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On photocatalytic membrane reactors in water and wastewater treatment: recent experiences and perspectives

Sylwia Mozia

Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

West Pomeranian University of Technology, Szczecin
Institute of Chemical Technology and Environment Engineering
ul. Pułaskiego 10, 70-322 Szczecin, Poland
tel. +48 91 449 48 72, e-mail: sylwia.mozia@zut.edu.pl

Outline

1. **A brief introduction to membrane processes**
2. **Photocatalytic membrane reactor (PMR) – what is it?**
3. **Examples of possible applications of PMRs for treatment of real water and wastewater:**

(I) Example 1: **Treatment of effluents from a municipal wastewater treatment plant** (MWWTP) in a PMR utilizing ultrafiltration (UF) – application of a **polymeric membrane**

(II) Example 2: **Treatment of lake water** in a PMR and a hybrid system coupling UVC/H_2O_2 and UF – application of a **ceramic membrane**

4. Conclusions and future trends

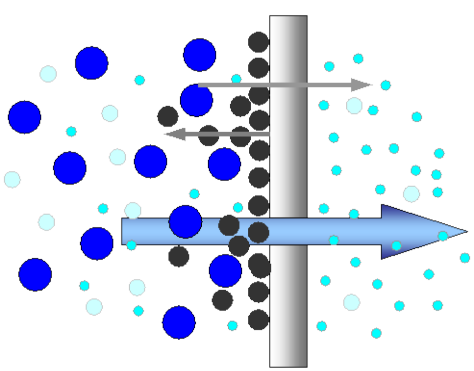
A brief introduction to membrane processes

Membrane – what is it?

membrane

structure, having lateral dimensions much greater than its thickness, through which transfer may occur under a variety of **driving forces**

(Terminology for membranes and membrane processes (IUPAC Recommendations 1996)



Membrane processes

Driving force

Transmembrane pressure ΔP

- ✓ Microfiltration (MF)
- ✓ Ultrafiltration (UF)
- ✓ Nanofiltration (NF)
- ✓ Reverse osmosis (RO)

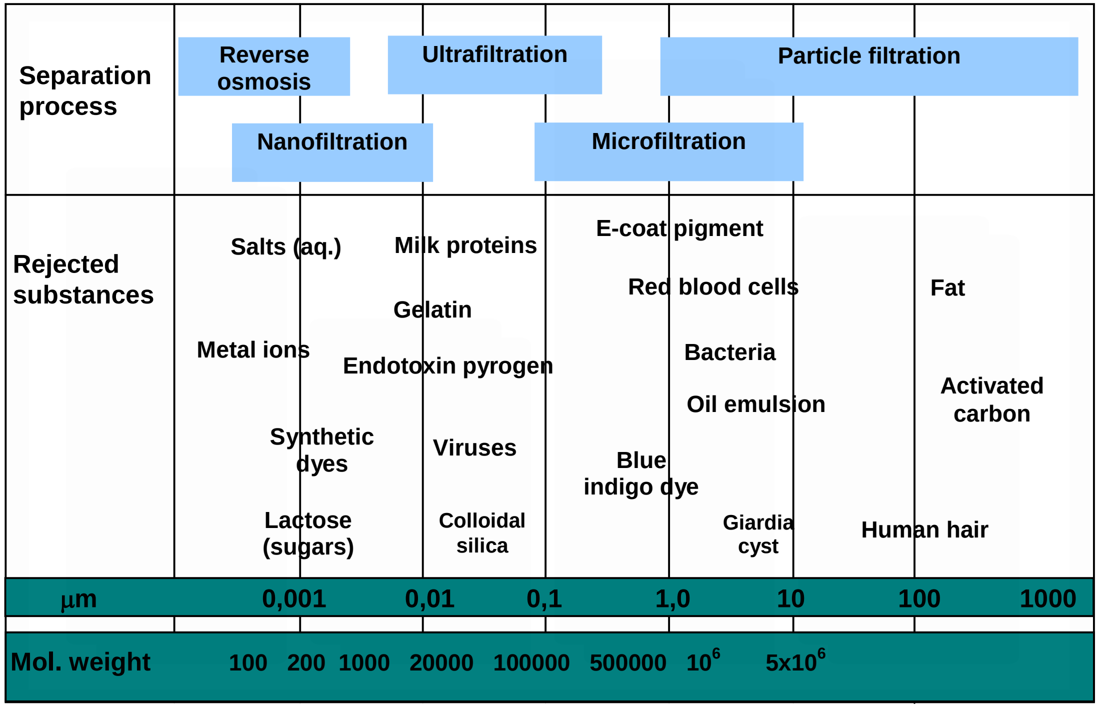
Concentration (or partial pressure) difference Δc, Δp

- ✓ Dialysis
- ✓ Pervaporation (PV)
- ✓ Membrane distillation (MD)
- ✓ Gas separation (GS)
- ✓ Liquid membranes (LM)
- ✓...

Electrical potential difference ΔE

- ✓ Electrodialysis (ED, EDR)
- ✓ Membrane electrolysis (ME)
- ✓...

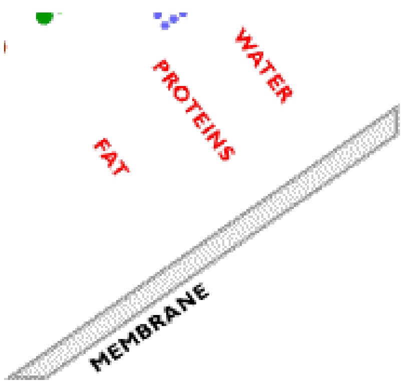
Pressure driven membrane processes



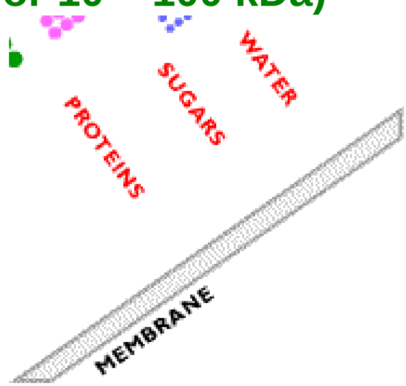
driving force: transmembrane pressure (TMP)

- MF: TMP < 0.3 MPa
- UF: TMP 0.1 – 1 MPa
- NF: TMP 0.5 – 3 MPa
- RO: TMP 1 – 8 (10) MPa

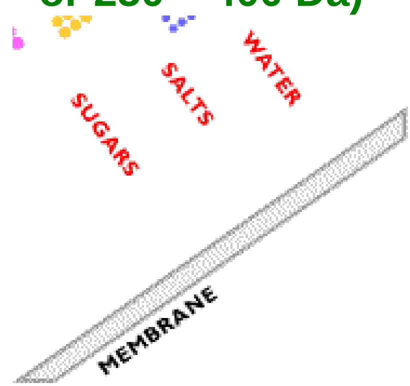
MF (0.1 – 10 um)



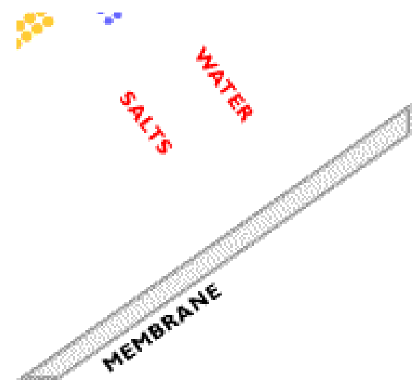
UF (1 – 100 nm or 10 – 100 kDa)



NF (< 2nm or 250 – 400 Da)



RO (< 125 Da)



Streams in membrane separation processes

feed

permeate

a portion of feed stream which passes through the membrane; in case of water/wastewater treatment it contains mainly water and substances that were not rejected by the membrane

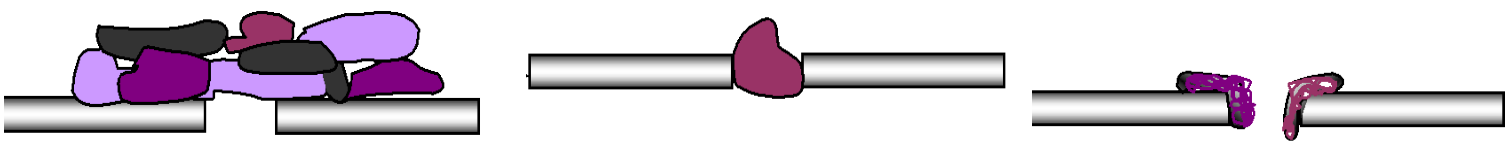
retentate (concentrate)

a portion of feed stream which does not pass through the membrane; a concentrated solution containg components rejected by the membrane

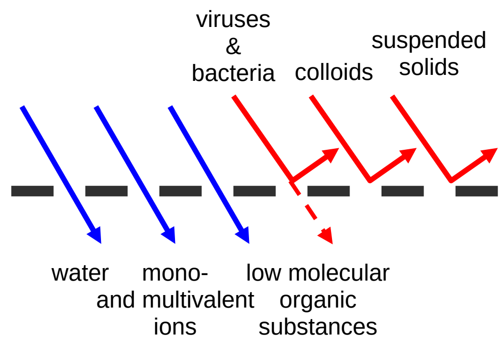
The product of a membrane process can be either permeate or retentate, or sometimes both streams.

