UV-activated peroxydisulfate ($S_2O_8^{2-}$) oxidation as a pre-treatment for wastewater in reverse osmosis plants

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Bavarian Research Network BayWater

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5. Bayrische Staatsbrauerei Weihenstephan *,#
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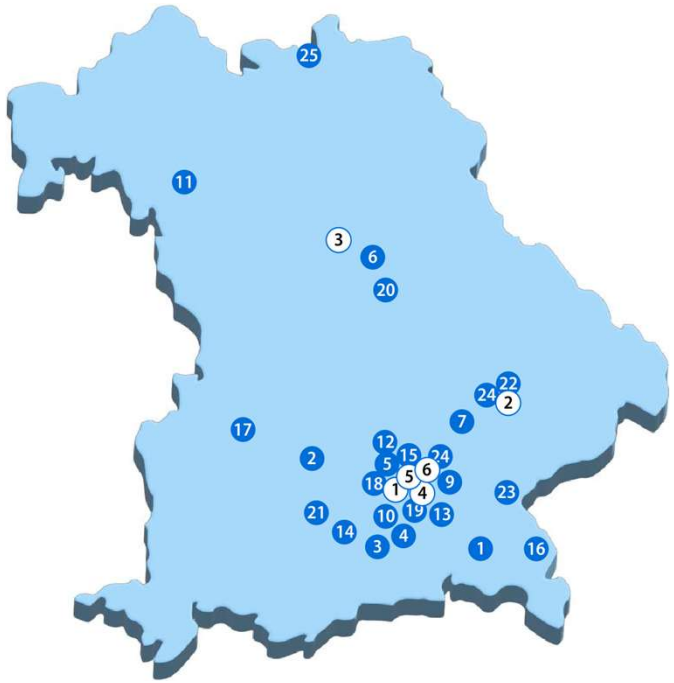
BayWater - Academic Partners

1. Professur Functional Materials for Food Packaging (FMP, TUM)
2. Sensorik Applikations Zentrum (SappZ, OTH Regensburg)
3. Polymer Optical Fiber Application Center (POF-AC, TH Nürnberg)
4. Lehrstuhl für Analytische Chemie und Wasserchemie (IWC, TUM)
5. Lehrstuhl für Systemverfahrenstechnik (SVT, TUM)
6. Forschungszentrum für Brau- und Lebensmittelqualität (BLQ, TUM)



- 6 academic partners
- 25 industry partners
- 6 sub-projects
- 7 academic positions
- Duration of 3 years (October 2024 – October 2027)

TH Nürnberg, POF-AC:

- Fiberoptic Sensors for Biofouling Detection
- UV-pre-treatment with UV-LEDs

Bavarian Research Network BayWater

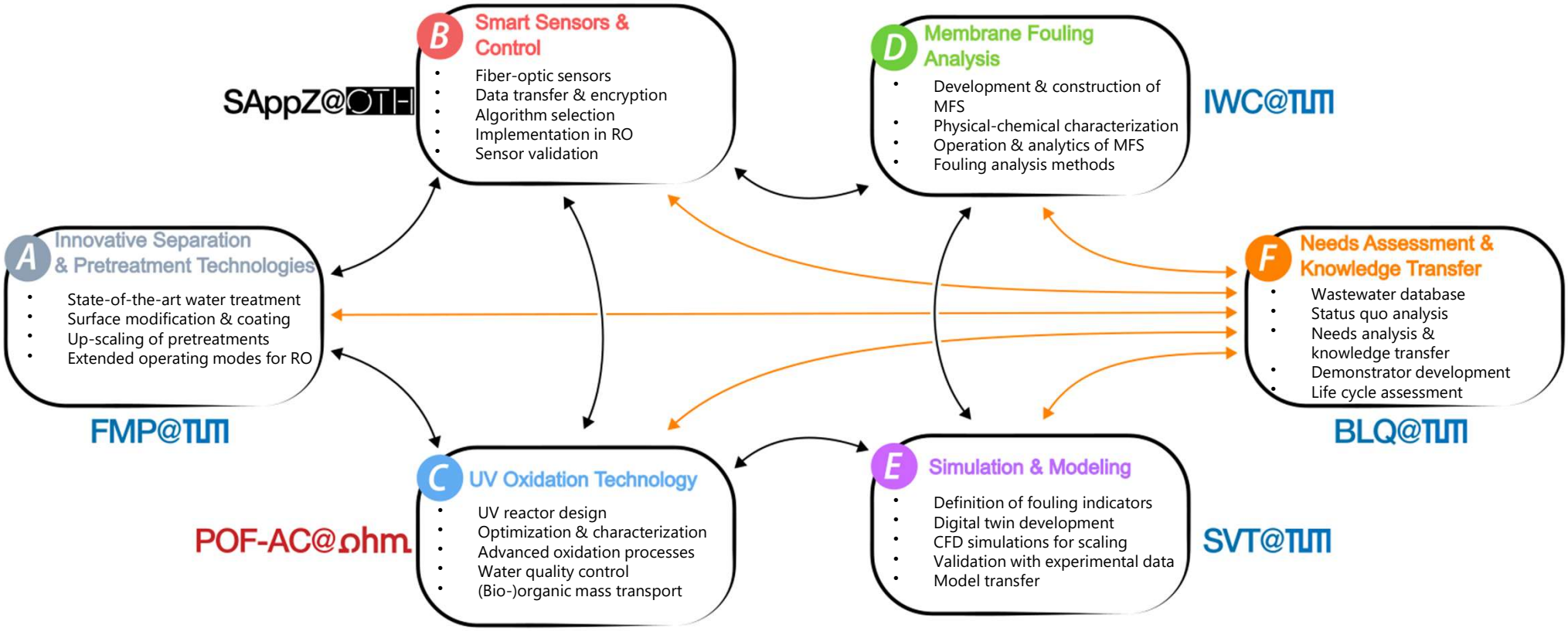
Objectives:

- Using water wisely: We are reducing water consumption in **various industries** and focusing on the **circular economy** – efficiently and sustainably
- Clean water through **innovative technology**: Modern filtration processes and membrane technologies purify water efficiently and consume little energy
- Simulation-based process optimization: Using digital tools to **tailor recycling solutions to specific needs**
- **Industrial implementation** and demonstration: New technologies are tested directly in collaboration with companies

Industries:

- Beverage and food industry (Adelholzener Alpenquellen GmbH, Andechser Molkerei Scheitz GmbH,…)
- Mechanical engineering industry (BMW AG, MTU Aero Engines AG,…)
- Electrical Engineering & Sensor Technology (Endress+Hauser Conducta GmbH & Co. KG Infineon Technologies AG, …)
- Chemical industry (Wacker Chemie AG, MSD Intervet International GmbH,…)

Organization: Subprojects in BayWater



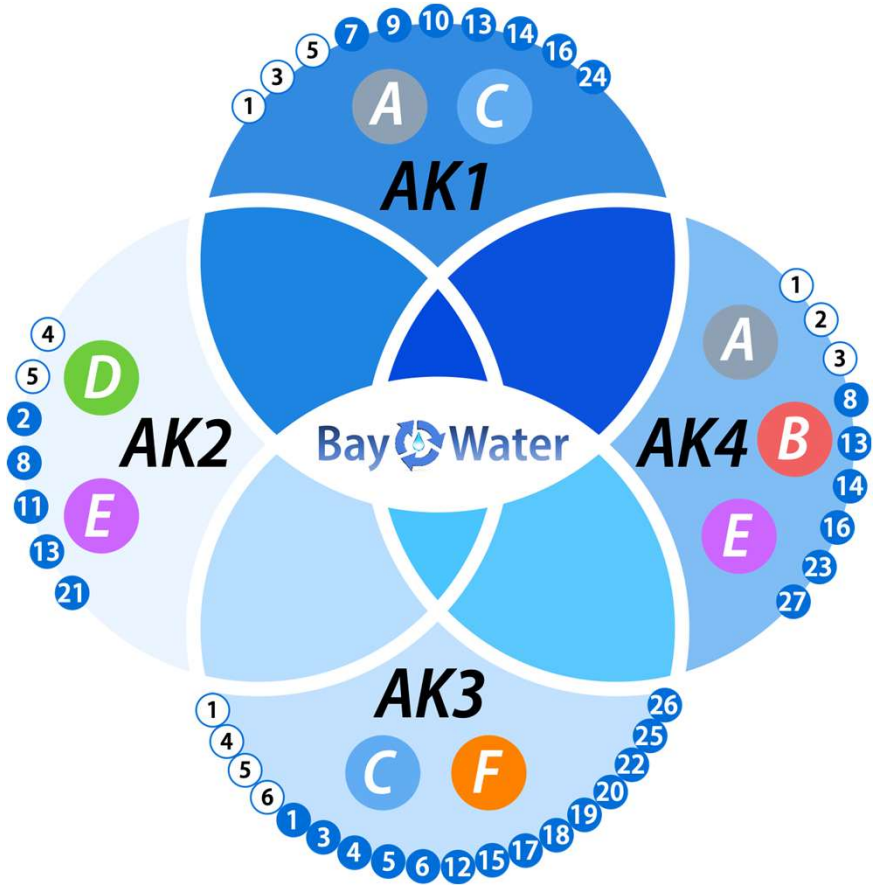
Organization: Intersecting Issues with SMBs

AK1: Pretreatment Strategies and Operational Methodology

- New pretreatment strategies
- RO operating modes
- Combining pretreatment and operation

AK2: Membrane Fouling Analysis and Digital Twin

- Susceptibility to membrane fouling
- Prediction for different water types
- Modeling in the digital twin



