GDAŃSK UNIVERSITY OF TECHNOLOGY

Application of photocatalysis for degradation of pharmaceuticals

Gdańsk, 8th February 2023

The project "Improving quality of BSR waters by advanced treatment processes" (acronym: AdvIQwater) has received funding from the European Union, Interreg Baltic Sea Region Programme (2021-2027).

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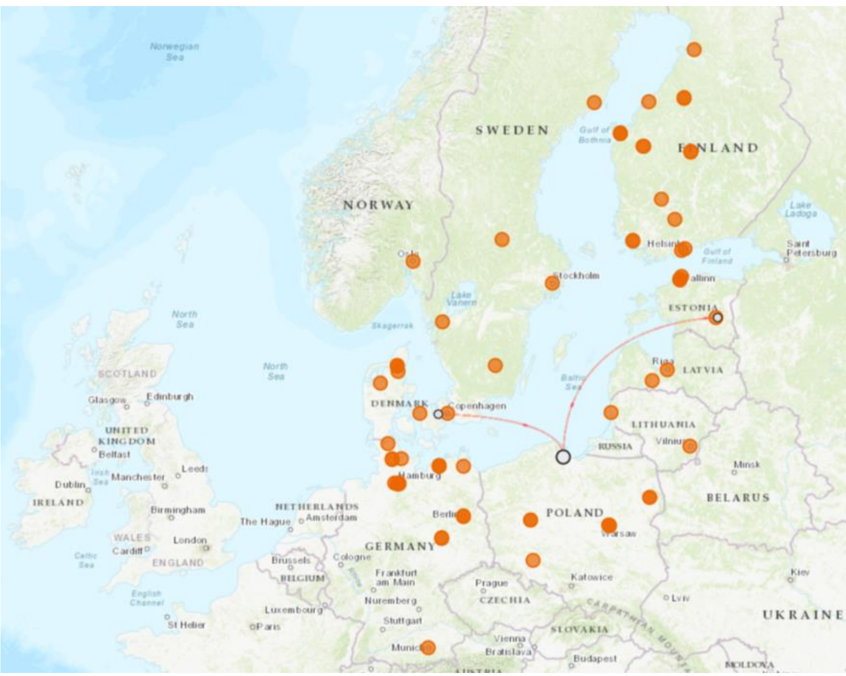
Laboratory of Photocatalysis



Anna Zielińska-Jurek, PhD. DSc. Eng. Assoc. Prof.

Department of Process Engineering and Chemical Technology, Poland

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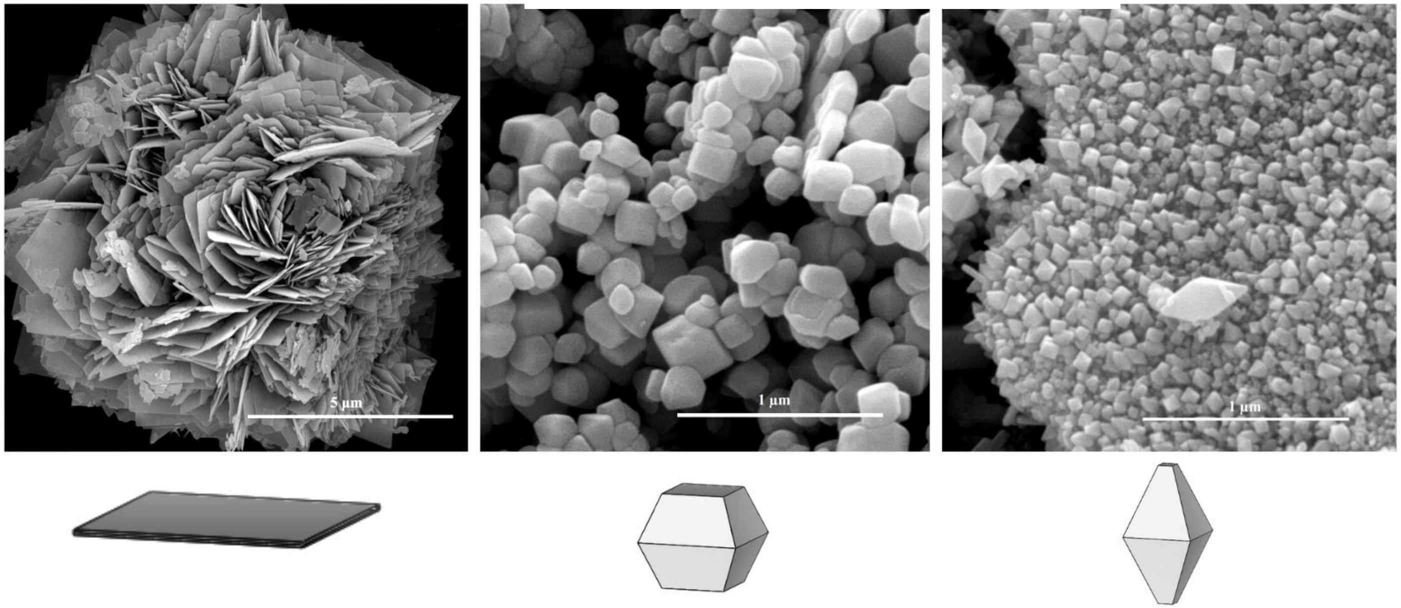

Photocatalytic Research Group

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Photocatalysis can provide solutions for many environmental challenges facing the modern world

Extensive research is devoted mainly to photocatalytic oxidation of emerging contaminants present in water and air. However, photocatalysis can also be applied to the production of fuels like hydrogen or as a green route to obtain valuable chemicals.

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Team of Photocatalysis


Anna Zielińska-Jurek


Izabela Wysocka


Agnieszka Fiszka-Borzyszkowska


Izabela Malinowska


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Agnieszka Sulowska


Marta Kowalkińska


Anna Grzegórska

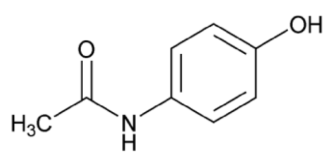
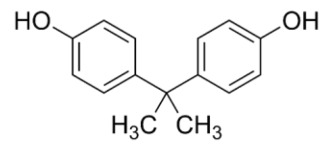
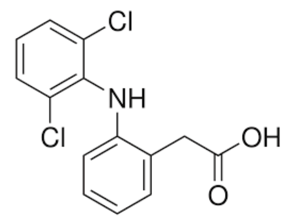
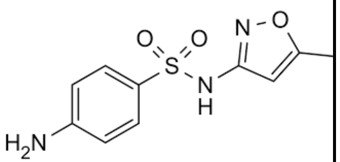
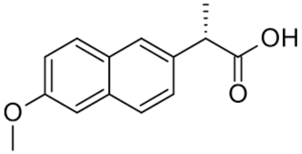
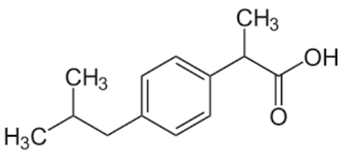
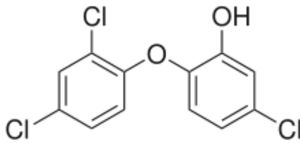
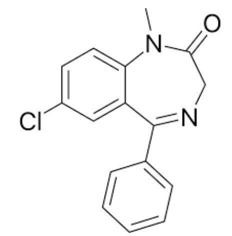
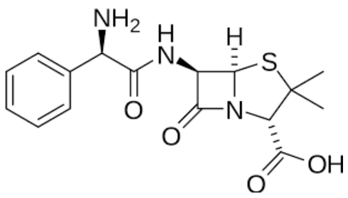
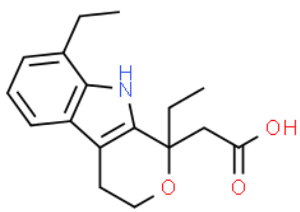
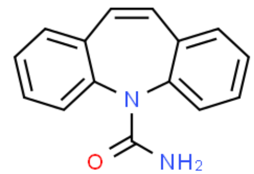
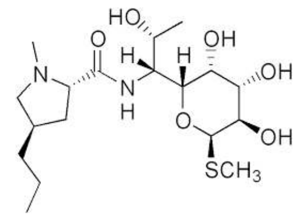

Elvana Cako

Our photocatalysis team is working in four areas of activities:

- Air and Water Remediation
- New Materials
- The conversion of CO_2 and water into chemicals and fuels using solar energy
- Design photocatalytic reactors

Environmental fate of pharmaceuticals in water

Table 1. List of target pharmaceuticals not-susceptible to biodegradation

 **Acetaminophen** (analgesic)	 **Bisphenol A** (plasicizer)	 **Diclofenac** (antiphlogistic)	 **Sulfamethoxazole** (antibiotic)
 **Naproxen** (analgesic)	 **Ibuprofen** (antiphlogistic)	 **Triclosan** (antiseptic)	 **Diazepam** (anticonvulsant)
 **Amoxicilin** (antibiotic)	 **Etodolac** (analgesic)	 **Carbamazepine** (anticonvulsant)	 **Lincomycin** (antibiotic)