Membranes in water and wastewater treatment - problems to solve:

Permeate flux decline due to membrane fouling → deposition of contaminants on the membrane surface or within its pores



MF/UF membranes are not efficient in separation of low molecular organic contaminants → low permeate quality



Solution:

PMR

What is a photocatalytic membrane reactor?

Photocatalytic Membrane Reactor (PMR)

A hybrid system in which
the photocatalytic degradation
and membrane separation
occur simultaneously

PMR
=
PHOTOCATALYSIS:

- decomposition and mineralization of contaminants
- synthesis of useful organic compounds

+
MEMBRANE PROCESS:

- retention of photocatalyst in the reaction environment
- possibility of recovery and reuse of the photocatalyst in further runs
- control of a residence time of reagents in the reactor
- possibility of selective separation of products
- realization of a continuous process with simultaneous separation of reagents and photocatalyst from the solution

PMRs - classification

PMR

- with a photocatalyst supported in/on the membrane (photocatalytic membranes)
- with a photocatalyst suspended in the reaction mixture

according to the manner of photocatalyst introduction into the reactor

- gaseous phase
- liquid phase

according to the reaction environment

Driving force: ΔP:

- ❑ microfiltration
- ❑ ultrafiltration
- ❑ nanofiltration

Driving force: Δc, Δp:

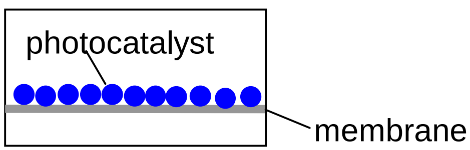
- ❑ pervaporation
- ❑ dialysis
- ❑ membrane distillation

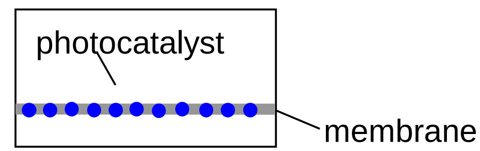
according to the membrane technique applied (liquid phase reactions)

PMRs with photocatalytic membranes

FUNCTION OF THE MEMBRANE:

photocatalyst support

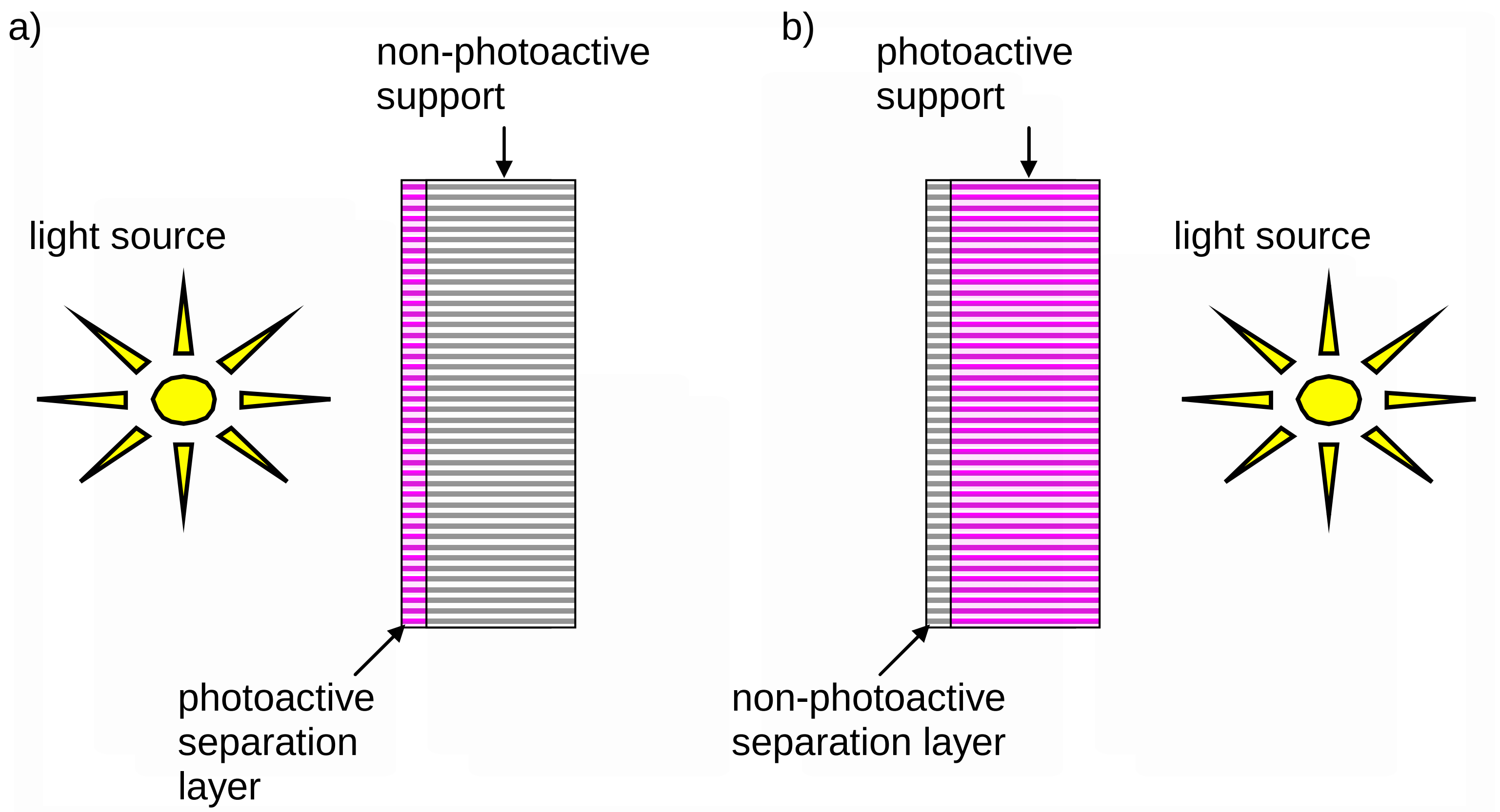




separation of the molecules present in the solution (initial compounds and products or by-products of their decomposition)

PMRs with photocatalytic membranes

PHOTOCATALYTIC MEMBRANES

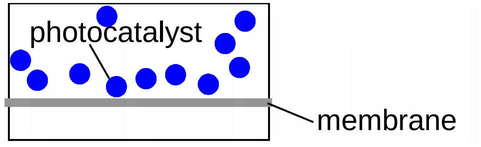


S. Mozia, Separation and Purification Technology, 73 (2010) 71–91

PMRs with photocatalyst in a slurry

FUNCTION OF THE MEMBRANE:

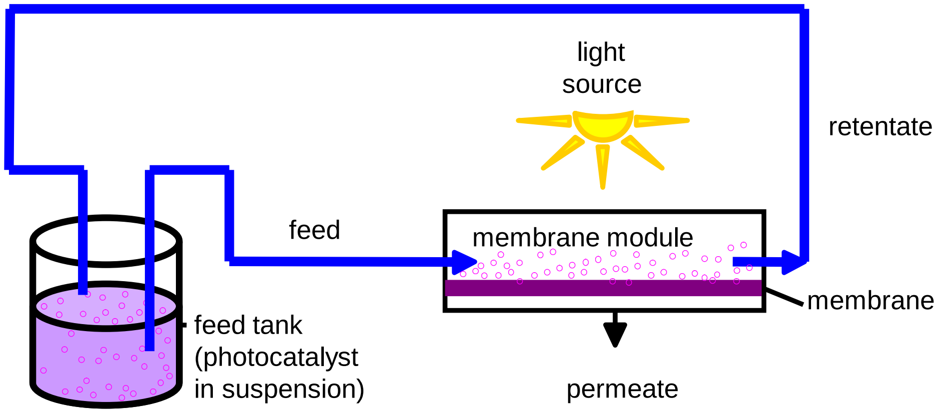
- **separation of photocatalyst particles**



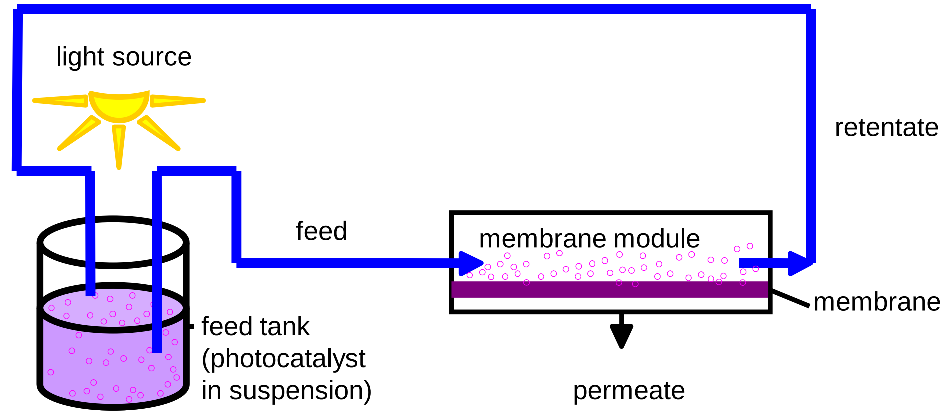
- **separation of the molecules present in the solution (initial compounds and products or by-products of their decomposition)**

