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The growing problem of water pollution with pharmaceuticals. Challenges, prospects and solutions.

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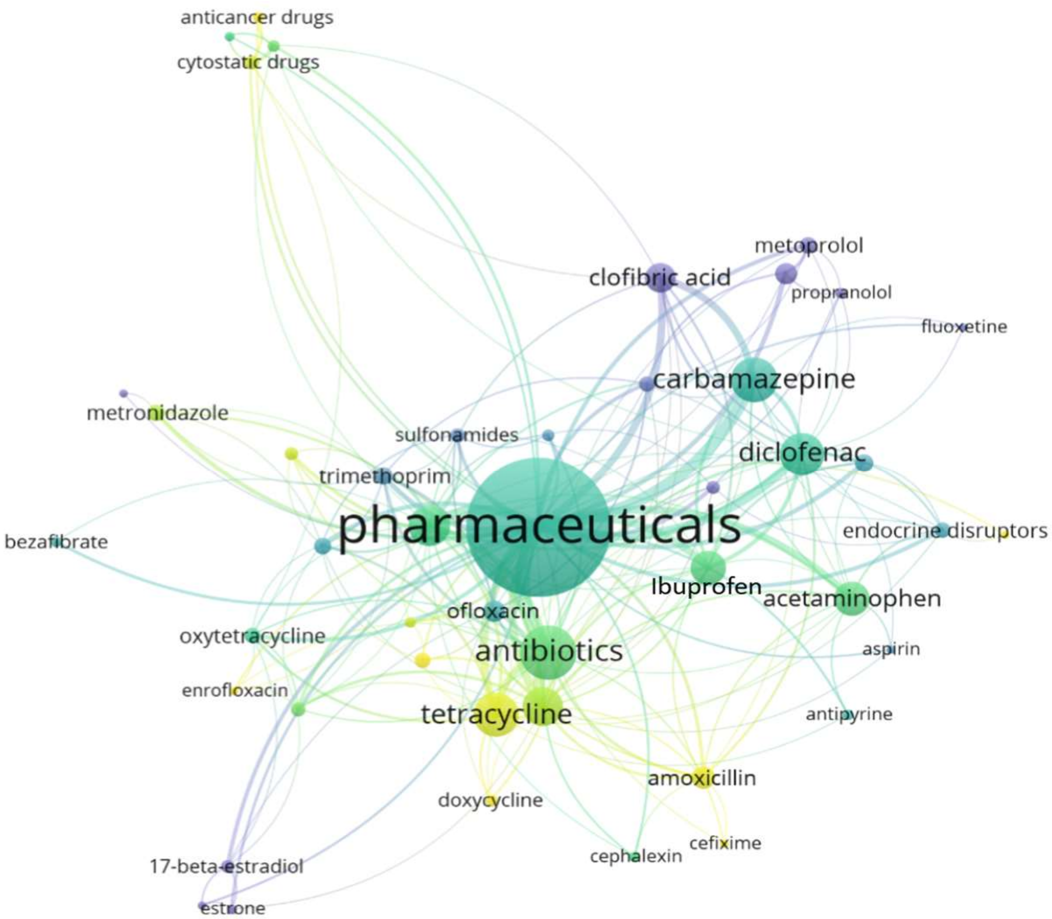
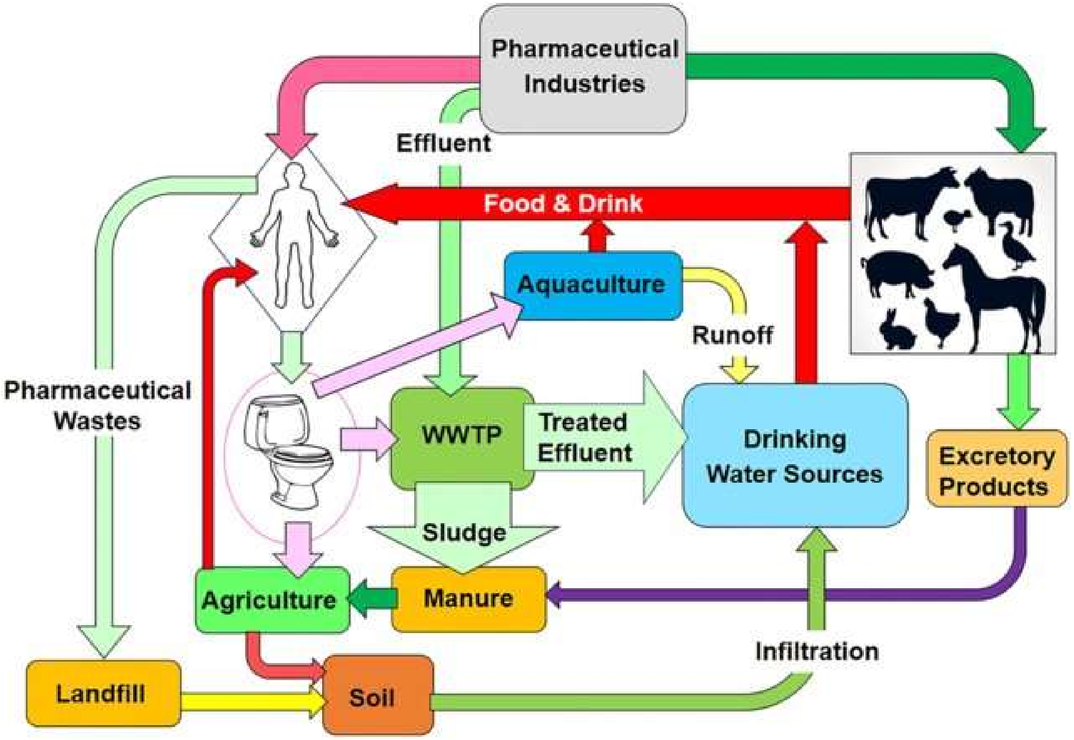
Pharmaceuticals in modern medicine