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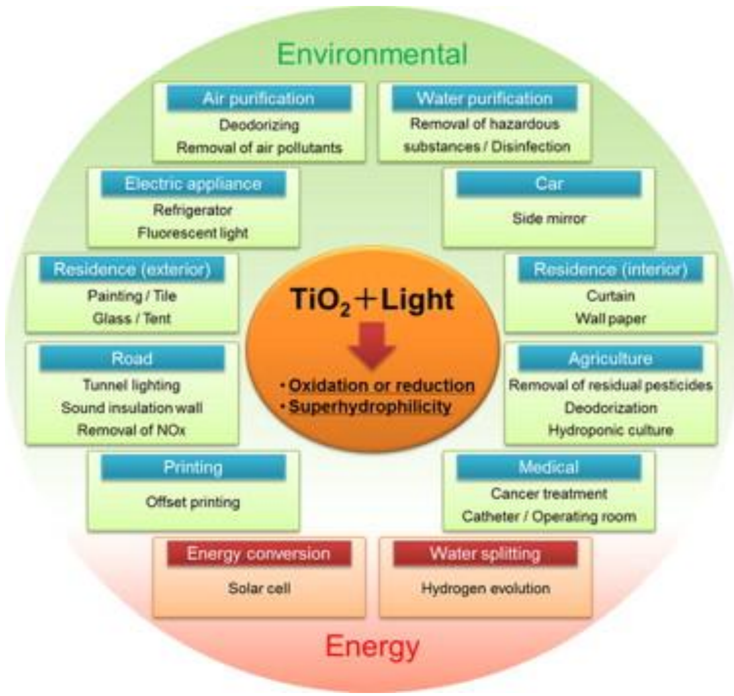
Active Pharmaceutical Ingredients (API)

Pharmaceutical compound	Molecule	Influent (μg/L)	Effluent (μg/L)	Removal efficiency (%)
Analgesics and anti-inflammatory	Naproxen	5.08	0.93	82
	Ibuprofen	13.48	3.48	74
	Acetaminophen	36.7	0.04	95
Antibiotics	Doxycyclin	0.65	0.42	35
	Ciprofloxacin	0.62	0.23	62
	Ofloxacin	0.48	0.17	64
	Sulfamethoxazole	0.32	0.26	18
	Tetracyclin	46.8	2.34	95
Antiepileptics	Carbamazepine	0.73	0.77	not removed
	4-Aminoantipyrine	1.51	0.67	55
	Diclofenac	1.04	0.68	34
Desinfectant	Triclosan	0.85	0.19	77

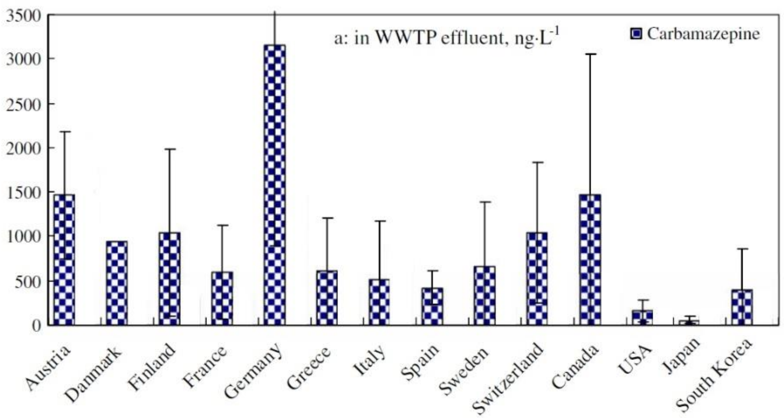


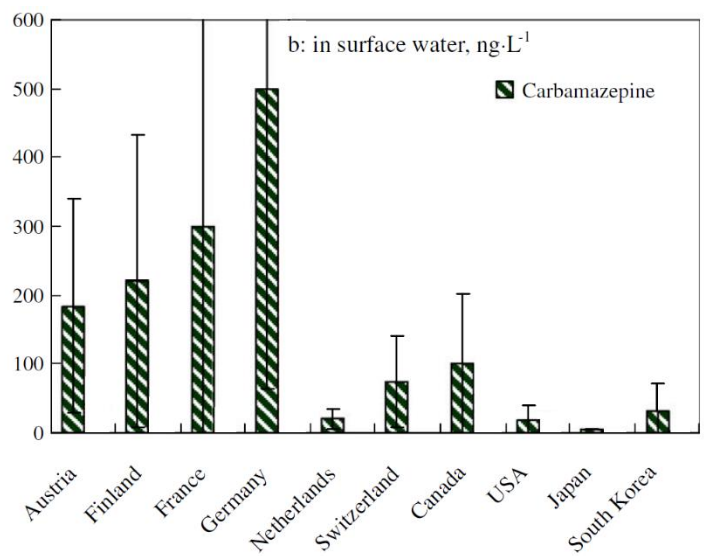
Two projects granted from Polish National Science Center

NATIONAL SCIENCE CENTRE POLAND

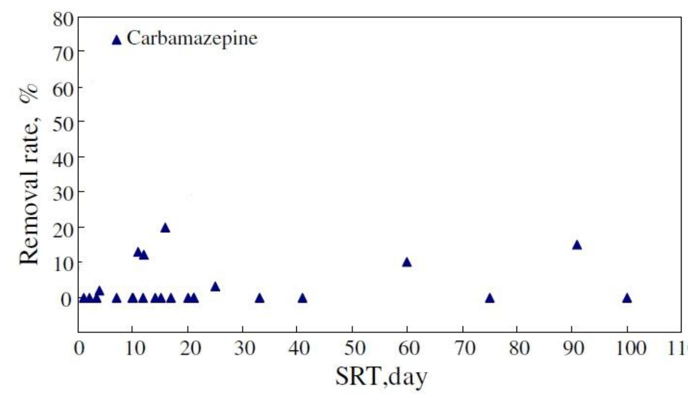
- Design, synthesis, and physicochemical characterization of 2D nanosheet-based hybrid photocatalysts for degradation of pharmaceuticals – Sonata Bis 8 (2019-2022)
- Synthesis, physicochemical properties and characteristics of the photocatalytic TiO_2 nanocomposites based on spinel and hexagonal ferrites used for oxidation of organic contaminants in the aqueous phase – Sonata 12 (2016-2018)

Carbamazepine

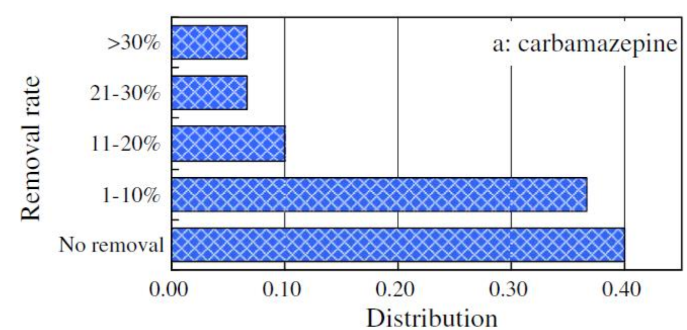




- Carbamazepine - dibenzazepine derivative with antiepileptic and psychotropic activity, also well established in treatment of severe pain syndromes associated with neurological disorders, such as trigeminal neuralgia.