PMRs with photocatalyst in a slurry: configurations

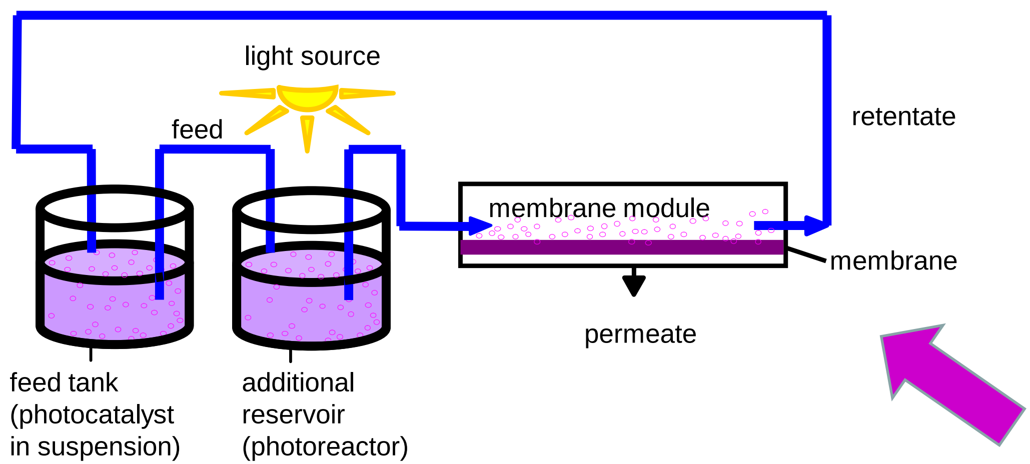
A. Photocatalytic reaction conducted in a membrane module



B. Photocatalytic reaction conducted in the feed tank



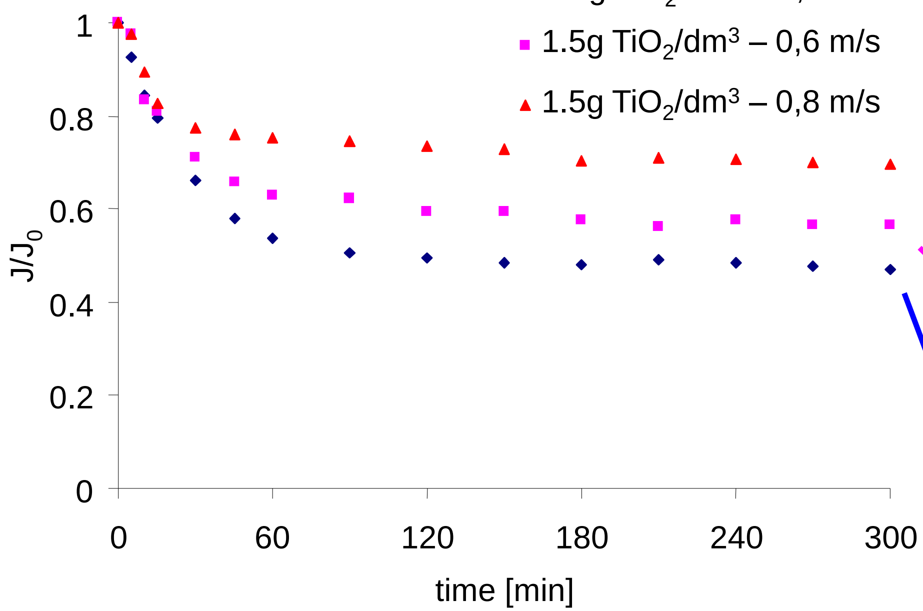
C. Photocatalytic reaction conducted in an additional reservoir (photoreactor) located between the feed tank and membrane module



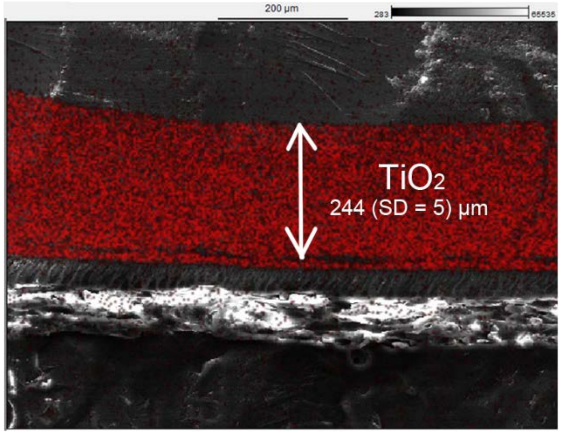
S. Mozia, A.W. Morawski, R. Molinari, L. Palmisano, V. Loddo, Chapter 6 in "Handbook of membrane reactors, Volume 2: Reactor types and industrial applications", Ed. A. Basile, Woodhead Publishing Limited, 2013, pp. 236-295

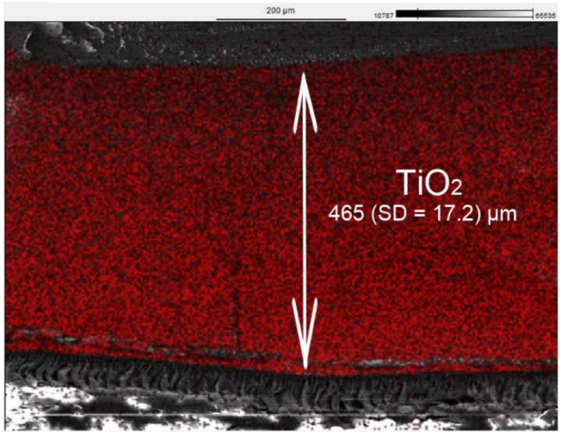
Example 1: Treatment of effluents from a municipal wastewater treatment plant (MWWTP) in a PMR utilizing ultrafiltration (UF) – application of a polymeric membrane

Influence of photocatalyst on permeate flux

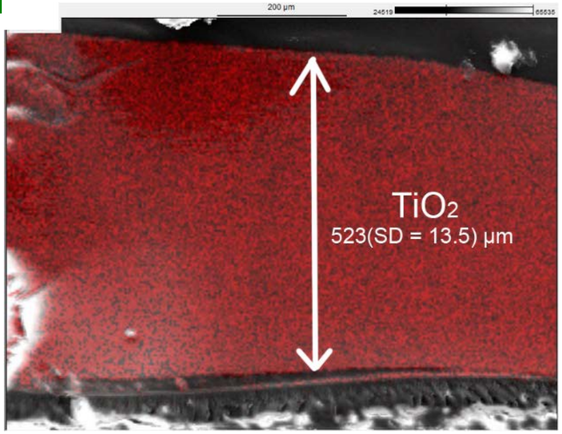


membrane fouling by TiO_2 particles
→ deterioration of permeate flux during filtration of TiO_2