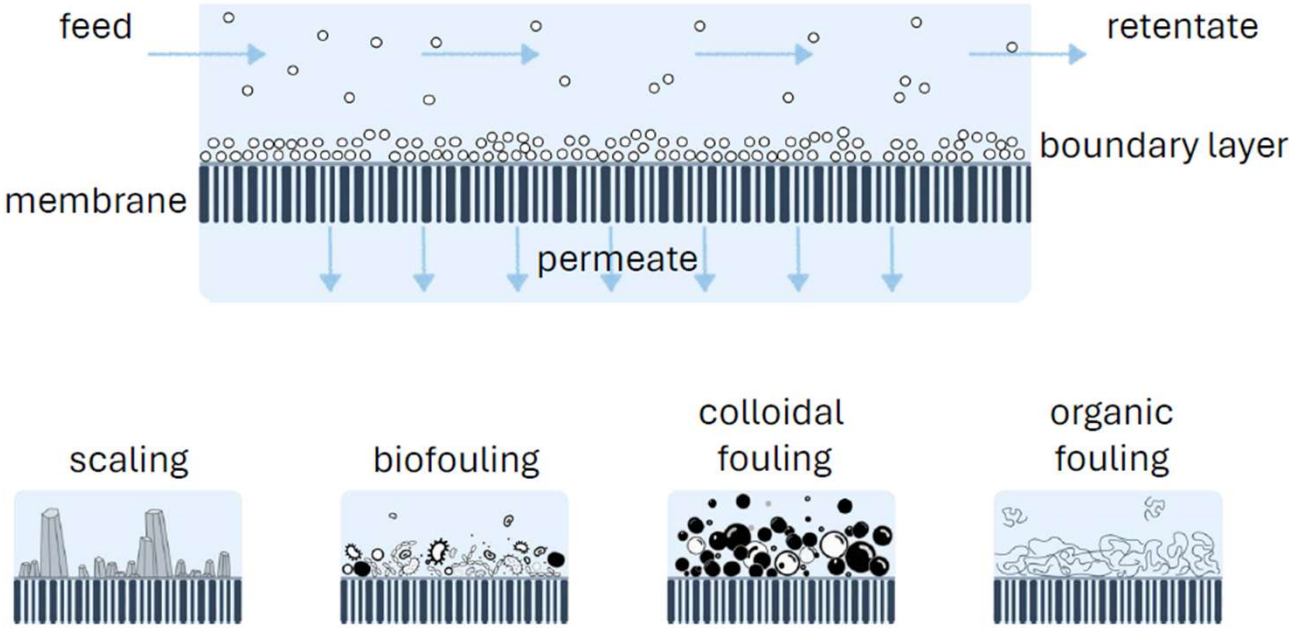
AK4: Online Sensing and Predictive Maintenance

- Analysis of demonstrator data
- Development of new sensor technology
- Early Detection of Operational Events

AK3: Demonstrator Plants and Science Transfer

- Dissemination of Results
- Method Validation in Industry
- Operation of Demonstrators

A central challenge in **R**everse **O**smosis: Membrane fouling



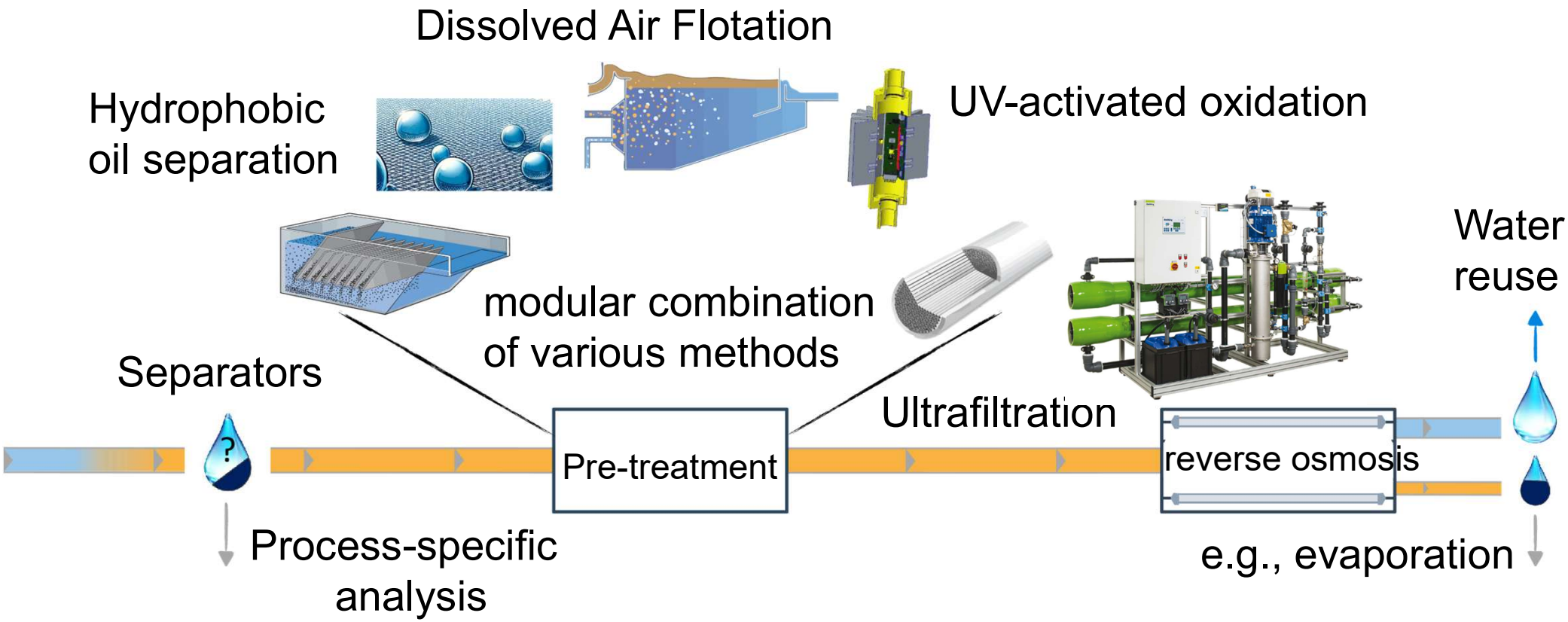
Fouling reduces flow performance and increases maintenance.
It is categorized into:

1. **Particulate and colloidal fouling** – microparticles and suspended solids
2. **Organic fouling** – oils, fats, and other organic compounds
3. **Scaling** – deposition of dissolved salts
4. **Biofouling** – growth of microorganisms

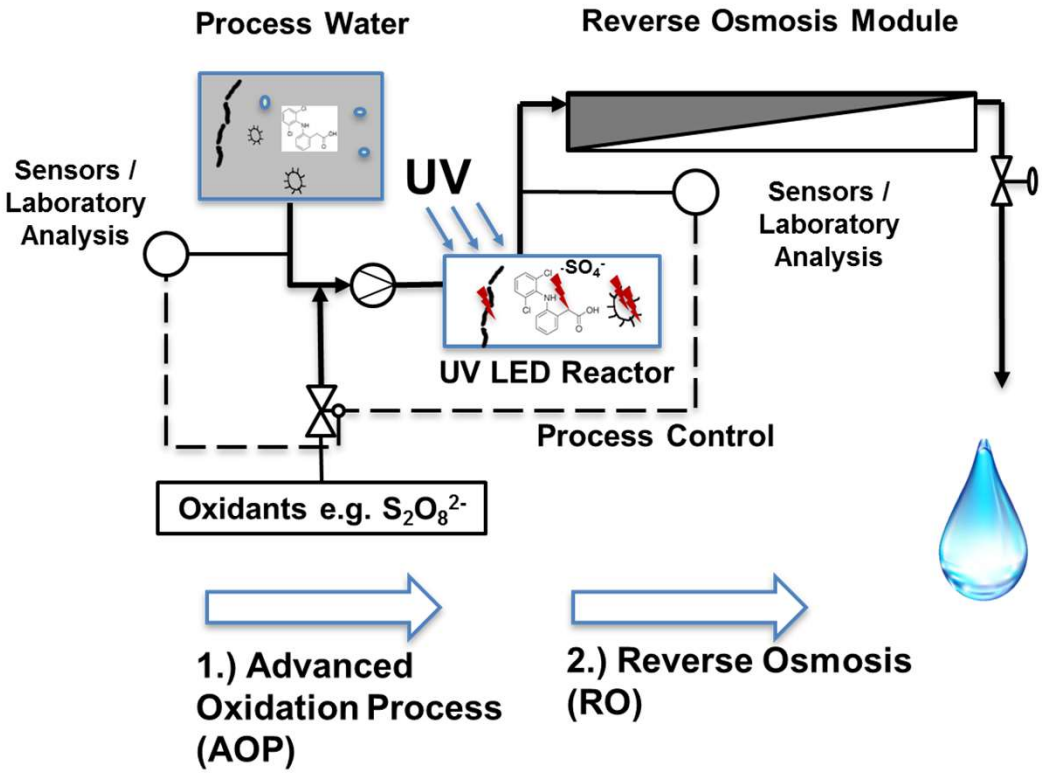
- Drawback: membrane fouling prevents continuous operation of the RO system
- Membrane Fouling is up to 40% Biofouling and leads to up to 30% of operating costs

[1],[2],[3],[4]

Mitigation by pretreatment



UV-activated peroxydisulfate oxidation



Goal of the Advanced Oxidation Process (AOP)

- Sufficient removal of micropollutants and microorganisms to reduce biofouling and organic fouling of the RO membrane
- Prevent damage to the RO membrane caused by radicals and oxidants generated during AOP