Fate of pharmaceuticals in the environment



Clean Technologies and Environmental Policy (2020) 22:11–42

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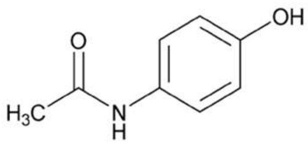
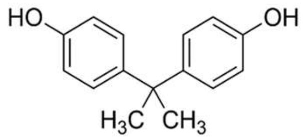
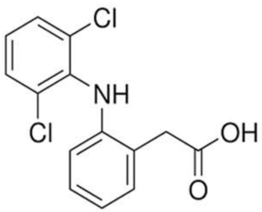
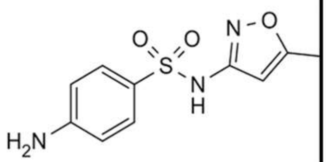
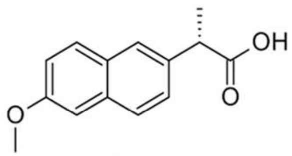
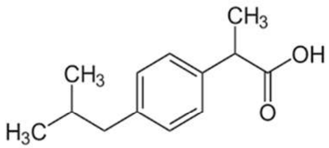
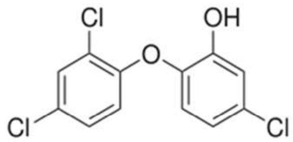
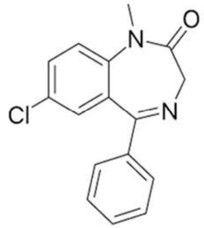
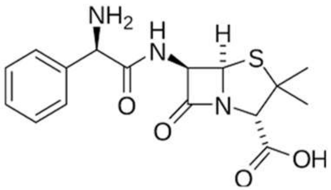
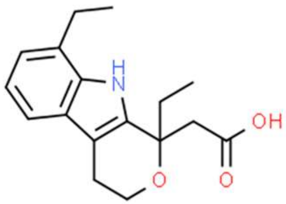
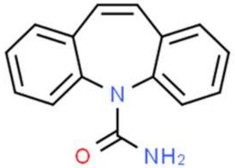
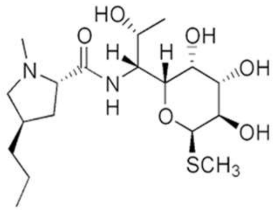
Environmental fate of pharmaceuticals

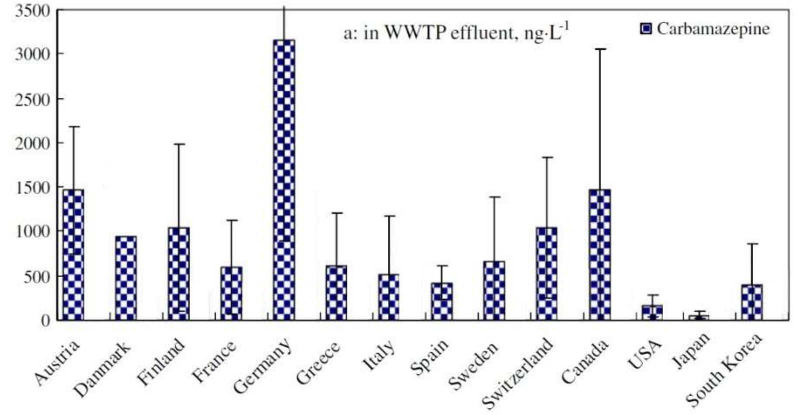
Table 1. List of target pharmaceuticals not susceptible to biodegradation