- Carbamazepine shows **low sorption** properties and **high persistence** to biodegradation



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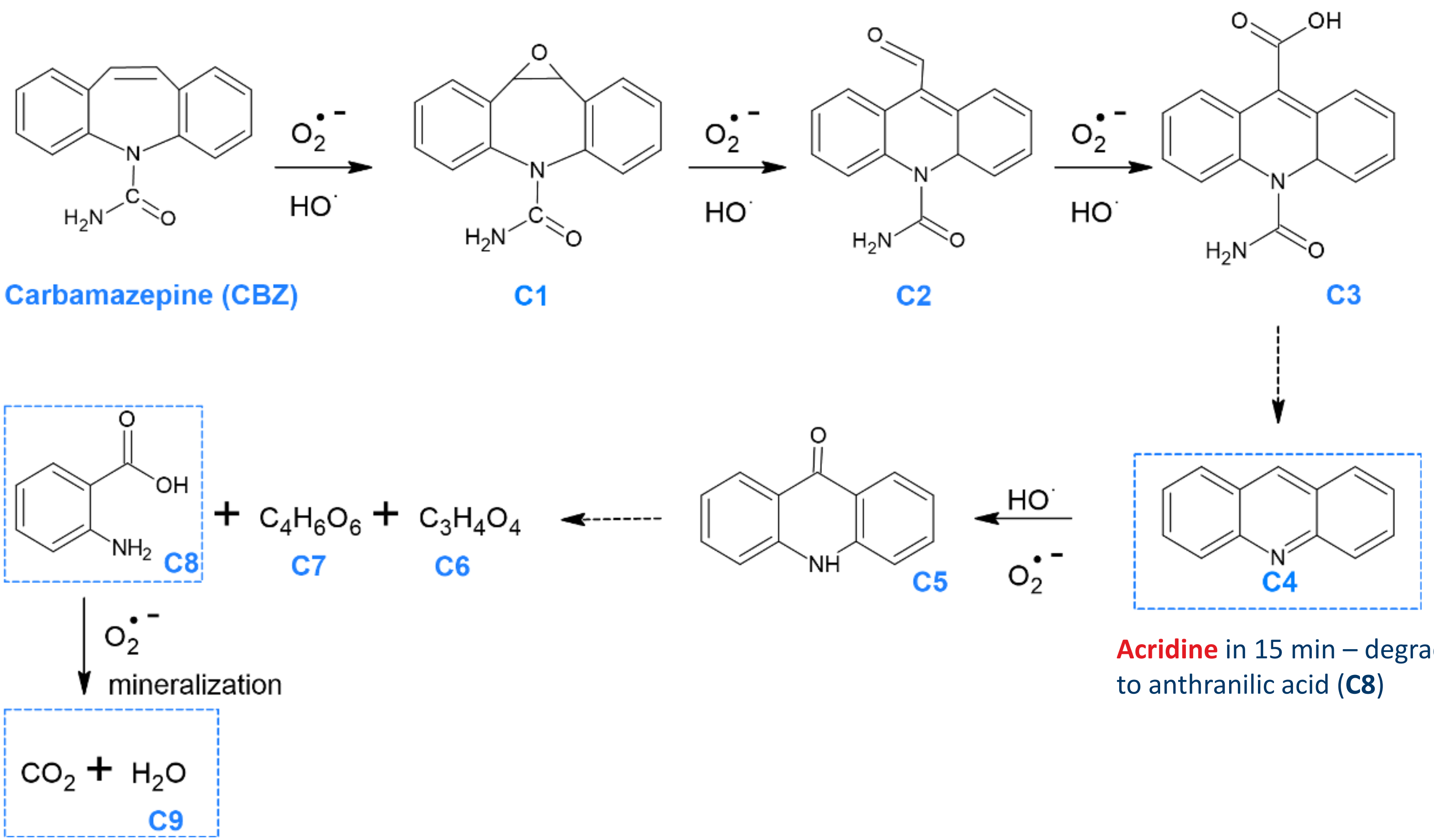
Carbamazepine degradation pathway



Acridine in 15 min – degradation to anthranilic acid (**C8**)

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Acetaminophen

- Acetaminophen (paracetamol) - member of the analgesic and antipyretic drugs group.
- It is included in the WHO Model List of Essential Medicines in 2019. One of the top 200 drugs prescribed overall the world.
- Acetaminophen is used as an antipyretic (fever reducer) and as an analgesic (pain reliever) due to migraine, headache, muscular aches, neuralgia, backache, toothache, and general pain.
- Acetaminophen generate chloramines, which are toxic.
- Acetaminophen gives rise to highly toxic N-acetyl-p-benzoquinone imine and 1,4-benzoquinone upon chlorination treatment.
- **Detected in** wastewater treatment plants, rivers and muds with concentrations in the range 6-65 µg/L.

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Scientific tasks

1. Can we identify improved strategies for treating pharmaceuticals & WW-derived micropollutants?

- *redox transformation to inactive byproducts*
- *selective*
- *sustainable*

2. What are the mechanisms controlling micropollutant redox transformations?

- *kinetics*
- *transformation products*
- *effects of water quality & non-target constituents*

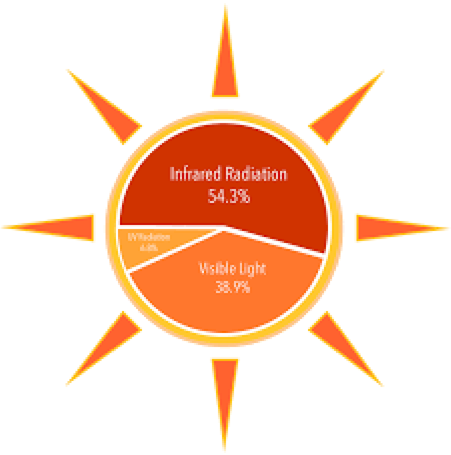
3. Removing the drop of poison in the ocean of water. How low should we go?

- *oxidation vs. mineralization ?*
- *Which pharmaceuticals/metabolites?*

Scientific tasks

4. New solutions should be **sustainable**

- *Energy efficient*
- *Limited chemical inputs*
  - Advanced Oxidation Technologies
  - Heterogeneous photocatalytic processes



Light and **oxygen** are two of the most important abiotic factors involved in the environmental fate of xenobiotics, in aquatic systems and/or in the surface of soils

Advanced Oxidation Processes

OH·

In-situ production of hydroxyl radicals (·OH)

oxidizing agent	oxidation potential [V]
hydroxyl radicals	2.89
Fenton’s reagent	2.76
ozone	2.07
hydrogen peroxide	1.78
hypochlorous acid	1.49
chlorine	1.36

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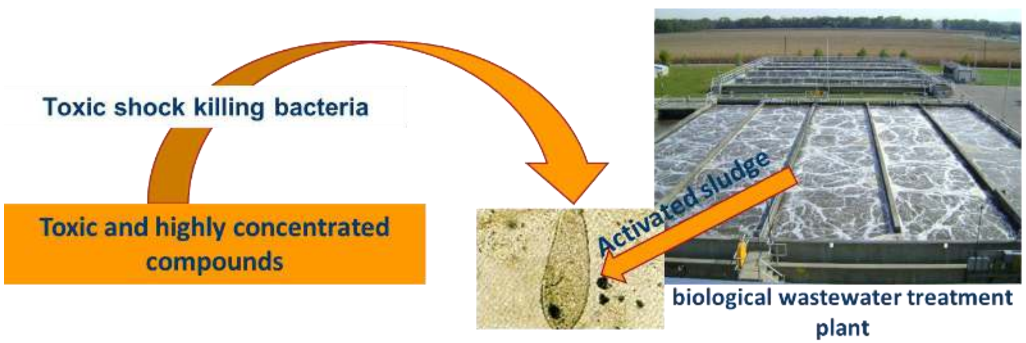
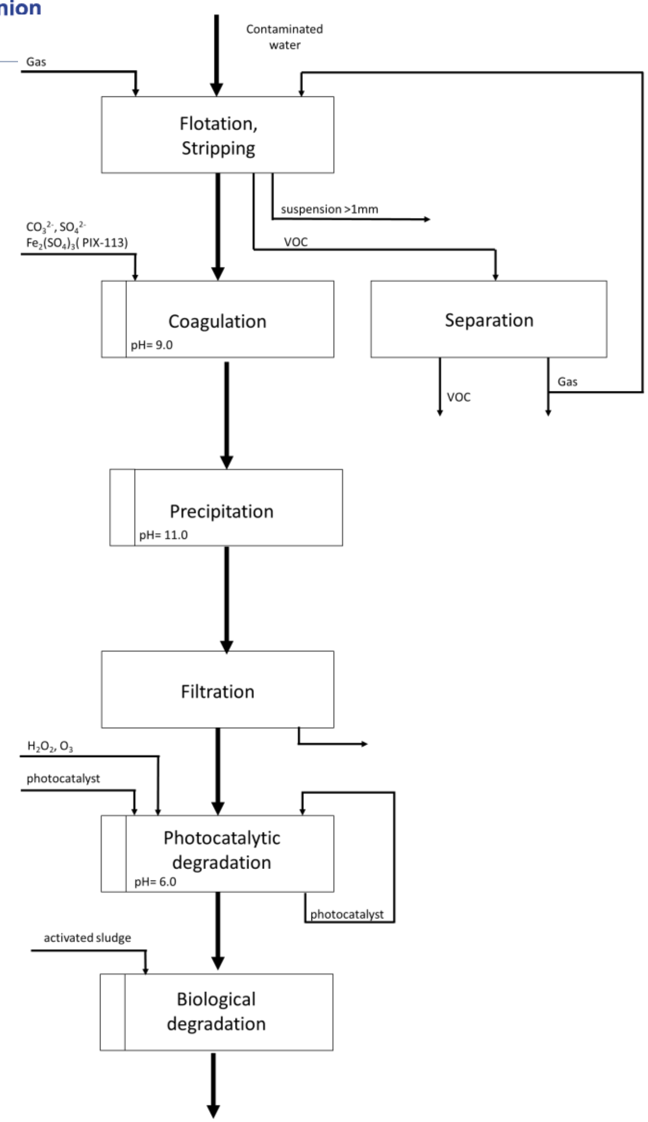
Advanced Oxidation Processes