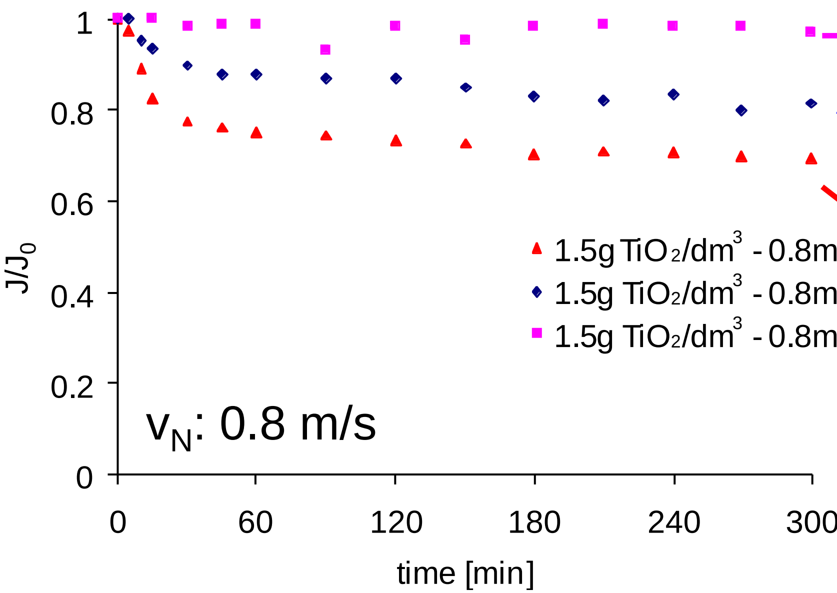


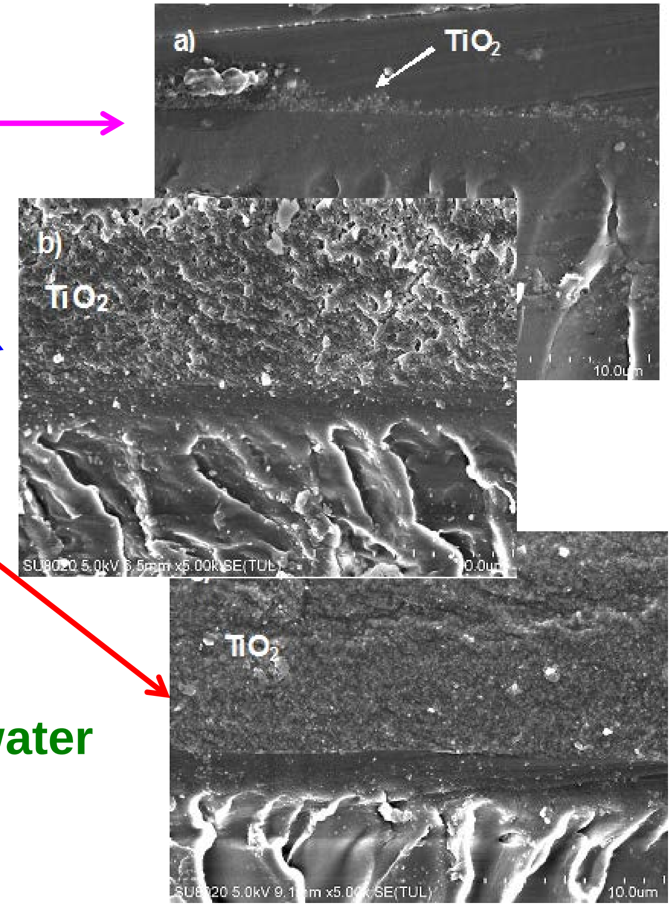
feed: TiO_2 in distilled water



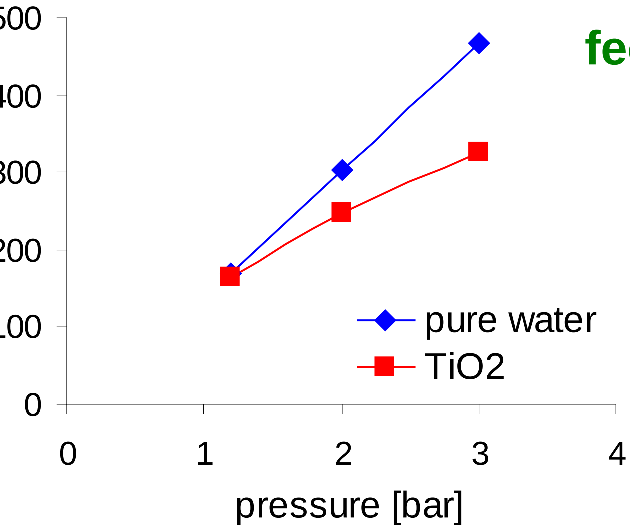
- membrane: PES, UE10 (Trisep Corp.), MWCO: 10 kDa
- 1.5 g TiO_2P25/dm^3
- TMP: 3 bar

Influence of photocatalyst on permeate flux



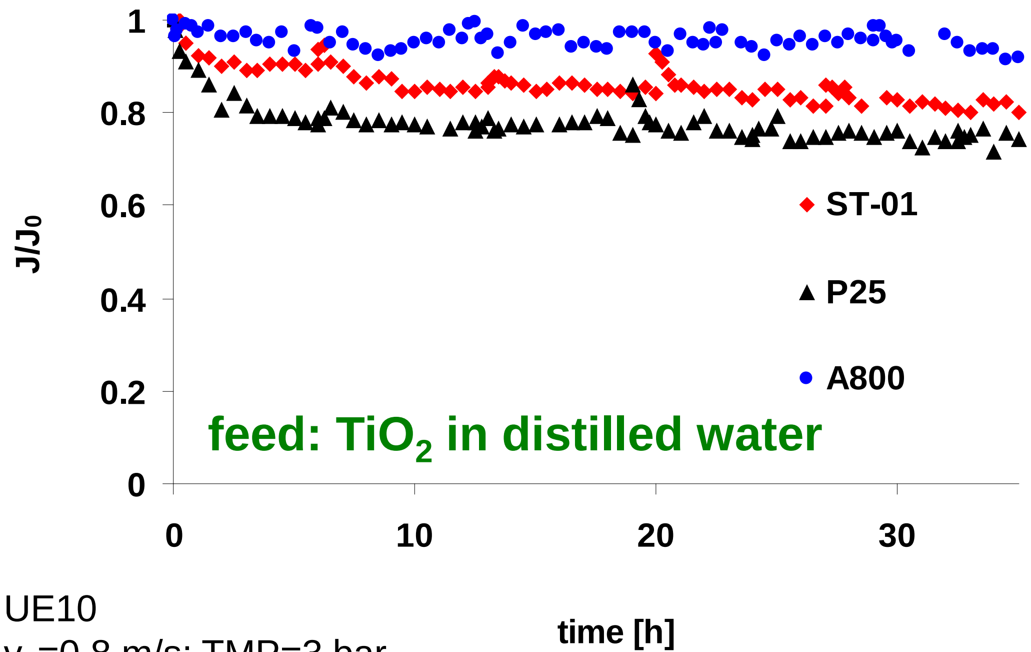


feed: TiO_2 in distilled water



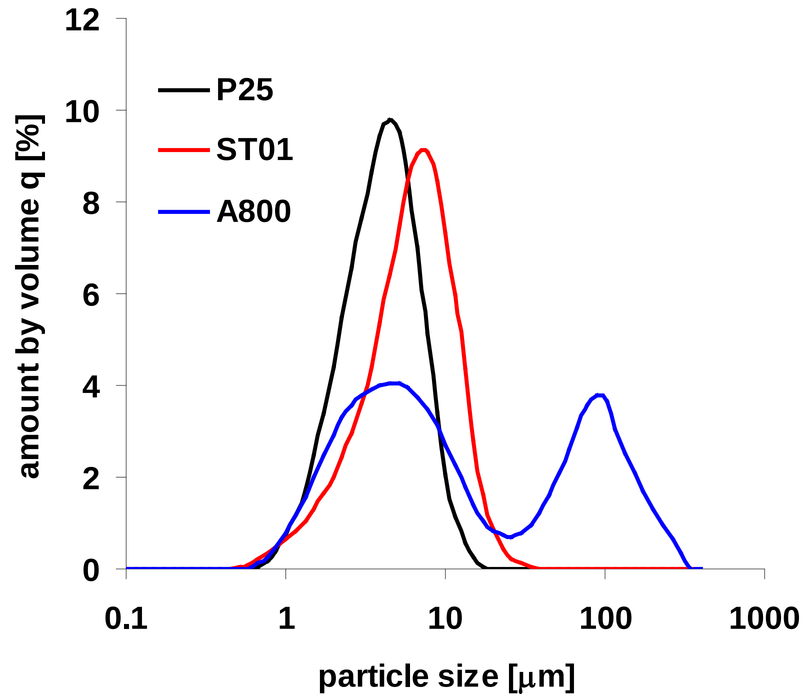
How to avoid membrane fouling?
1. Careful selection of process conditions:
- Transmembrane pressure (TMP)
- Feed flow rate

Influence of photocatalyst on permeate flux



large particles, non-uniform distribution

small particles, uniform distribution



UE10
v_F=0.8 m/s; TMP=3 bar
0.5 $gTiO_2/dm^3$

Photocatalyst	Specific surface area S_{BET} [m^2/g]	Anatase over rutile ratio (A:R)	Crystallite size of anatase [nm]
A800	6	2:98	51
P25	51	80:20	22
ST-01	252	100:0	8

How to avoid membrane fouling?
2. Selection of a photocatalyst

What is the infuence of photocatalysis on permeate flux during treatment of wastewater?