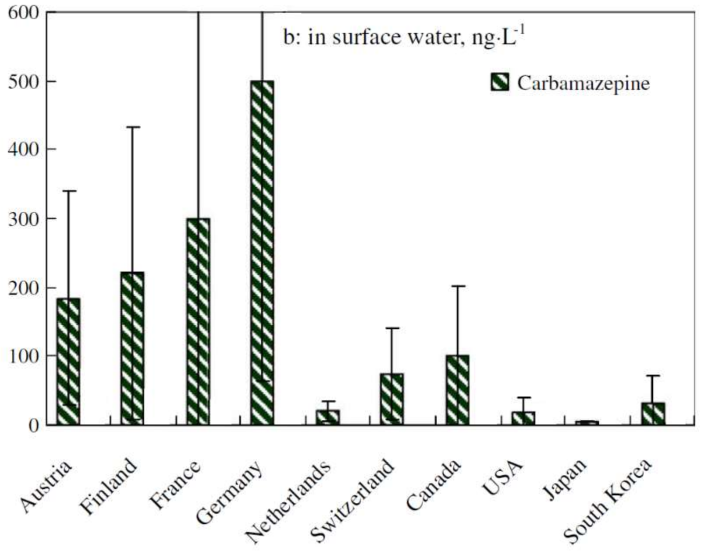
 **Acetaminophen** (analgesic)	 **Bisphenol A** (plasticizer)	 **Diclofenac** (antiphlogistic)	 **Sulfamethoxazole** (antibiotic)
 **Naproxen** (analgesic)	 **Ibuprofen** (antiphlogistic)	 **Triclosan** (antiseptic)	 **Diazepam** (anticonvulsant)
 **Amoxicilin** (antibiotic)	 **Etodolac** (analgesic)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

Active pharmaceutical ingredients (API)

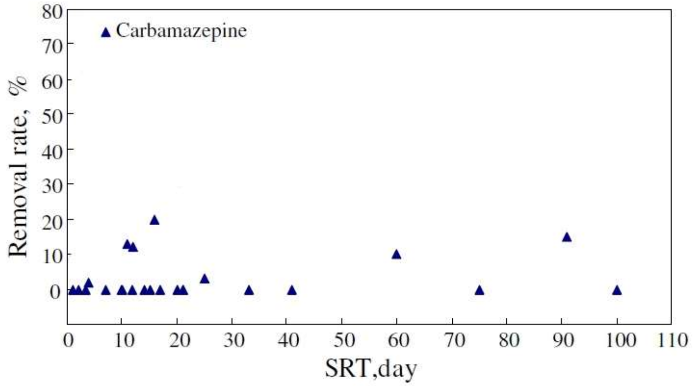
Pharmaceutical compound	Molecule	Influent (µg/L)	Effluent (µg/L)	Removal efficiency (%)
Analgesics and anti-inflammatory	Naproxen	5.08	0.93	82
	Ibuprofen	13.48	3.48	74
	Acetaminophen	36.7	0.04	95
Antibiotics	Doxycycline	0.65	0.42	35
	Ciprofloxacin	0.62	0.23	62
	Ofloxacin	0.48	0.17	64
	Sulfamethoxazole	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

Carbamazepine

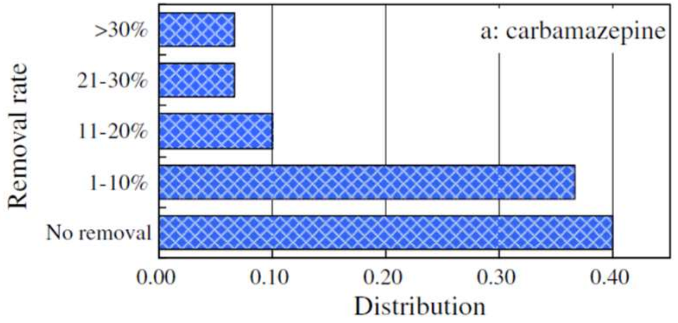




- Carbamazepine - dibenzazepine derivative with antiepileptic and psychotropic activity, also well established in treatment of severe pain syndromes associated with neurological disorders, such as trigeminal neuralgia.



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



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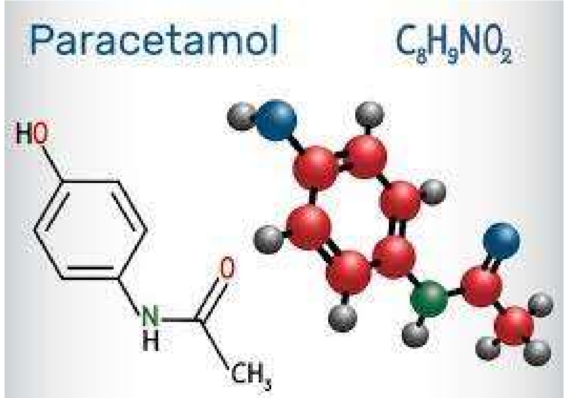
Acetaminophen



- 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 from 6 to 65 µg/L.