- Ability to reduce the concentration of contaminants from several-hundreds ppm (mg/dm^3) to less than a few ppb (µg/dm^3)



- biologically toxic or non-degradable materials such as aromatic, pesticides, petroleum etc.
- high concentrated (to increase /BOD/COD/ - biodegrability)
- volatile organic compounds in wastewater
- to treat effluent of secondary treated wastewater - **tertiary treatment**



Method for treating of flow back water after shale gas exploration, Patent PL 414343 (2020)

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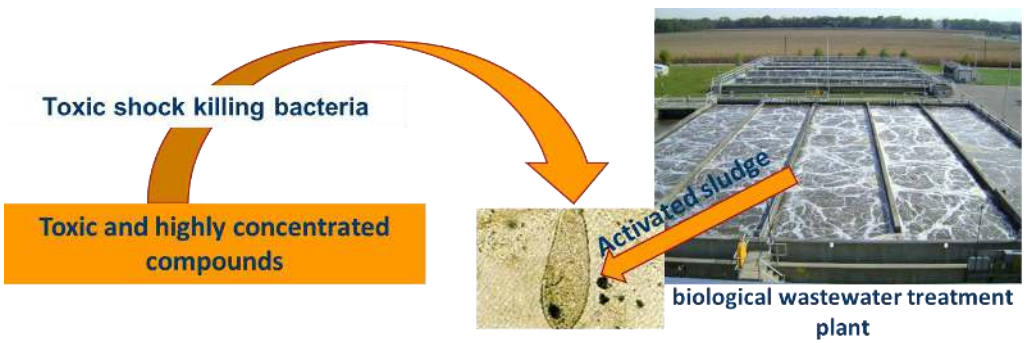

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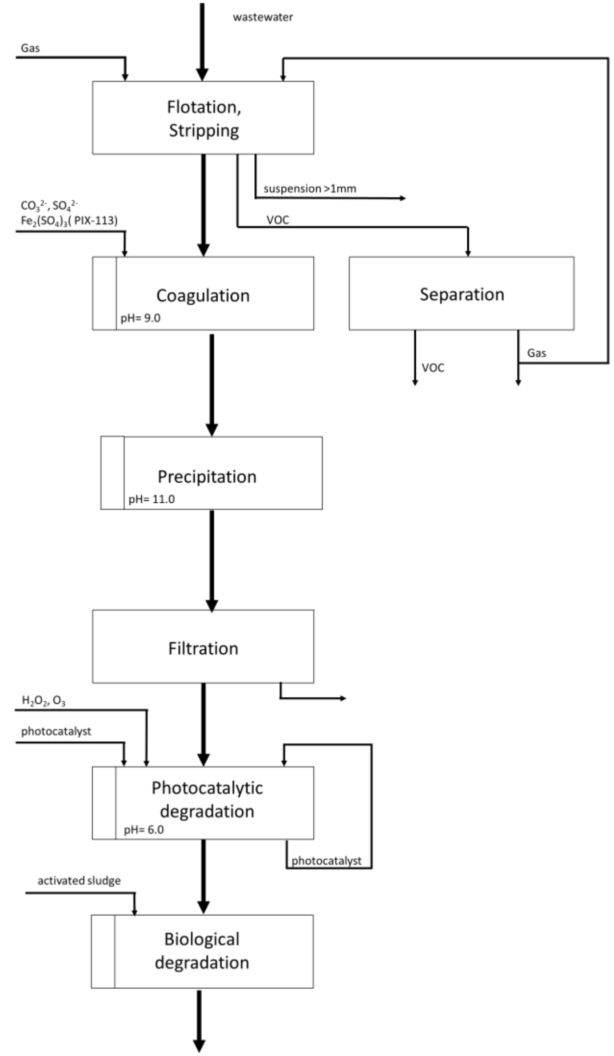
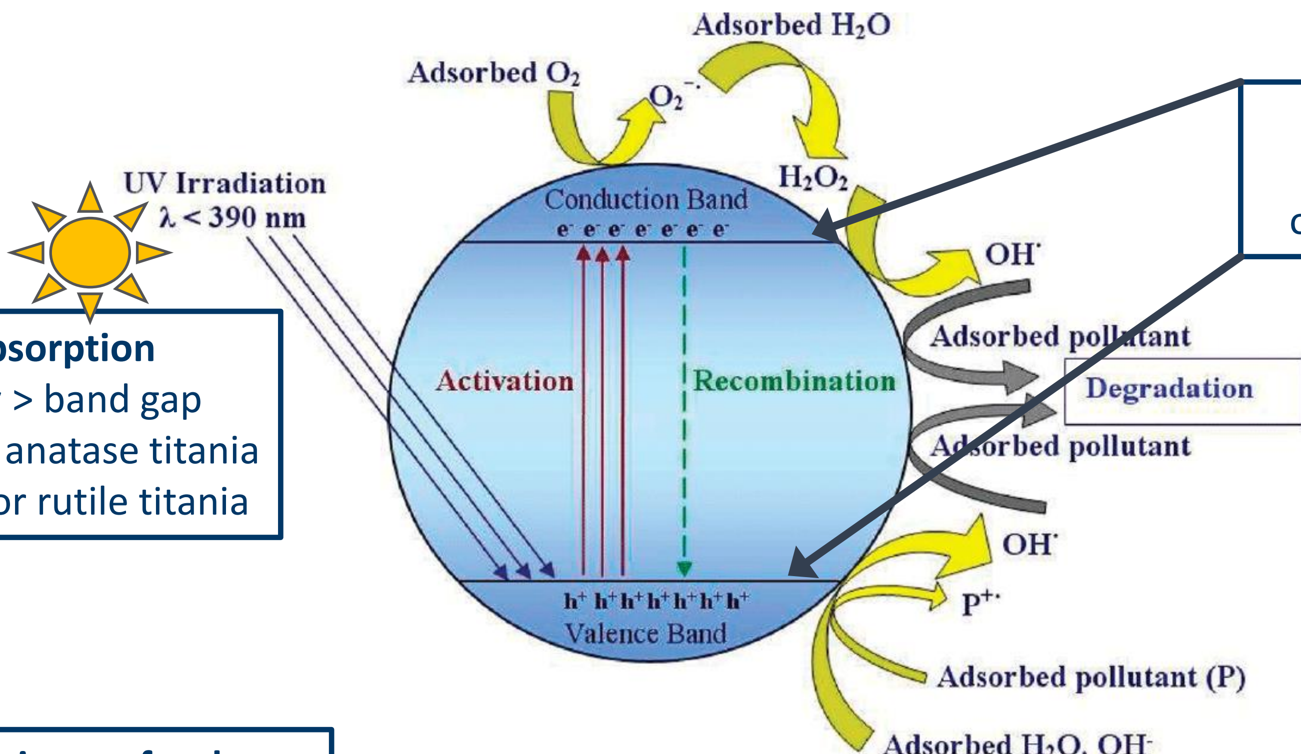


A. Zielińska-Jurek, J. Hupka, Method for treating of flow back water after shale gas exploration, Patent PL 414343 (2020)

How semiconductor is working ?



1. Light absorption
Energy > band gap
3.2 eV for anatase titania
3.06 eV for rutile titania

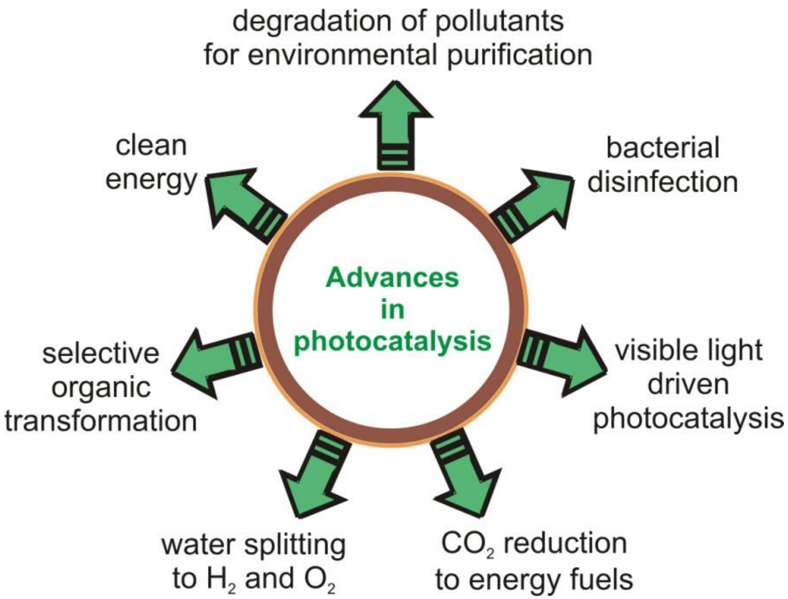
2. Activation
(generation
of charge carriers)