Treatment of wastewater in PMR utilizing UF

Municipal sewage treatment plant
with a capacity of 418 000 equivalent citizens

mechanical treatment
sieves, screens, grit chamber, primary settling tanks

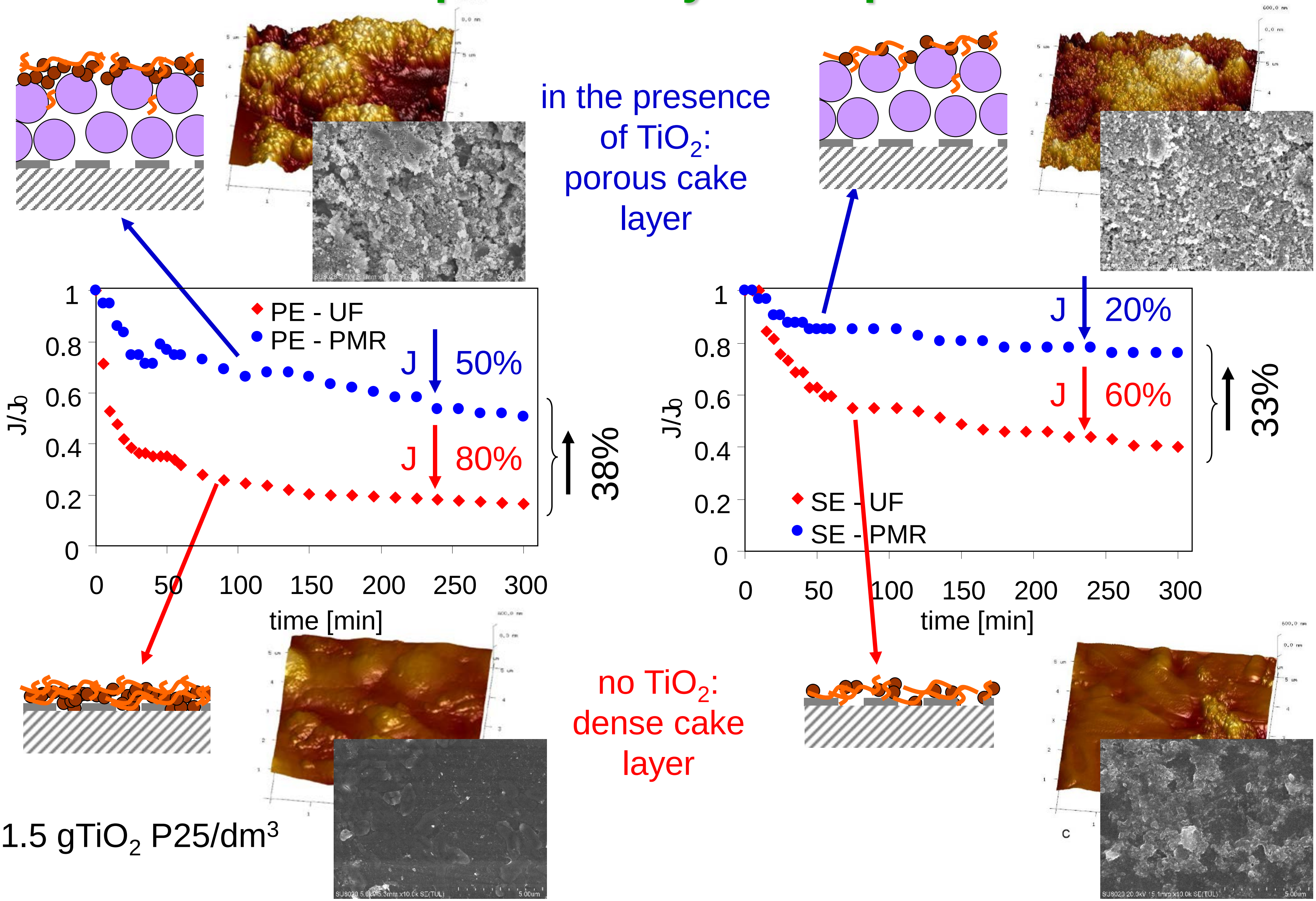
biological treatment
pre-denitrification, dephosphatation, nitrification

secondary settling tanks

Typical parameters of primary (PE) and secondary (SE) effluents applied in the experiments

Parameters	PE	SE
TOC [mg/dm^3]	70 - 80	12 - 19
DOC [mg/dm^3]	49 - 54	11 - 18
TIC [mg/dm^3]	58 - 100	42 – 58
pH	7.5 - 8.5	7.2 - 8.5
Conductivity [µS/cm]	1020 - 1170	1040 - 1130
TDS [ppm]	710 - 780	730 - 790
Turbidity [NTU]	75 - 110	1 - 4
N-NH_4^+ [mgN/dm^3]	43 - 50	5 - 8

Influence of photocatalysis on permeate flux

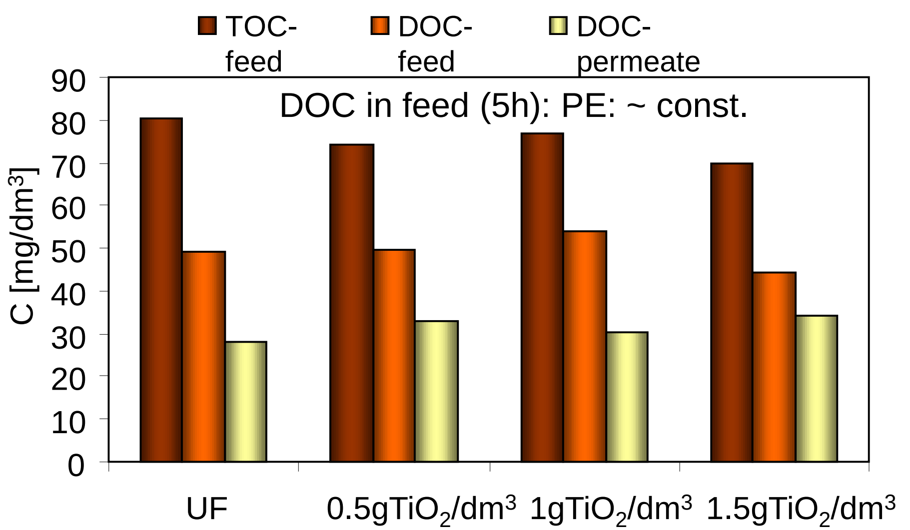


Increase of the permeate flux in the presence of TiO_2 P25

Will PMR be effective in treatment of wastewater?

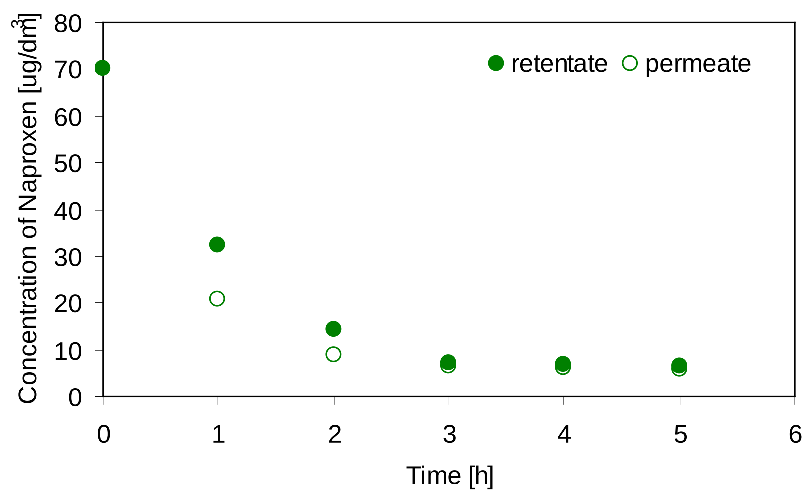
Removal of organic contaminants

Mineralization of large molecular organic contaminants proceeds slowly. Overall treatment efficiency depends more on membrane separation than photocatalysis.



Concentration of TOC and DOC in primary effluents (initial feed) and in permeate after 5h of UF or PMR process

Low molecular organic contaminants and products of their decomposition are not rejected by UF membranes. Overall treatment efficiency depends on effectiveness of photocatalysis.



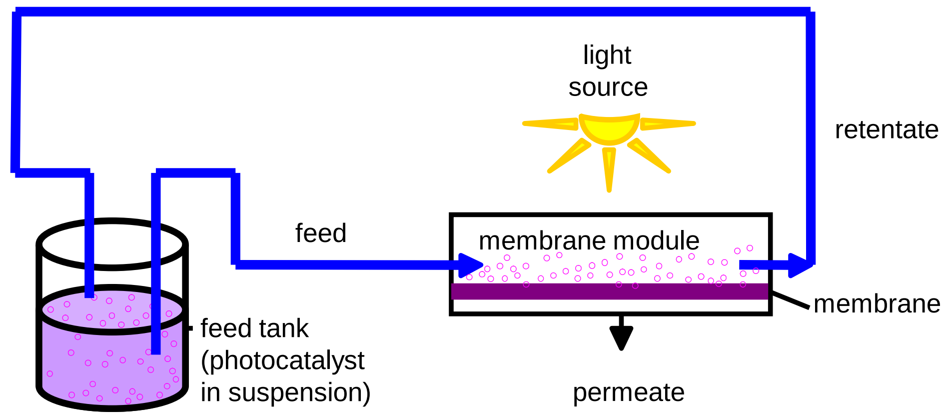
Non Steroidal Anti-Inflammatory Drug
Naproxen sodium salt (MW 252 g/mol)
Feed: Naproxen in primary effluents

Possible application: post-treatment (polishing) of water/wastewater containing low concentrations of harmful or persistent organic contaminants (tens ug/dm^3 or lower), e.g. pharmaceuticals or endocrine disrupting compounds.