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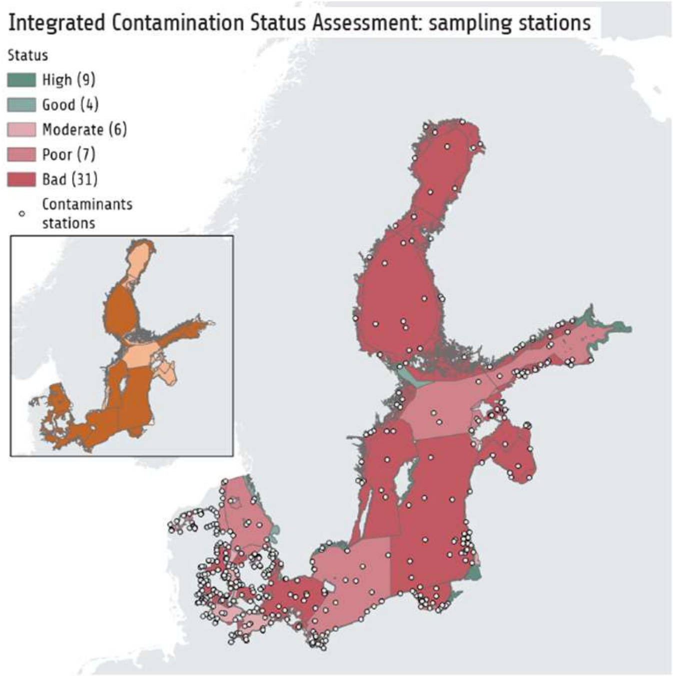
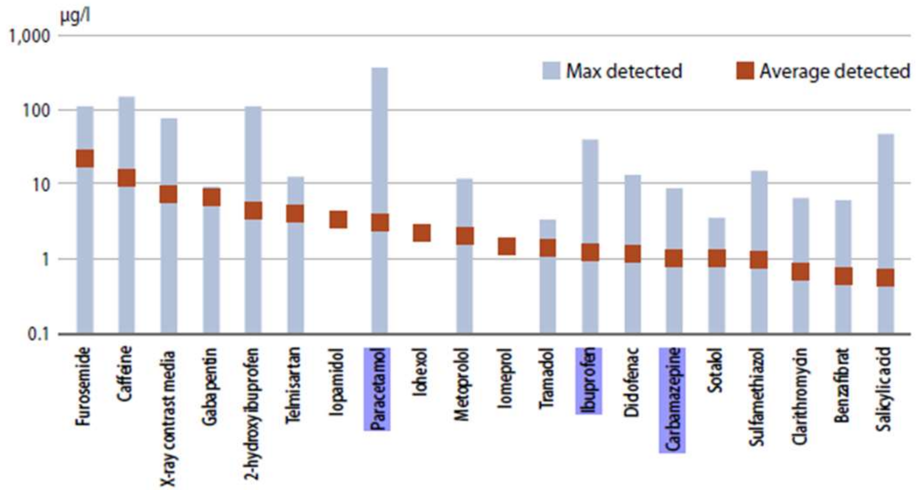
Why do we need to improve the quality of surface waters?

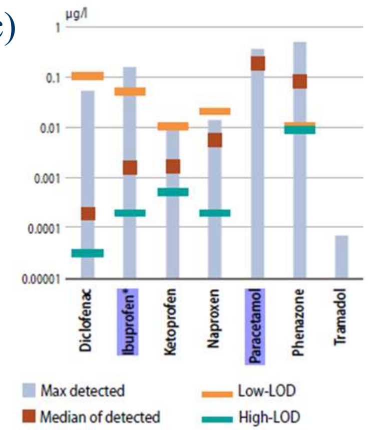
a)



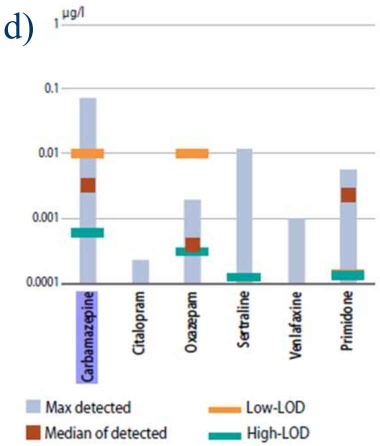
b)



c)



d)



Status of the Baltic Sea, related to pharmaceuticals presence (a), pharmaceuticals detected in wastewaters (b), and marine waters (c,d), in the Baltic Sea Region*

*Source: HELCOM, Pharmaceuticals in the aquatic environment of the Baltic Sea region A status report International Initiative on Water Quality-IIWQ, 2017.