Process optimization and control

Why AOP: good efficiency for oxidizing various contaminants

Why $S_2O_8^{2-}$-based AOP: high achievable radical formation yield; reagents are easy to store and transport

Why UV-LED for activation: long life-time, mercury-free

UV-activated peroxydisulfate oxidation: Radical Generation

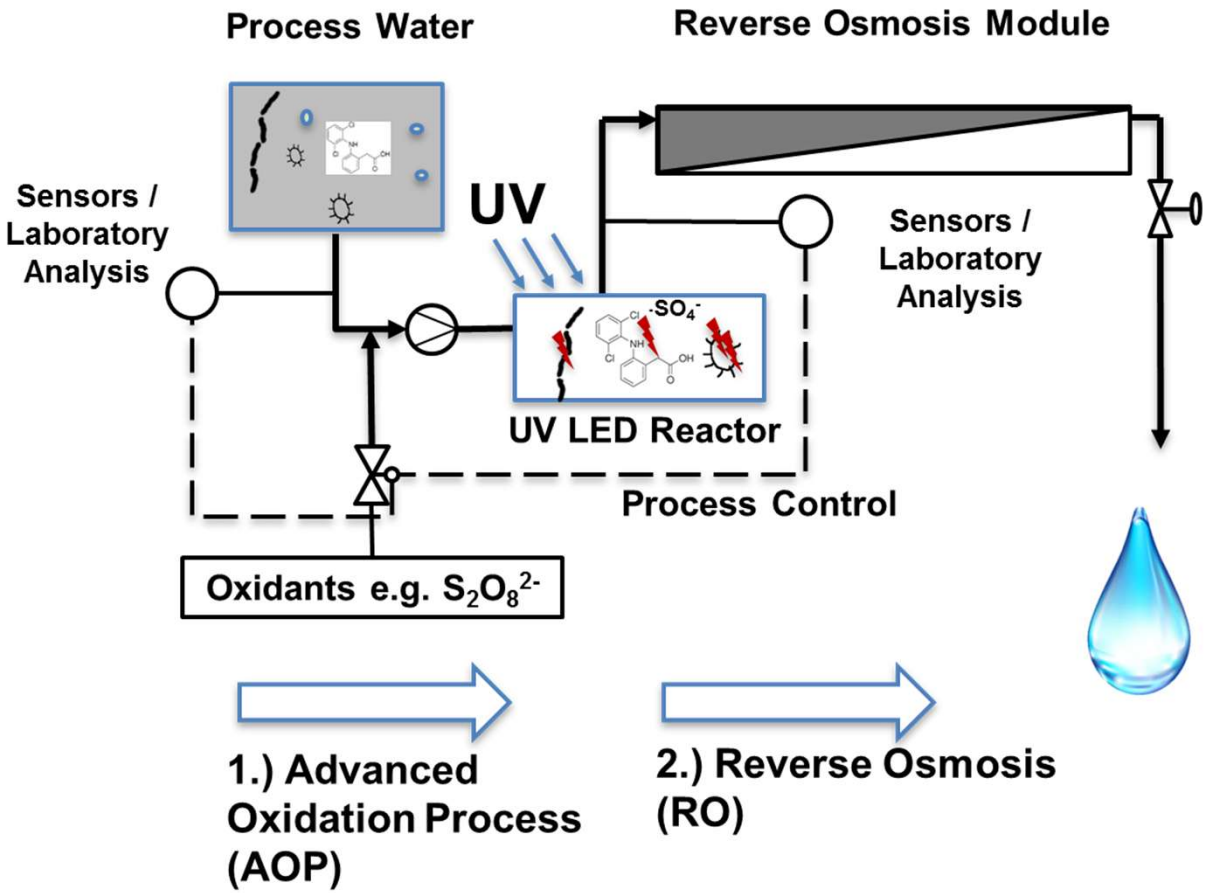


Photo-Irradiation of Peroxydisulfate (PDS)