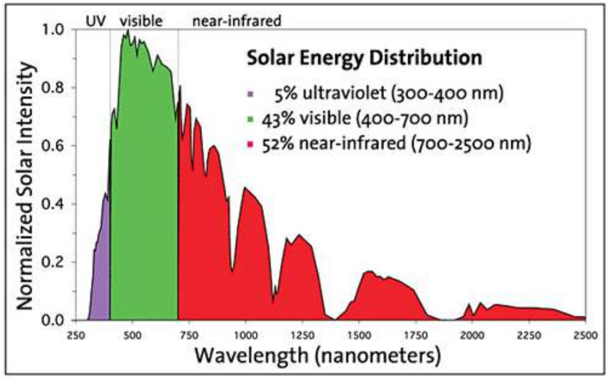
3. Migration of charge carriers to the surface (or volume recombination of charge carriers)

4. Redox reactions
(or surface recombination
of charge carriers)

Advances in TiO_2-based photocatalysis

Goals:





- ○ Development of a new light harvesting assemblies
- ○ Elucidation charge transfer processes
- ○ Improvement of quantum yield efficiency
- ○ Characterize kinetics and mechanism of xenobiotics oxidation
- ○ Identify strategies for improving chemical selectivity

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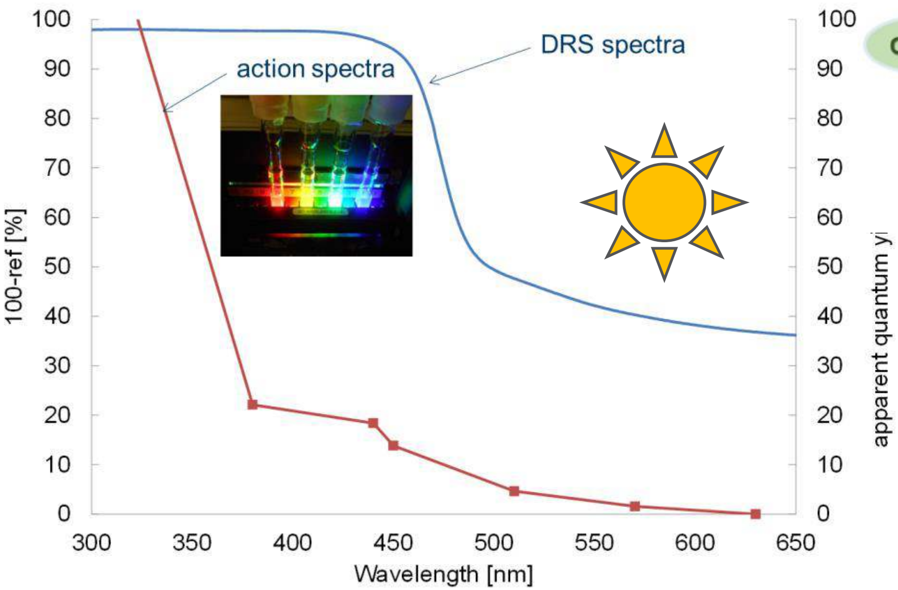
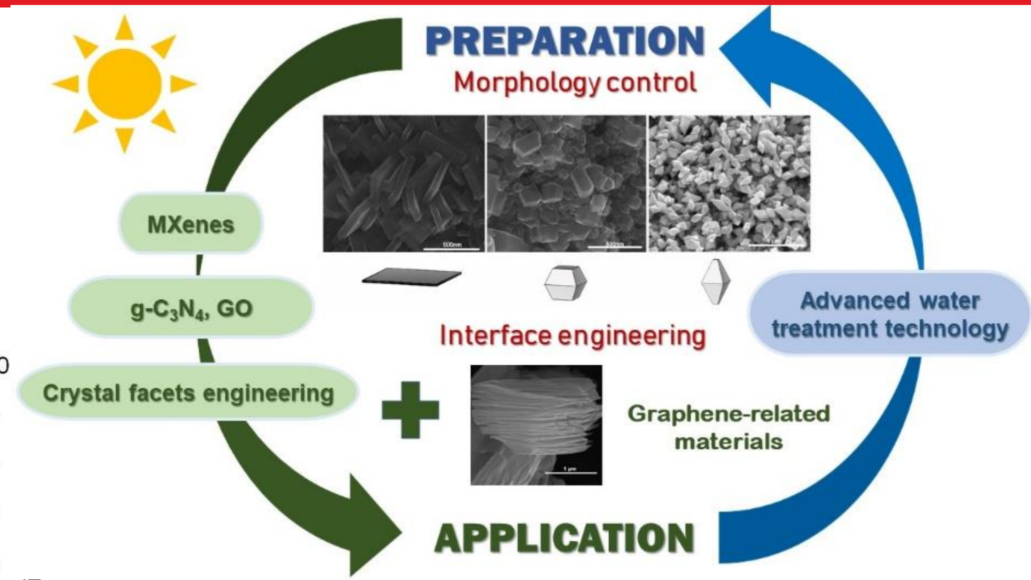
Experimental design

Visible light activated photocatalyst

- doped or modified with metals
- doped or modified with nonmetals





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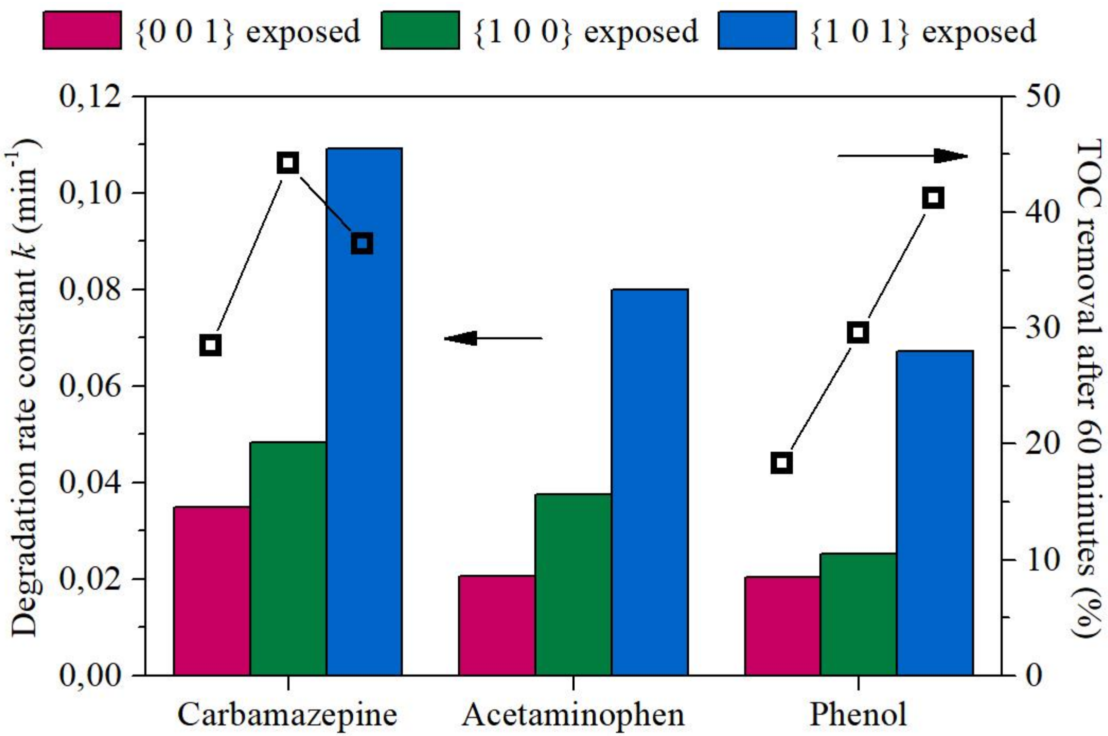
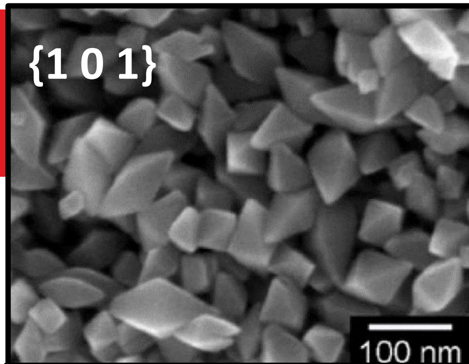
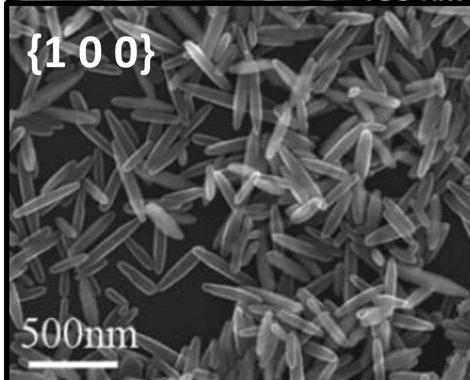
The surface chemistry of photocatalytic materials