Stability of polymeric membranes in PMRs

Stability of polymeric membranes in PMRs

PMR with a light source located in the vicinity of membrane surface



a danger of destruction of the polymeric membrane structure by UV light or hydroxyl radicals

Resistance of membranes to UV:

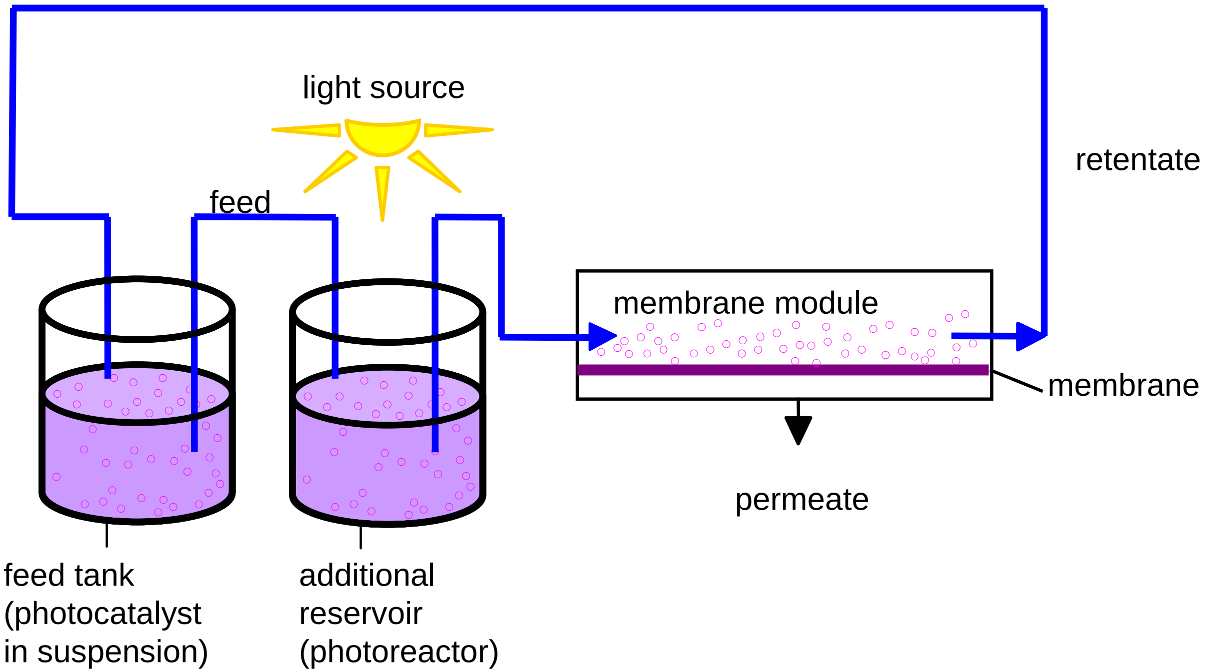
polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF)

polypropylene (PP), polyacrylonitrile (PAN) and cellulose acetate (CA) -CH-

polyethersulfone (PES) ≈ polysulfone (PSU) $-SO_3^-$

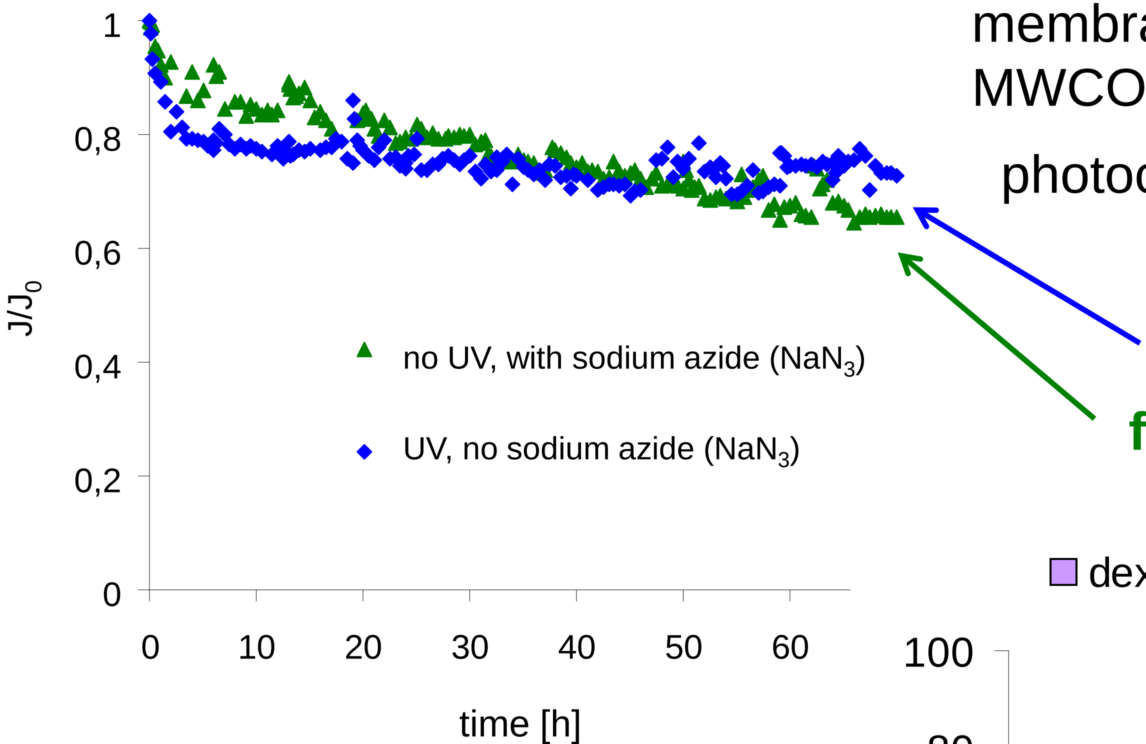
Stability of polymeric membranes in PMRs

PMR with a light source under or inside an additional reservoir (photoreactor)



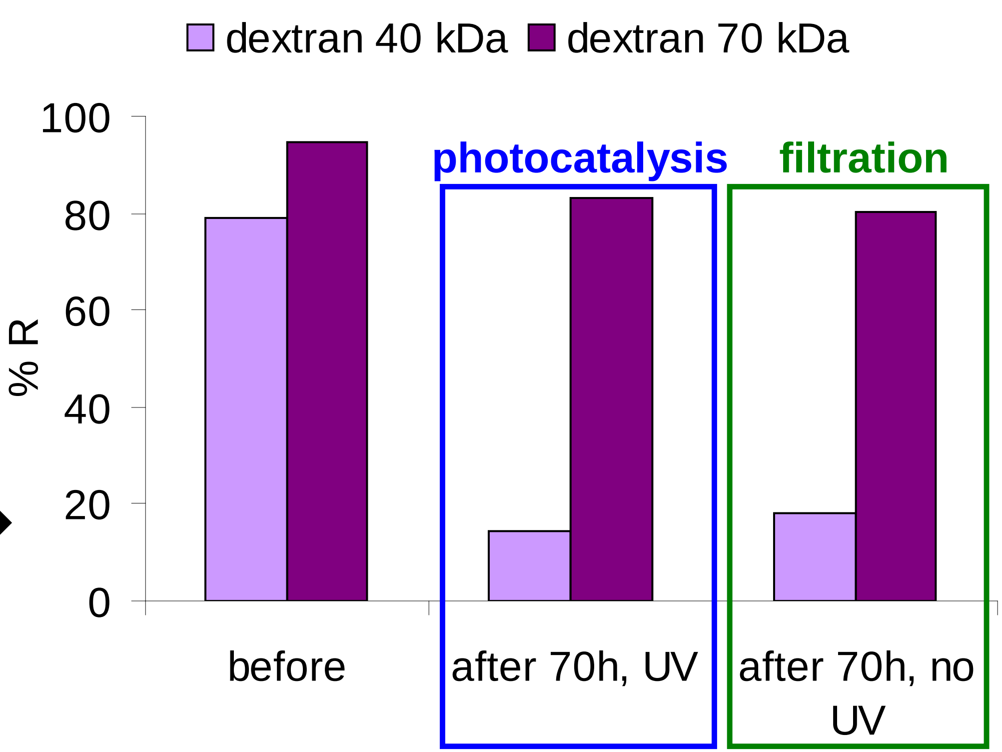
NO RISK OF DESTRUCTION OF POLYMERIC MEMBRANES BY UV LIGHT

Stability of polymeric membranes in PMRs



membrane: PES, UE10 (Trisep Corp.)
MWCO: 10 kDa

photocatalyst: AEROXIDE® TiO_2 P25



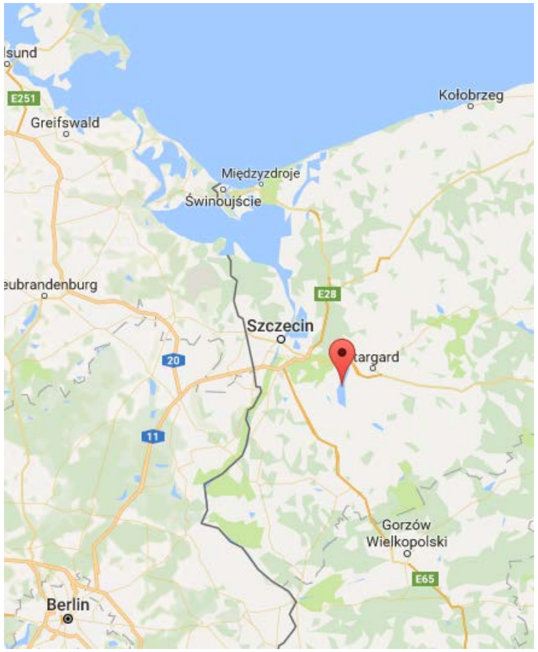
loss of separation properties due to membrane skin layer damage, regardless of presence or absence of UV → abrasive action of TiO_2 particles

