency 75 – 100 %)
- operation time of GAC filters dependent on sorption behaviour of micropollutants!
**GAC Process**

**Tap water:**
\[ C_{0,\text{Carbamazepin}} = 0.9 \, \mu g/L, \quad C_{0,\text{Iopromide}} = 1 \, \mu g/L \]

- Carbamazepine in effluent of column 2
- Iopromide in effluent of column 2

**GAC filter, effluent column 2:**
- GAC type: NORIT GAC 830
- \( h = 1 \, m \) (column 1 and 2)
- \( m_{\text{GAC}} = 1200 \, g \)
- \( v_F = 10 \, m/h \)

**Operating time in d**

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**IWW**
**GAC Process**

**Tap water:**
\[ C_{0,\text{Carbamazepin}} = 0.9 \, \text{µg/L}, \quad C_{0,\text{lopromide}} = 1 \, \text{µg/L} \]

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**Specific throughput in m³ water/kg GAC**
Breakthrough curves of different pharmaceuticals (incl. contrast agents) in GAC-Filter test

Quelle: Marcus, 2005
Oxidation with Ozone (as O$_3$)

- usually addition of approx. 1-2 mg O$_3$ per mg DOC
- ozone (as O$_3$) reacts selectively with substances which can be easily oxidised.
- the degradation rate for micropollutants depends strongly on the type of substance and ambient conditions (e.g. pH).
Rate Constant and Half Life Period (for 1 mg/L Ozone) for Some Pharmaceuticals Reacting with O₃ und ClO₂ (pH = 7)

Source: Ternes, 2006

Huber et al., 2005, Water Res.
Oxidation with Ozon (radical formation)

- during ozonation formation of highly reactive OH-radicals, which react non-selectively and their rate constants are between $10^7$ and $10^9$ L/(mol s)
- concentration ratio of OH-radicals and ozone (usually $\sim 10^{-9}$) is too low
- concentration ratio can be increased by Advanced Oxidation Processes (AOP) up to $\sim 10^{-6}$
Main Topics

- Actual problems and challenges of drinking water treatment

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- Non-conventional processes
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  - Membrane filtration

- Conclusions
Removal of Micropollutants by AOP

- Rate constants for the reaction of ozone respectively OH-radicals with pharmaceuticals 
  (Huber et al. 2003, Baus et al. 2007)

  - **AOP**
    - $\text{O}_3/\text{H}_2\text{O}_2$ (Peroxon-Process)
    - UV/$\text{O}_3$
    - UV/$\text{H}_2\text{O}_2$
    - Fe(II)/$\text{H}_2\text{O}_2$ (Fenton-Process)

- Radicals react non-selectively. But especially hydrogen carbonate ions and the natural organic matter act as scavengers

- Removal in % of pharmaceuticals in Lab experiments using ozone and hydrogen peroxide(data from Zwiener und Frimmel, 2000)
Some Critical Aspects Concerning O$_3$-Oxidation or Photolysis

- **Using ozone**
  - possible formation of substances, which may cause more problems due to their toxicity and removal efficiency than the substances in the raw water before the oxidation step (e.g. NDMA)
  - by-product formation (e.g. bromate, less with the Peroxon-Process)

- **Using UV**
  - high energy consumption (more than by the use of NF and RO for TDS < 5,000 mg/L)
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Principle of Membrane Filtration Processes

Flow Direction

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Flow Direction</th>
<th>Pore Size</th>
<th>Pressure Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse Osmosis (RO)</td>
<td></td>
<td>no pores</td>
<td>Δp = 5 - 100 bar</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td></td>
<td>d_pore ≈ 1 nm</td>
<td>Δp = 3 - 10 bar</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td></td>
<td>d_pore ≈ 10-50 nm</td>
<td>Δp = 0.1 - 5 bar</td>
</tr>
<tr>
<td>Microfiltration (MF)</td>
<td></td>
<td>d_pore ≥ 50 nm</td>
<td>Δp = 0.1 - 2 bar</td>
</tr>
</tbody>
</table>

**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 substances:
  - ions, polyvalent
  - ions, monovalent
Main Applications

- **RO:** Desalination of seawater and brackish water

- **NF/LPRO:** Removal of hardness, sulfate, colour, NOM (Natural Organic Matter), increasingly org. micropollutants (LPRO=Low Pressure Reverse Osmosis)