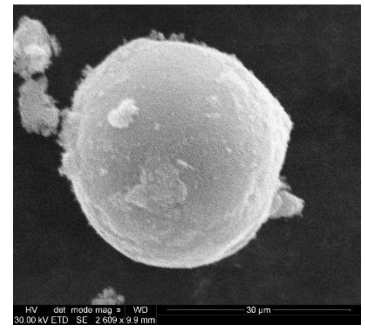


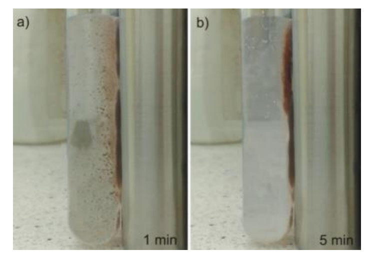


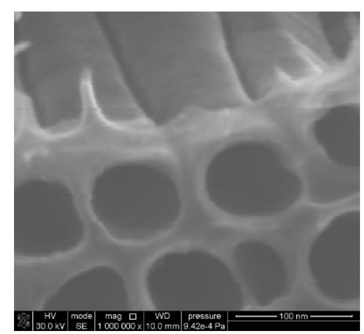


Experimental system

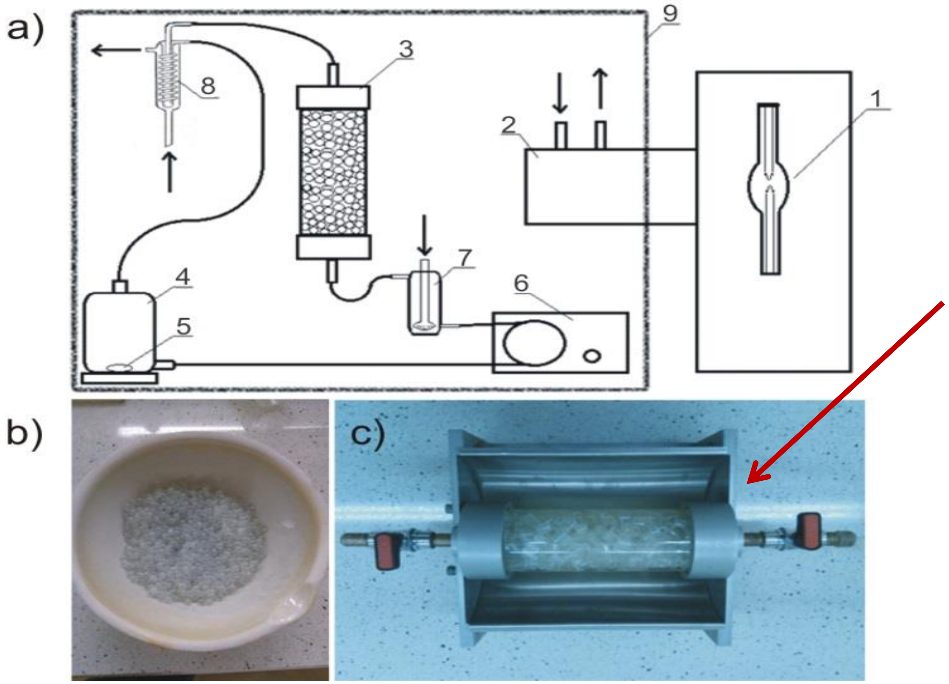
1. Visible light activated photocatalyst
   - doped or modified with metals
   - doped or modified with nonmetals
2. Separable photocatalysts
   - immobilized on microspheres
   - with magnetic properties
   - oriented structures as thin films
3. Scale-up of photoreactor





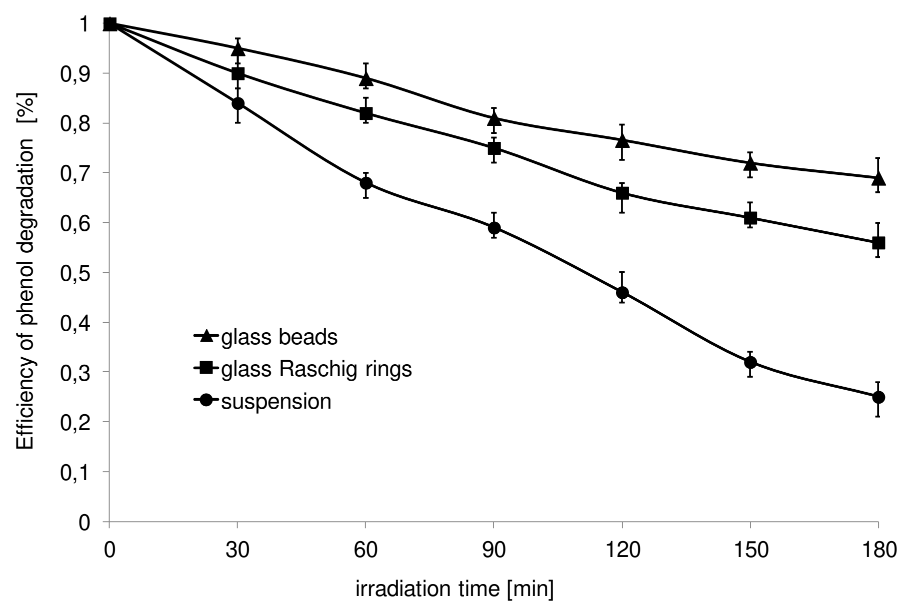


Immobilization of TiO_2 nanoparticles on solid substrate



a) Experimental setup: 1-2) Irradiation source: UV-Vis, light flux 150 W/m^2, 3) photoreactor with parabolic mirror, 4) storage tank, 5) magnetic stirrer, 6)peristaltic pump, 7) bubbling, 8) cooling water, **b)** glass beads (5 mm diameter); **c)** photoreactor filled with Raschig rings.

Photoreactor, made of a cylindrical quartz tube (i.d. 45 mm, length 130 mm) filled with Pt/I-TiO_2-coated glass beads or Raschig rings and positioned over an aluminum parabolic mirror. 0.5 dm^3 of phenol solution (0.2 mmol/dm^3) was pumped in a loop with a flow rate of 5 cm^3/min, λ>420 nm, 150W xenon lamp (flux=15 mW·cm^{-2})



Efficiency of phenol degradation in fixed bed photoreactor with Pt/I-TiO_2 coating on glass Raschig rings, glass beads and in the slurry system.