Example 2: Treatment of lake water in a PMR and a hybrid system coupling UVC/H_2O_2 and UF – application of a ceramic membrane

Treatment of surface water in PMR and UVC/H_2O_2–UF system

Miedwie Lake - source of drinking water for Szczecin, Poland

Water Treatment Plant ZPW „Miedwie”: max. production: 100 000 m^3 of water per day (at present: ca. 55 000 m^3/day)



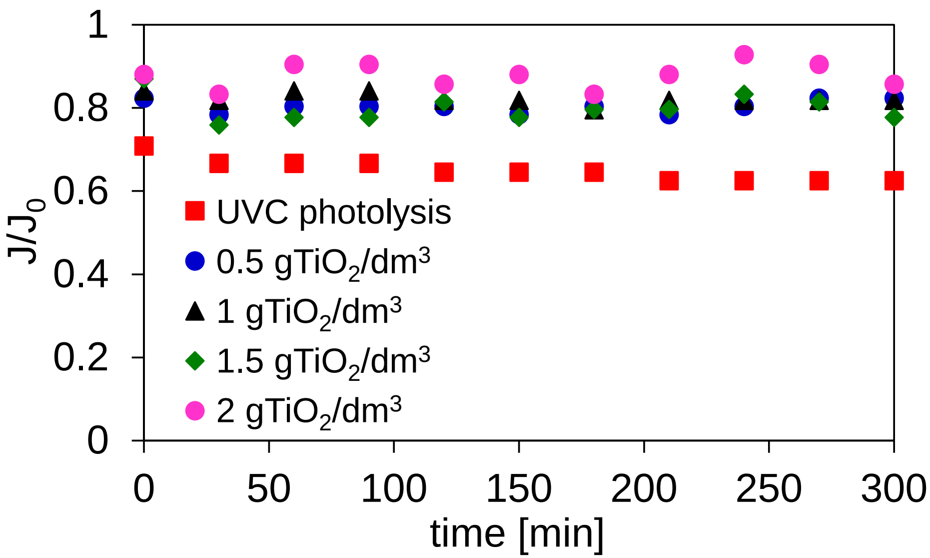
Water was collected after initial prefiltration through screens and sieves

Typical parameters of lake water applied in the experiments

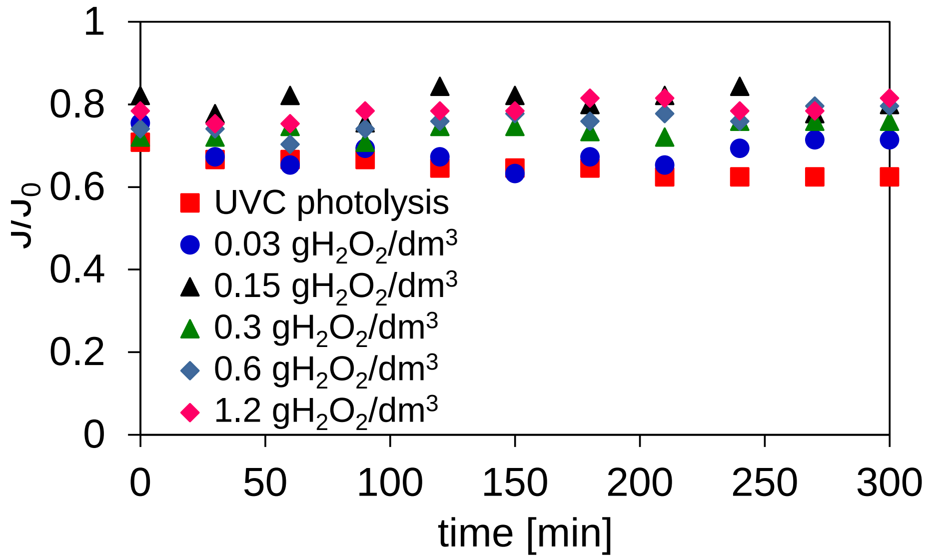
Parameter	Unit	Value
TOC	mg/dm^3	8.1-8.7
Conductivity	µS/cm	555-573
Absorbance UV_{254}	cm^{-1}	0.1568-0.1707
Turbidity	NTU	0.54-1.66
pH	-	7.0-7.9
Cl^-	mg/dm^3	41.2-42.2
NO_3^-	mg/dm^3	0.8-1.7
SO_4^{2-}	mg/dm^3	85.3-86.8
PO_4^{3-}	mg/dm^3	0-0.1
Na^+	mg/dm^3	23.4-24.0
K^+	mg/dm^3	4.9-5.4
Ca^{2+}	mg/dm^3	63.1-67.2
Mg^{2+}	mg/dm^3	16.5-17.1

Influence of AOPs on permeate flux

PMR



UVC/H_2O_2–UF

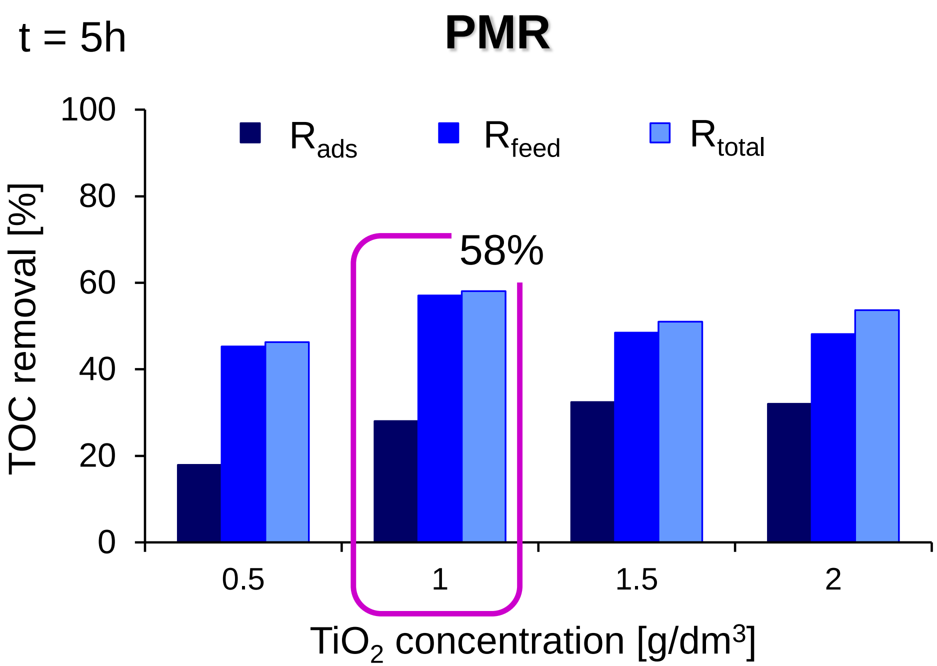


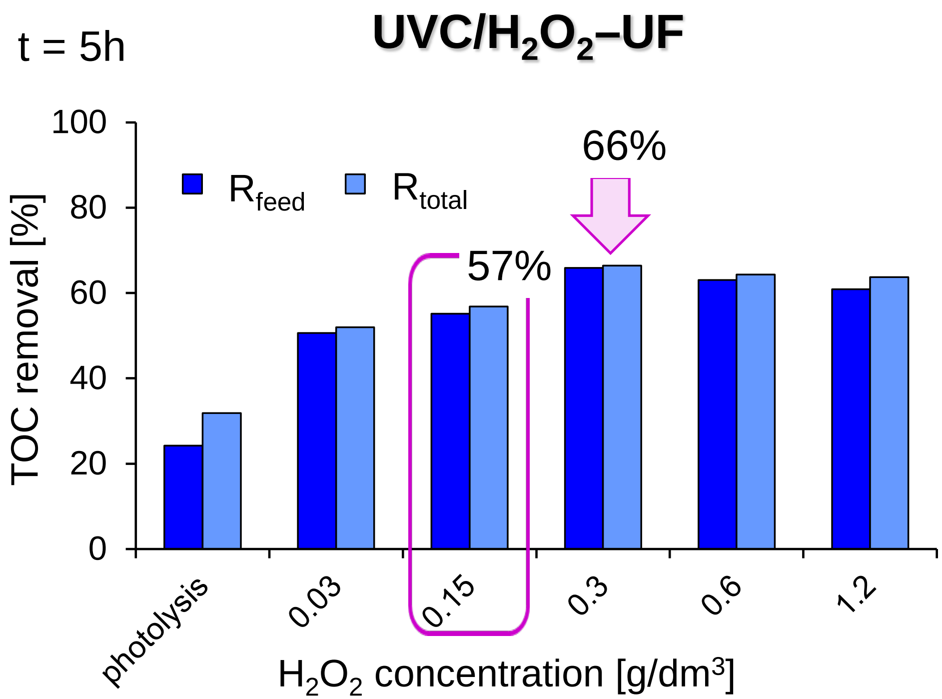
→ **Both AOPs** (TiO_2 photocatalysis and UVC/H_2O_2) have **positive influence** on UF membrane **fouling mitigation** during treatment of lake water

BUT

→ **Increase** of the permeate flux in the presence of **TiO_2 P25** was **slightly higher** than in the presence of **H_2O_2**

Removal of organic contaminants





→ **PMR:** the highest TOC removal rate: **1 gTiO_2/dm^3**.
UVC/H_2O_2 – UF: similar efficiency at **0.15 gH_2O_2/dm^3**.