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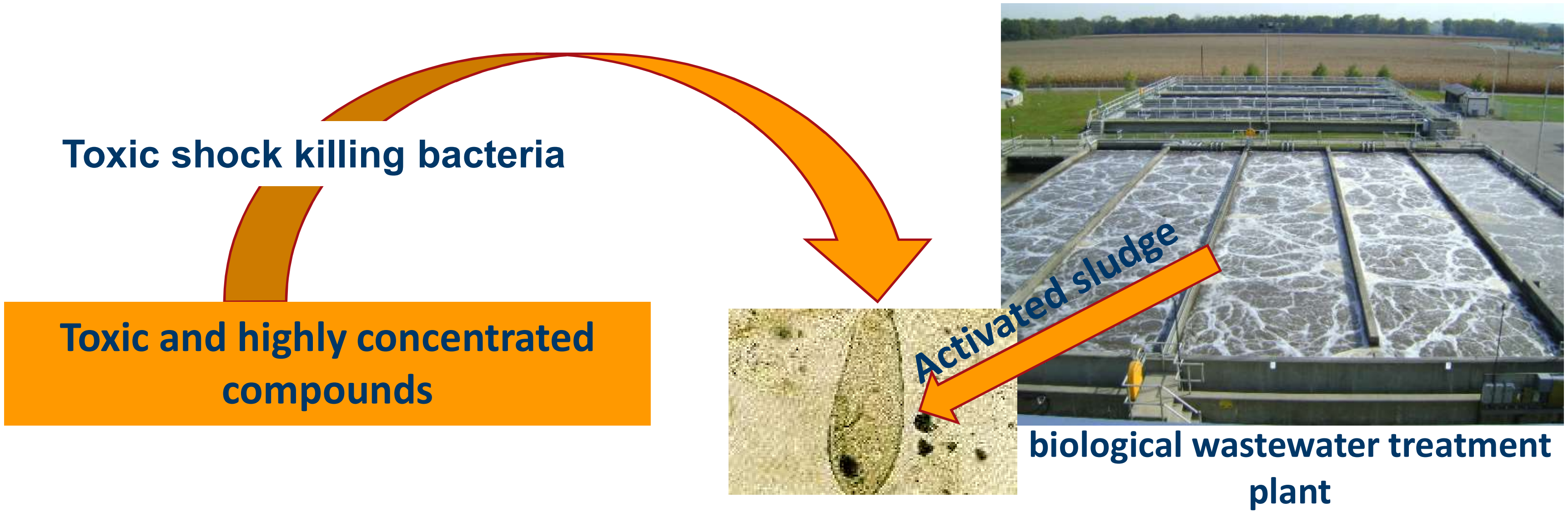
Why Advanced Oxidation Processes ?

- 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



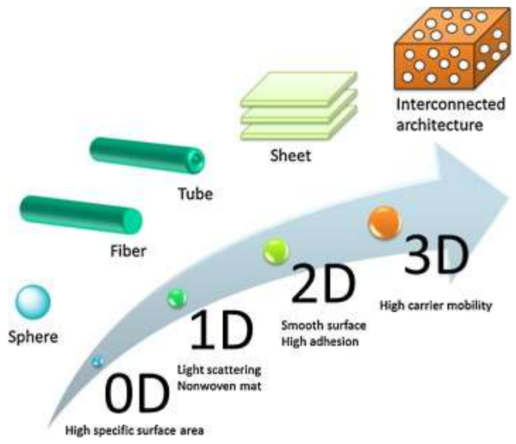
Advanced Oxidation Processes

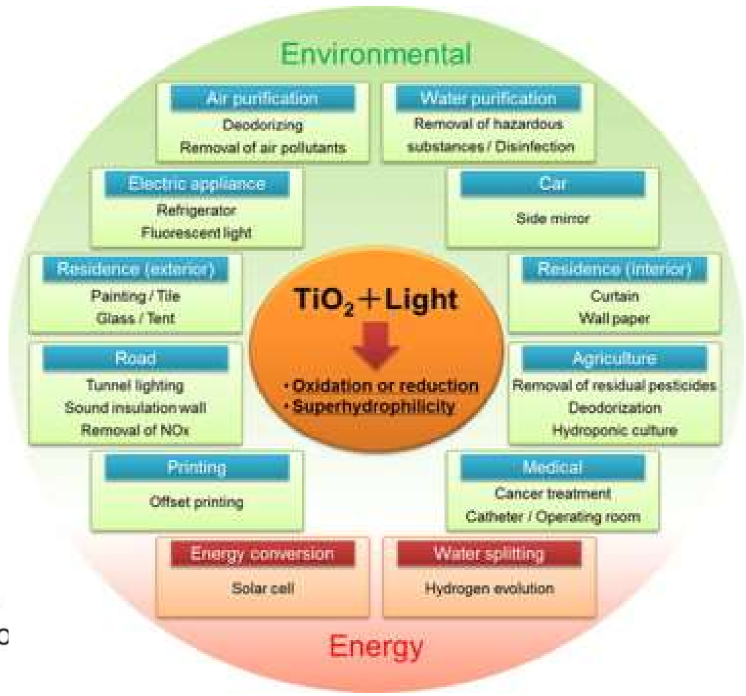
OH·

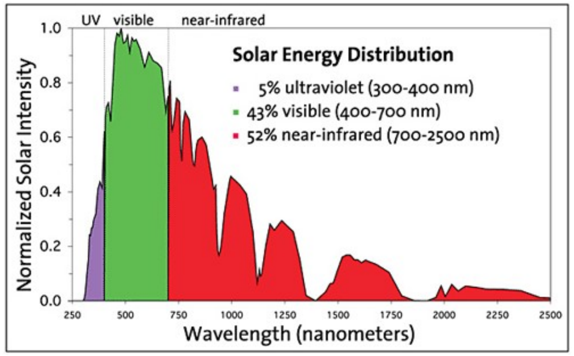
In-situ production of hydroxyl radicals (·OH) and sulfate radicals ($^{\bullet}SO_4^-$)