Primary Radical Generation

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\cdot-}$$

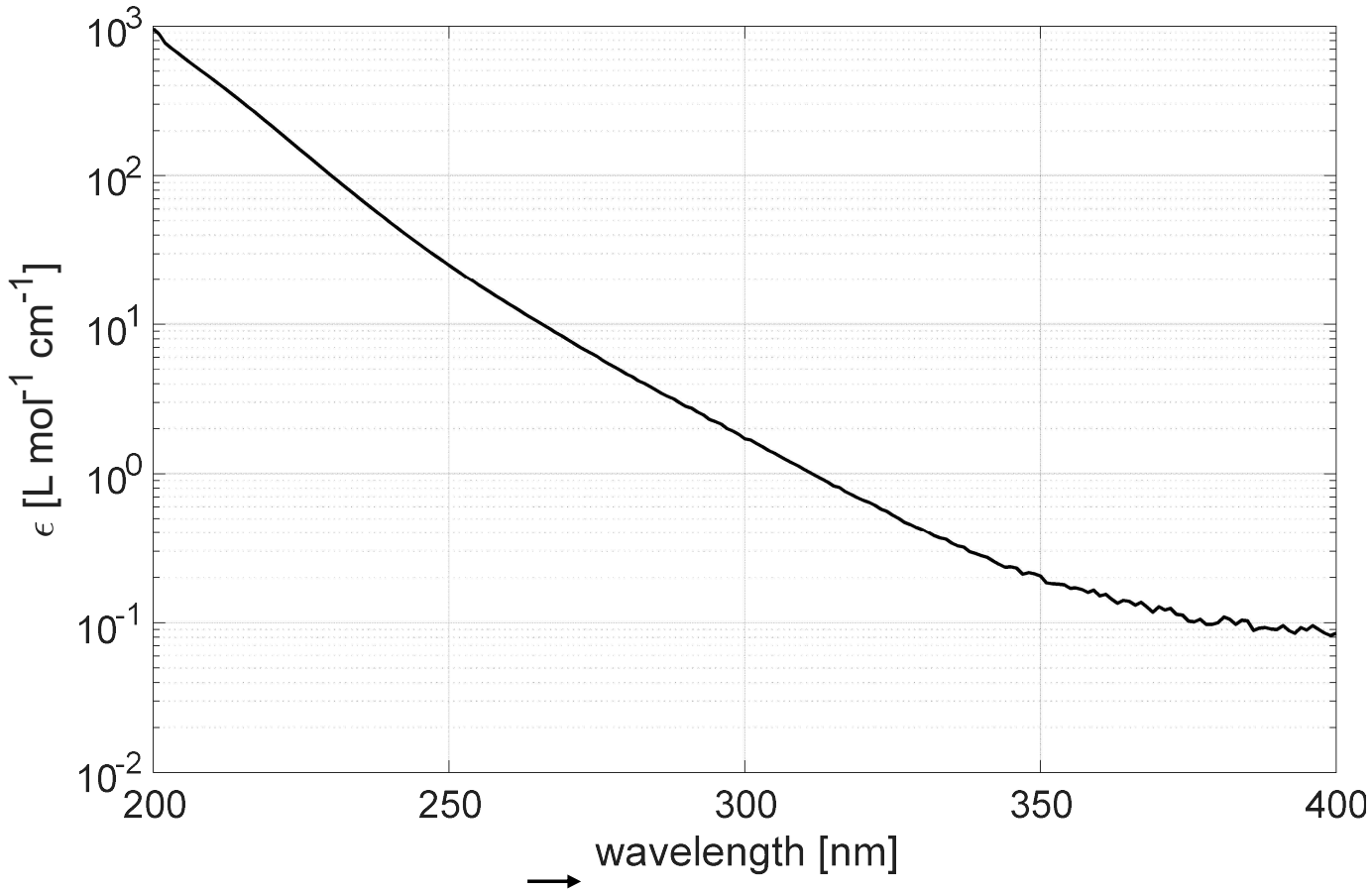
- Sulfate radical ($SO_4^{\cdot-}$)
- Redox potential: E_0 = 2.5 - 3.1 V
- Strong Oxidant with high **selectivity towards organic compounds**