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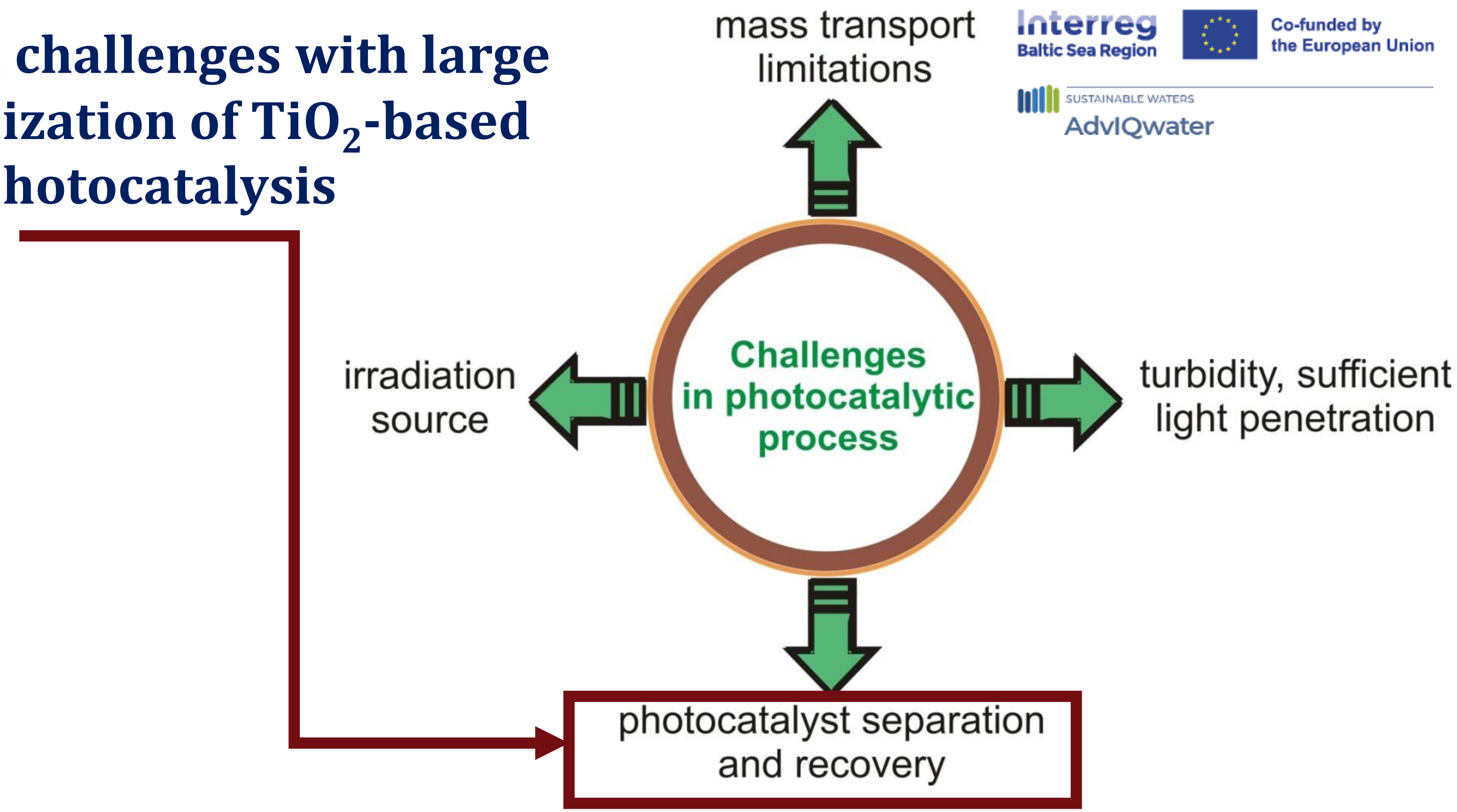
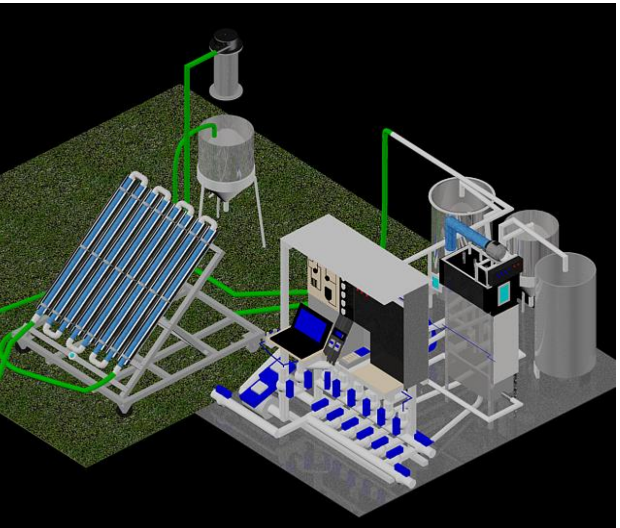
Technical challenges with large scale utilization of TiO_2-based photocatalysis





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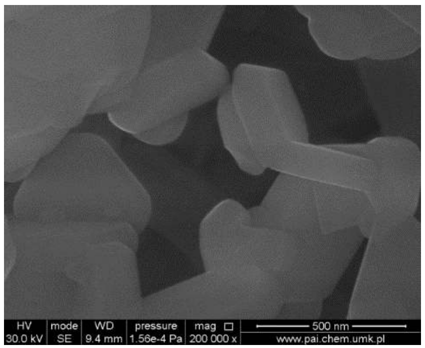
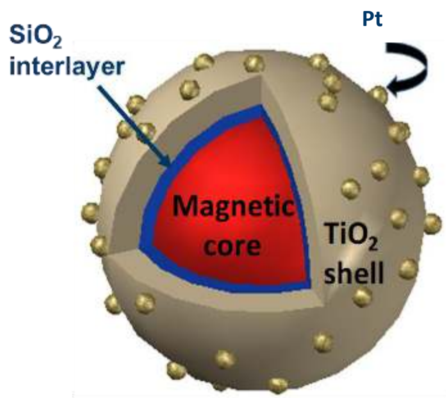
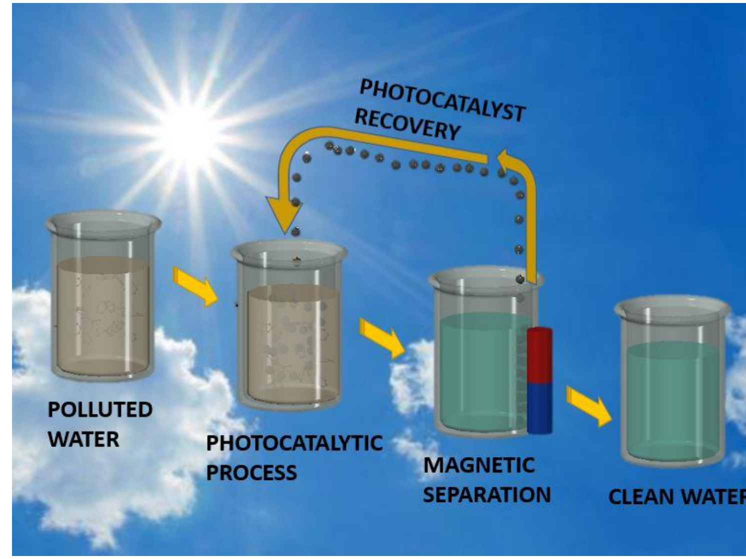
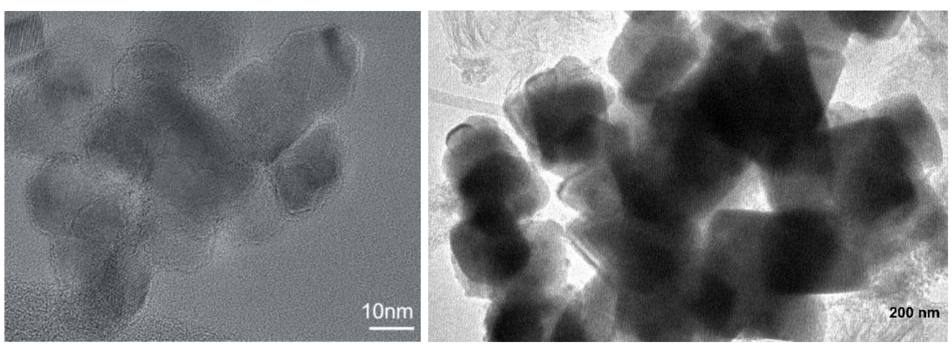
Magnetic photocatalysts



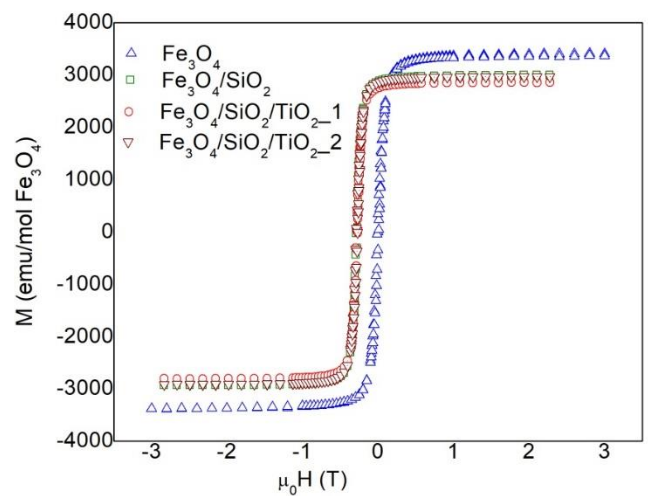
$BaFe_{12}O_{19}$ as a magnetic core







Spinels $CoFe_2O_4$ and Fe_3O_4 as a magnetic core



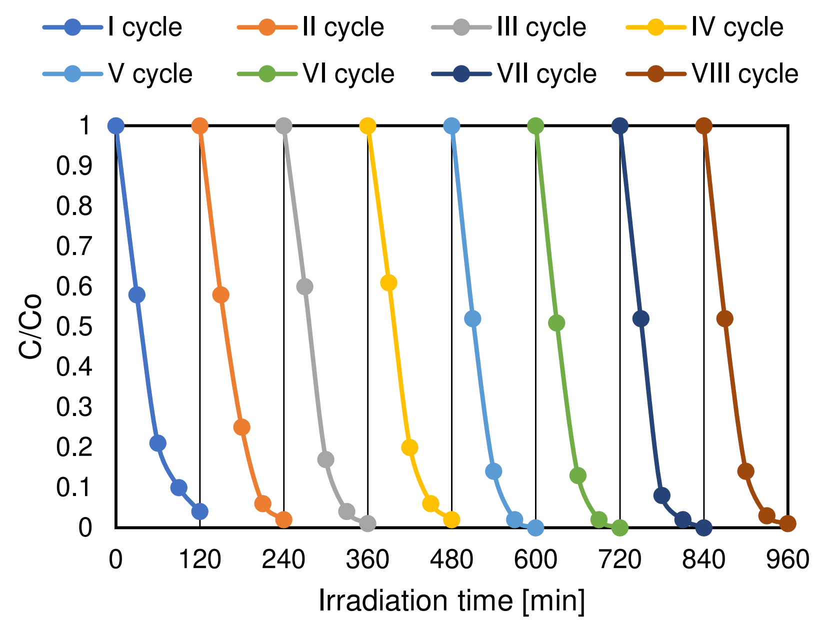
Magnetic hysteresis loops for Fe_3O_4 particles and $Fe_3O_4/SiO_2/TiO_2$ nanocomposites