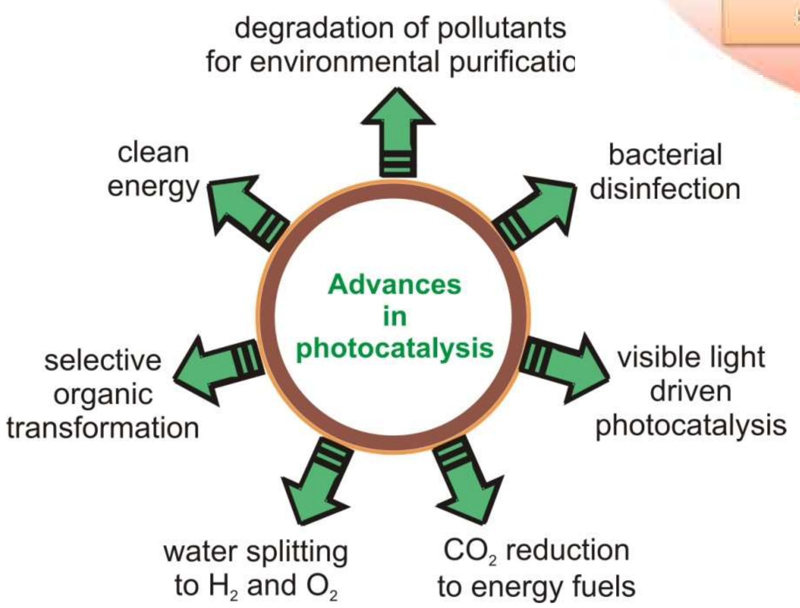
oxidizing agent	oxidation potential [V]
hydroxyl radicals	2.89
sulfate radicals	2.80
Fenton’s reagent	2.76
ozone	2.07
hydrogen peroxide	1.78
hypochlorous acid	1.49
chlorine	1.36