Secondary Radical Formation

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^{\cdot}$$

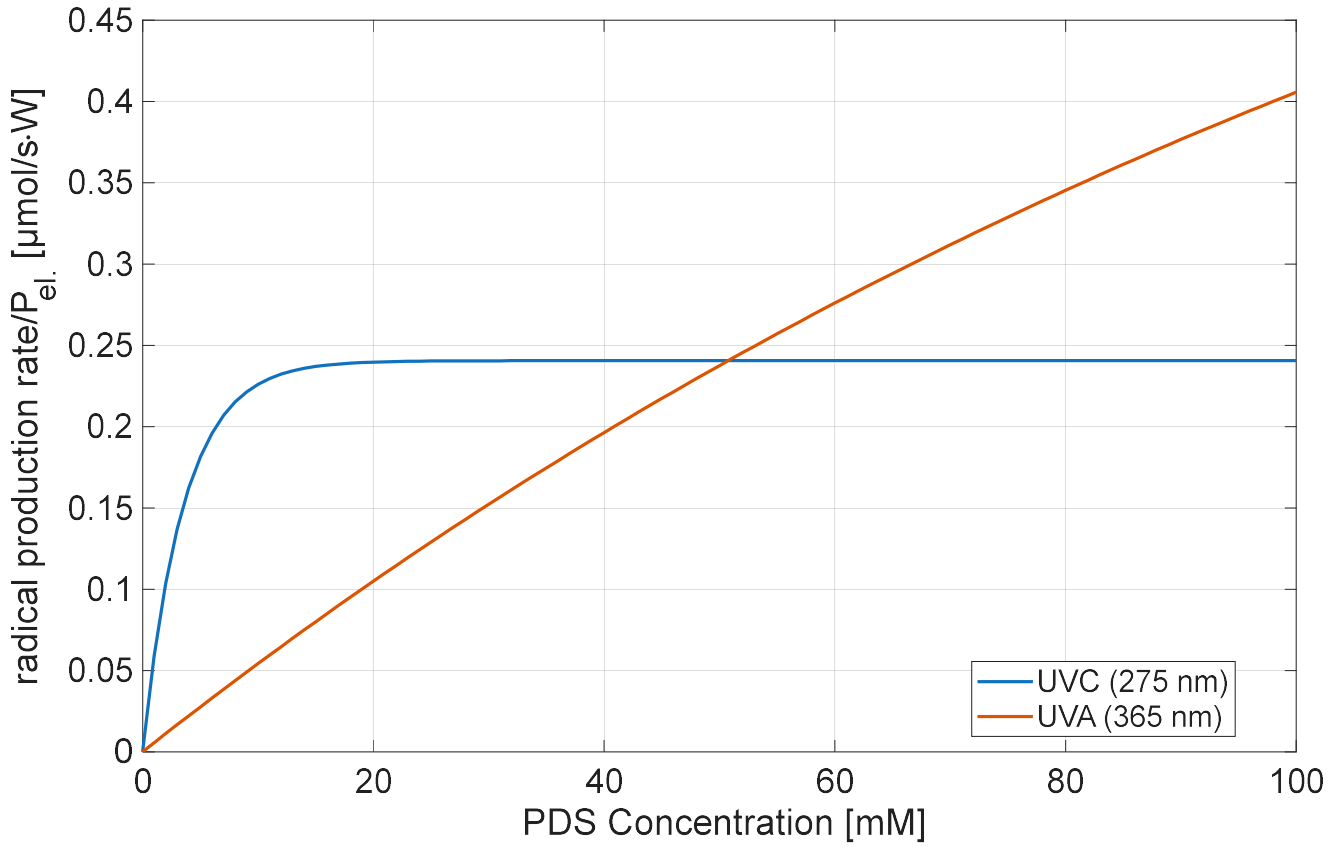
- Hydroxyl radical ($HO^{\cdot}$)
- Redox potential: E_0 = 1.9 - 2.7 V
- Higly reactive, **non-selective** oxidant

UV-activated **P**eroxy**D**i**S**ulfate oxidation: Wavelength dependency



- Radical production is highly wavelength-dependent
- Efficient activation is expected in the UVC range (200–280 nm)
- <5 mMol (<250 nm) and 20 mMol (>250 nm)
- pure absorption of PDS

UV-activated **P**eroxy**D**i**S**ulfate oxidation: Wavelength dependency

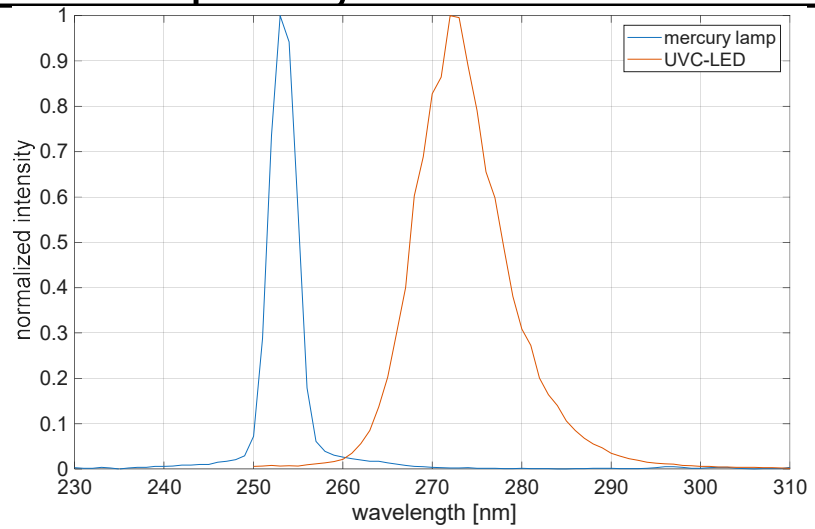


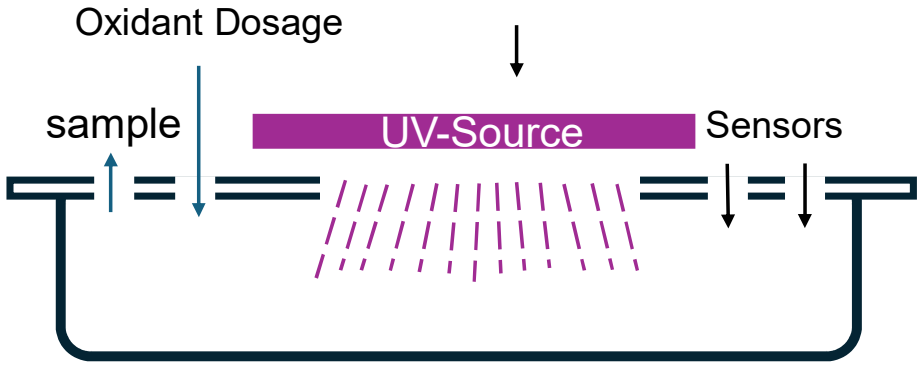
Assumptions:

- UVC LED with 7% efficiency
- mercury lamp with 37%
- optical length: 20 cm

Activation is also conceivable in the UVA range (320–400 nm) at higher doses of the oxidizing agent or higher optical powers UVA-Wave-lengths can not activate PDS effectively

UV-activated peroxydisulfate oxidation: Laboratory Setup

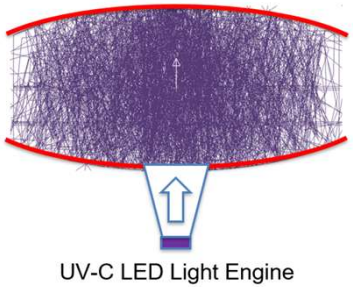




Goal of the Laboratory Setup

- Comparison between $S_2O_8^{2-}$ and H_2O_2
- Comparison between UV mercury lamps and UV LEDs
- Assessment of radical formation
- Determination of the UV doses required for successful AOPs for different wastewaters

Results are used for creating AOP-flow reactor

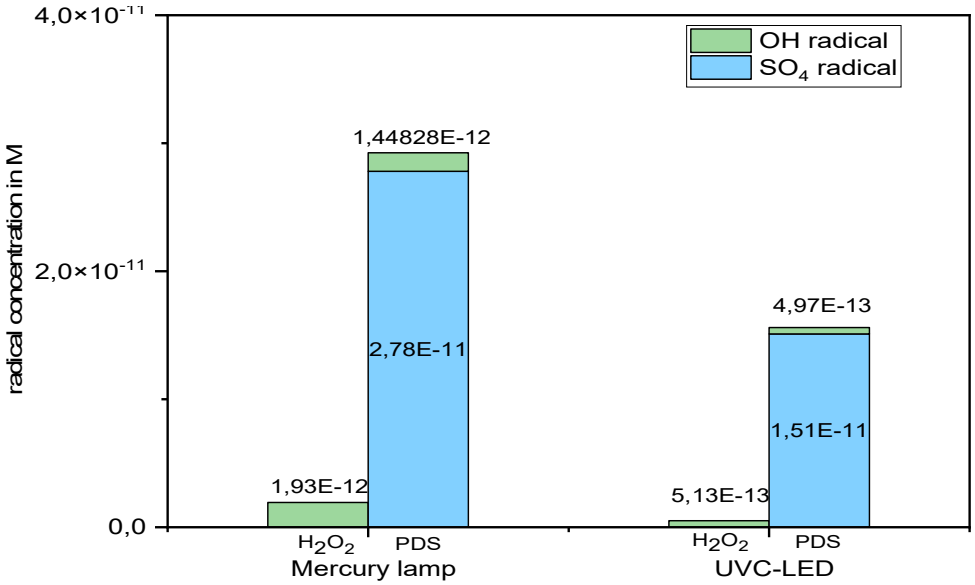


Process Characterization

radical concentrations → degradation rates of micropollutants

- HPLC-based five-chemical-probe method

Conditions: 1 mM PDS/ H_2O_2, pH = 7



- Diclofenac as model molecule
- HPLC-based five-chemical-probe method

Decay rate of diclofenac as ln (c/c_0)/time [s^{-1}]

	Only UV	UV/H_2O_2	UV/PDS
Mercury lamp	0.0055	0.01873	0.08199
UVC-LED	0.0101	0.01450	0.03420

Process Characterization

Results:

Activation Efficiency

- UVA-Wavelengths can not activate PDS effectively
- PDS-based AOPs had much higher radical concentrations
- UVC-LED-activated AOPs had lower radical concentrations
- UVC-LED-activation is applicable for PDS-based AOPs

Degradation Rates

- Diclofenac was more rapidly degradeted in PDS-based AOPs
- UVC-LED could be applied for PDS activation but could not effectively activate H_2O_2

Summary

Done

- ✓ Reactor characterization and UV irradiation flux determination: mercury lamp vs. UVC-LED
- ✓ Determination of steady-state radical concentrations: mercury lamp vs. UVC-LED, UV/PDS vs. UV/H_2O_2
- ✓ Degradation test of the model molecule diclofenac: mercury lamp vs. UVC-LED, UV/PDS vs. UV/ H_2O_2

Next to do

- ➢ HPLC vs. ELISA for the analysis of diclofenac degradation
- ➢ Further experiments of E. coli deactivation/elimination during AOP: mercury lamp, UV/PDS vs. UV/H_2O_2
- ➢ Use results for prototyping a UV-LED - flow reactor based on non-sequential raytracing

Sources

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