- **UF/MF:** Removal of suspended and colloidal substances, esp. microorganisms, in future possibly desinfection

- *(UF/MF in combination with PAC ⇒ Removal of organic micropollutants)*
LPRO/NF-Results with Polyfluorinated Tensides (PFOA)

<table>
<thead>
<tr>
<th></th>
<th>Tag1</th>
<th>Tag3</th>
<th>Tag5</th>
<th>Tag1</th>
<th>Tag4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rückhalt PFOA Versuch 1</td>
<td>99,6</td>
<td>99,7</td>
<td>99,8</td>
<td>99,9</td>
<td>96,1</td>
</tr>
<tr>
<td>Eingangskonzentration 100 µg/l</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rückhalt PFOA Versuch 2</td>
<td>96,9</td>
<td>97,3</td>
<td>99,95</td>
<td>99,96</td>
<td>98,0</td>
</tr>
<tr>
<td>Eingangskonzentration 10 µg/l</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- BW30
- XLE
- NF 90
- NF 270
Possibilities and Limits of LPRO / NF...

- Xenobiotics – also polar, persistent ones – are usually very good removable (e.g. Pesticides, PPCPs, PFT, MTBE, EDTA, different metabolites...)

- But: low retention of very small and uncharged molecules like Trichloroethene, Chloroform, NDMA (also using LPRO)

- Using „real“ NF the retention of substances with molecular weights between approx. 200 und 400 g/mole is strongly dependent on:
  - membrane material and membrane structure
  - substance!!!
  - water matrix

- Permeate is not comparable to the raw water with regard to the chemical composition

- Characteristics with regard to corrosion behaviour of the permeate are usually influenced negatively ⇒ Post Treatment!
Effective pretreatment step for particle removal necessary (no backwashing of spiral wounded modules)

Recovery only approx. 80 % (maximum 90 %) due to avoiding of scaling (clogging of the membrane)

In the concentrate are high concentrations of the retained pollutants (factor 5 – 10) and normally anti-scalants (10 – 50 mg/L)

Total costs (without pre- and post-treatment) are approx. 30-50 Cent/m³

Application may be more economical, if several conventional treatment steps can be replaced
Principle of the PAC / UF combination

**UF, flow direction**

**Solid Substances**
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  - viruses

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Use of PAC with Pressure Driven Membrane Filtration

Cross-Flow-Mode
(e. g. Cristal® process)
high energy consumption

Dead-End-Mode
low energy consumption
Removal of PNP with PAC/UF in Dead-End-Mode

Polym. cap. membrane, 
d = 0.8 mm, L = 1.2 m 
Membrane surface = 3.6 m² 
Flow rate = 360 L/h 
Flux = 100 L/(m² h)

PAC (NORIT SA UF) contact time around 1.3 min

PAC/UF Dead-End Mode, continuous PAC dosing (10 mg PAC/L) during UF-filtration cycles just before UF-module. 
UF-backwashing every 30 minutes

PNP concentration in permeate, run 1
PNP concentration in permeate, run 2

Mean PNP conc. in permeate
Theor. PNP equilibrium conc.
Polymer Membranes versus Ceramic Membranes

- Today low pressure membrane market for DW production is absolutely dominated by polymeric membranes
  - Strength: quite reasonable price
  - Weakness: relatively low mechanical stability, low tolerance against chemicals

- In manyfold industrial solid-liquid separation processes ceramic membranes are well established
  - Strength: high mechanical stability (also at high temperatures), highly resistant against chemicals, high permeability, intensive backwashing and cleaning processes possible
  - Weakness: relatively high price

- In Japan exist about 40 DWTP with ceramic membranes (the largest one with approx. 1,600 m³/h)
NGK Insulators Ltd. Ceramic MF-Membrane (Material: Al$_2$O$_3$)

Membrane surface area: 25 m$^2$

Feed Channel
$\varnothing$ 2.5 mm

Filtrate collecting channel

Raw water

Filtrate slits

Filtrate
Main Topics

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Conclusions
Conclusions

- With modern drinking water treatment technologies we can remove nearly all pollutions down to non-relevant concentrations (absolute zero will be impossible!)

  but

- our primary objective should always be to protect our water resources! This will allow us to keep the drinking water as natural as possible

Many thanks for your attention!