Recent advances in photocatalysis





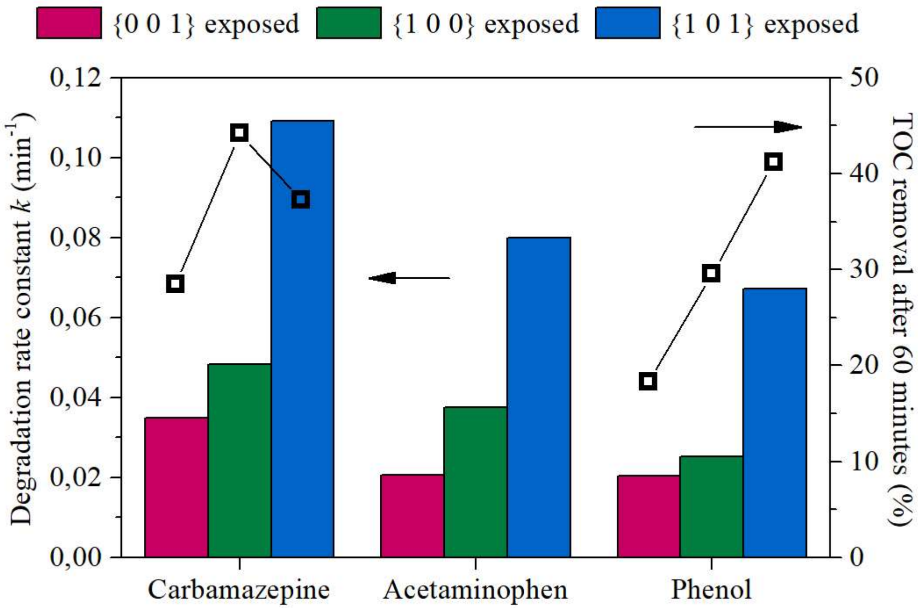


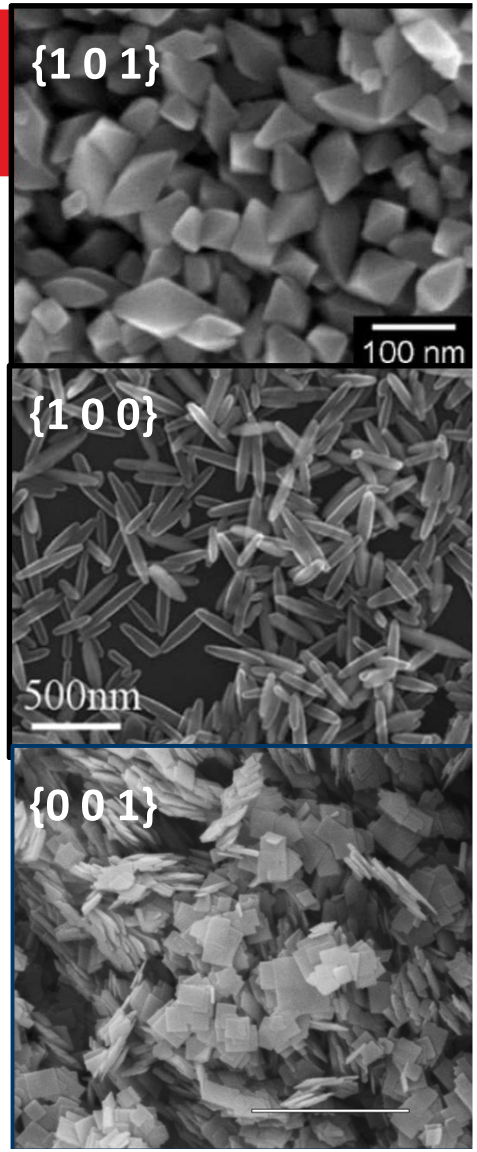


K. Nakata, A. Fujishima, J. Photochem. Photobiol. C: Photochem. Rev., 13 (2012) 169-189

- development of a new light harvesting assemblies
- elucidation charge transfer processes
- improvement of hydrogen generation efficiency

The surface chemistry of photocatalytic materials





The degradation process over the TiO_2 photocatalyst is mostly controlled by the distribution of surface trapped states, specific for each crystal facet (highest density for the {1 0 1} facets and the lowest for {0 0 1} one).

S. Dudziak, A. Fiszka Borzyszkowska, A. Zielińska-Jurek, Journal of Environmental Chemical Engineering 11 (2023) 109553

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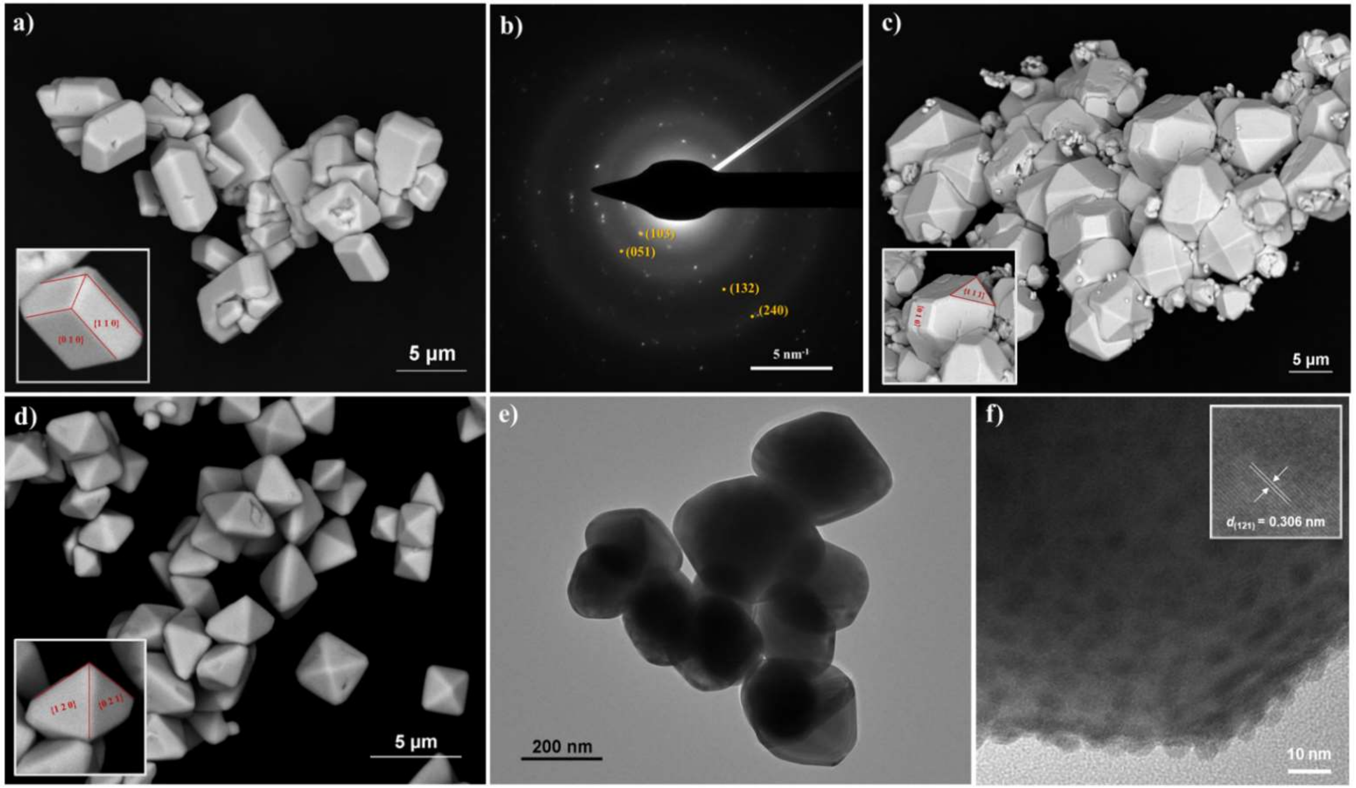
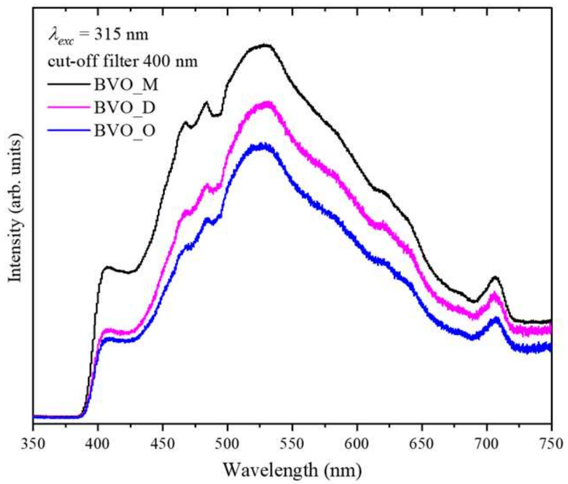
Crystal facets engineering of $BiVO_4$