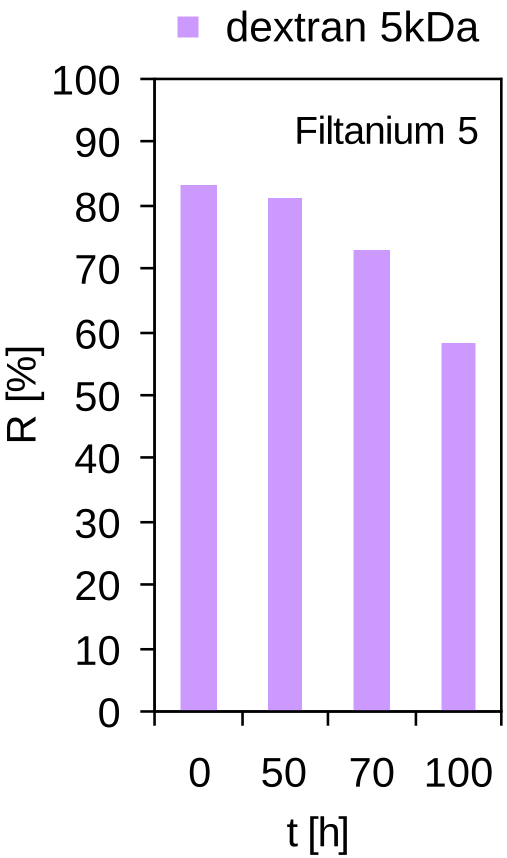
→ **Increase of H_2O_2** concentration up to 0.3 g/dm^3 → **improvement** of mineralization efficiency

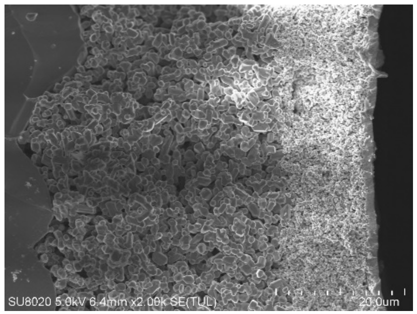
→ **Increase of TiO_2** concentration up to 1.5 g/dm^3 → **decrease** of mineralization efficiency

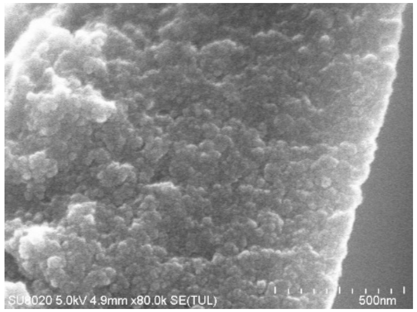
Stability of ceramic membranes in PMRs

photocatalyst: AEROXIDE® TiO_2 P25

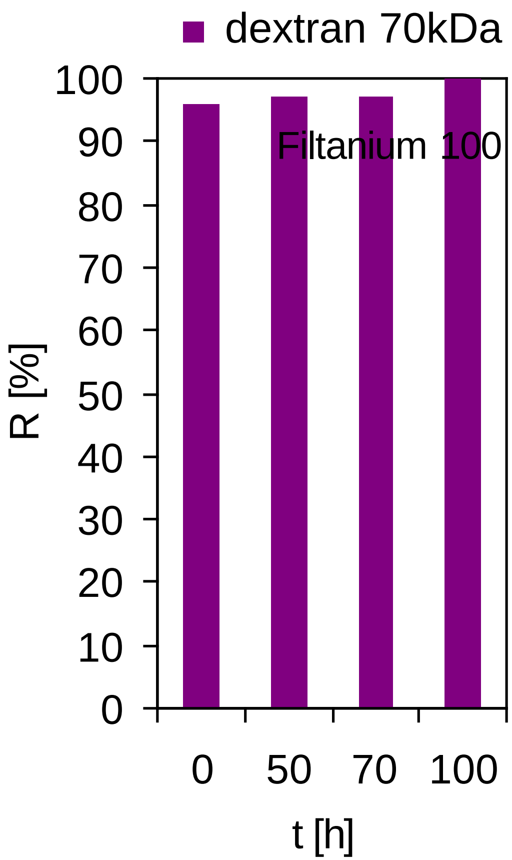
membrane: TiO_2 Filtanium 5kDa

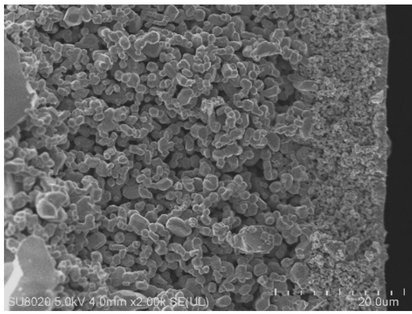


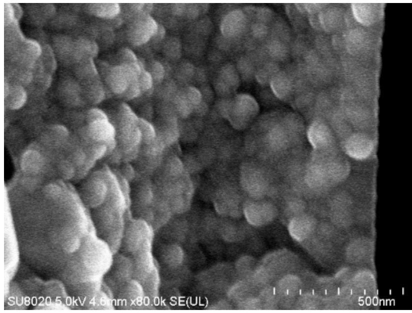




membrane: TiO_2 Filtanium 100kDa







Loss of separation properties → destruction of separation layer → abrasive action of TiO_2 in case of skin layer built of fine particles („fine UF" membrane)

No change in separation properties → no damage of separation layer

A short summary

Hybrid systems coupling AOPs with membrane separation, e.g. PMRs have a great potential in water/wastewater treatment and reuse.

Application of **AOPs** can result in **membrane fouling mitigation** and improvement of the **efficiency of organics removal**.

Application of **membrane separation** is especially advantageous when **retention of photocatalyst** in the reaction environment is necessary. Membrane allows to realize a **continuous process** with **simultaneous separation** of reagents (and photocatalyst) from the solution.

However, further investigations are still needed in order to **improve** the hybrid AOPs – membrane systems performance.

A **particular attention** should be paid to the selection of membranes for PMRs with reference to their resistance to:

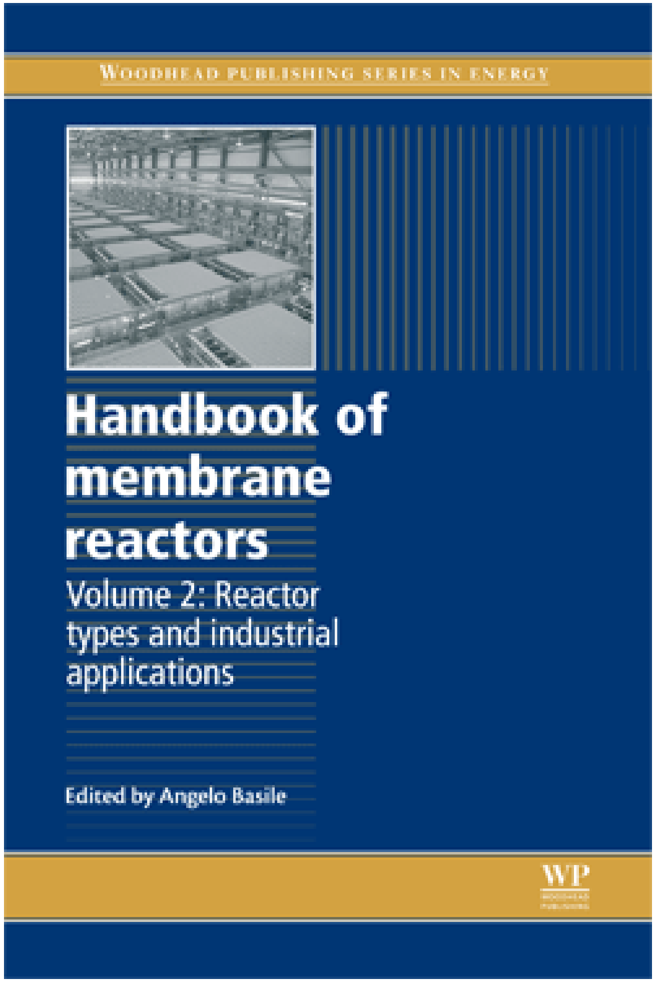
- damage by oxidative species
- abrasion by photocatalyst particles

It is very important to **investigate the real systems**, which focus on treatment of **natural waters and real wastewaters**. The number of reports concerning this subject is still limited, since most of the experiments have been conducted using model solutions.

Acknowledgments

Dominika Darowna
and Kacper Szymański

NATIONAL SCIENCE CENTRE
POLAND



"Handbook of membrane reactors, Volume 2: Reactor types and industrial applications", Ed. Angelo Basile, Woodhead Publishing Limited, Cambridge, UK, 2013

1. S. Mozia, A.W. Morawski, R. Molinari, L. Palmisano, V. Loddo, Chapter 6: "Photocatalytic membrane reactors: fundamentals, membrane materials and operational issues", pp. 236-295

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Thank you for your attention