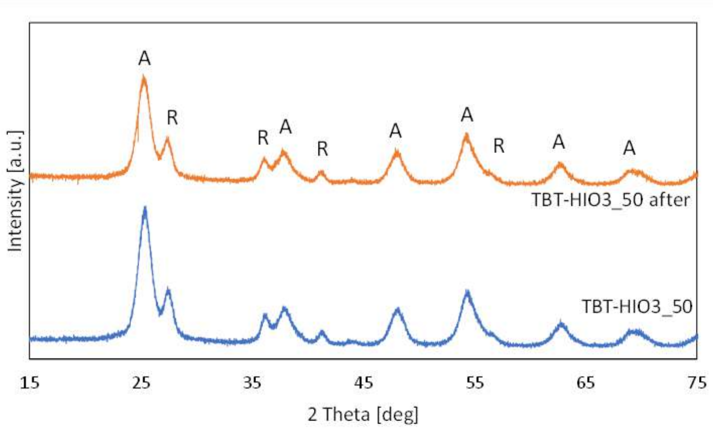
Photocatalyst stability

Tab. 1. Leaching of iron from $Fe_3O_4/SiO_2/TiO_2$ during dissolution and photodissolution analysis.

pH value	Parameters	Concentration of iron [$mg \cdot dm^{-3}$]
3	Absence of UV radiation	0.03
	Presence of UV radiation	0.04
5	Absence of UV radiation	0.00
	Presence of UV radiation	0.01
7	Absence of UV radiation	0.00
	Presence of UV radiation	0.01

A. Zielińska-Jurek, Z. Bielan, I. Wysocka, J. Strychalska, M. Janczarek, T. Klimczuk; *Journal of Environmental Management, 195 (2017) 157-165*





Results:

Up to eight 2-hour processes of carbamazepine photodegradation on the same dose of $Fe_3O_4/SiO_2/d\text{-}TiO_2\text{-}Pt$ magnetic photocatalyst, with no loss in photoactivity

S. Dudziak, Z. Bielan, P. Kubica, A. Zielińska-Jurek, Optimization of carbamazepine photo-degradation on defective TiO_2-based magnetic photocatalyst, Journal of Environmental Chemical Engineering 9 (2021) 105782

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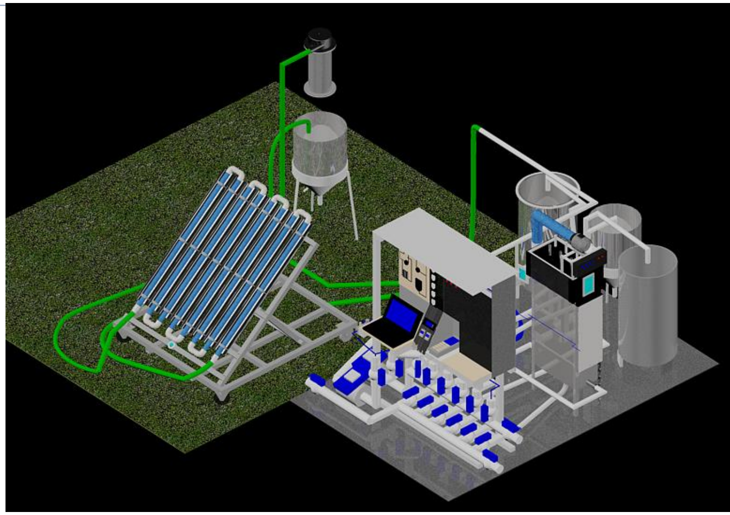
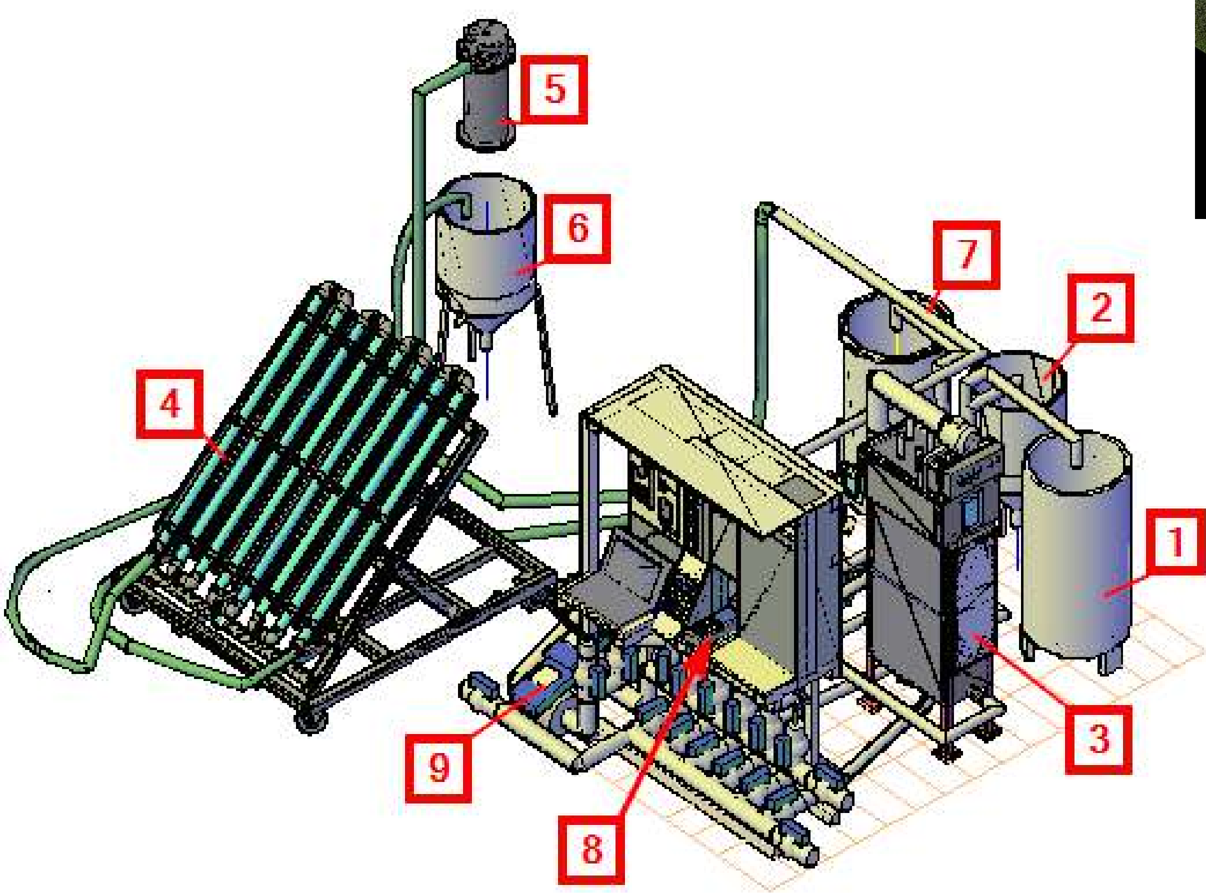
Photocatalytic treatment system





1. Coagulation module
2. Suspended photocatalyst
3. Photoreactor 2 (ALPR)
4. Photoreactor (NLPR)
5. Hydrocyclone
6. Tank
7. Photocatalyst separation unit
8. Control panel
9. Pump

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Photocatalytic system for degradation of emerging contaminants in water

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Floating laboratory PHOTON

PHOTON lab is adapted to marine research and analytical technology

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HISTORY IS WISDOM
FUTURE IS CHALLENGE

The project "Improving quality of BSR waters by advanced treatment processes" (acronym: AdvIQwater) has received funding from the European Union, Interreg Baltic Sea Region Programme (2021-2027).

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