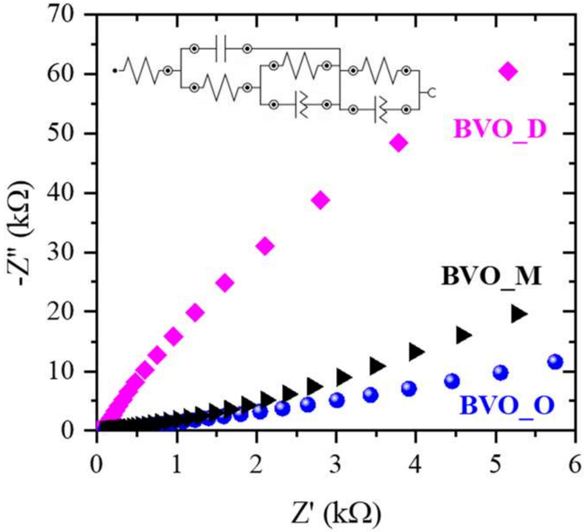


SEM images of **a)** BVO_D, **b)** SAED patterns of BVO_D, **c)** BVO_M, **d)** BVO_O, **e)** TEM and **f)** HRTEM images of BVO_O with calculated *d*-spacing in inset.

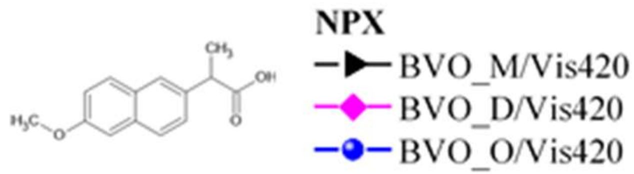
Crystal facets engineering of $BiVO_4$

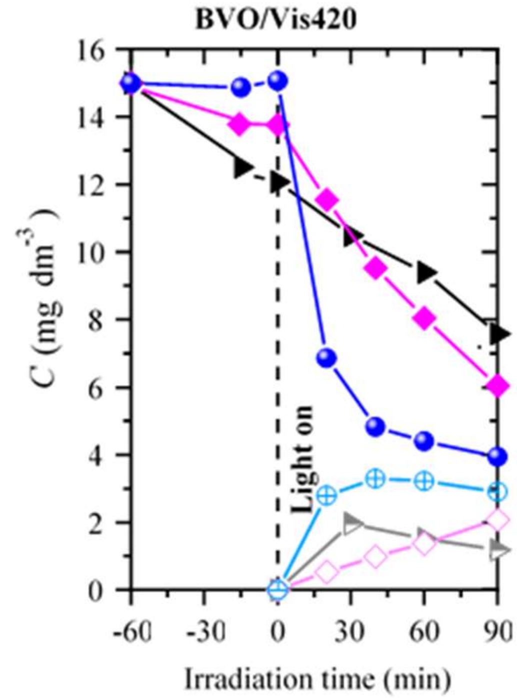


Photoluminescence spectra of faceted BVO

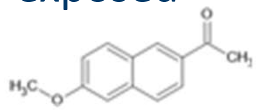


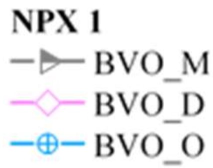
Nyquist plots of faceted BVO





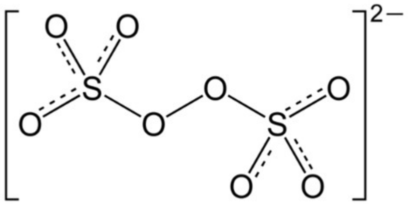
The highest photocatalytic activity was observed for BVO_O with exposed {1 2 0} and {0 2 1} facets.



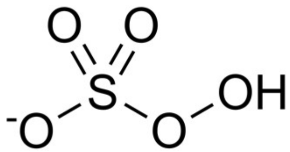


The order of the kinetics during photocatalysis is BVO_O > BVO_D > BVO_M

Peroxymonosulphate-assisted photocatalytic degradation of environmental pollutants



Peroxydisulfate (PDS)

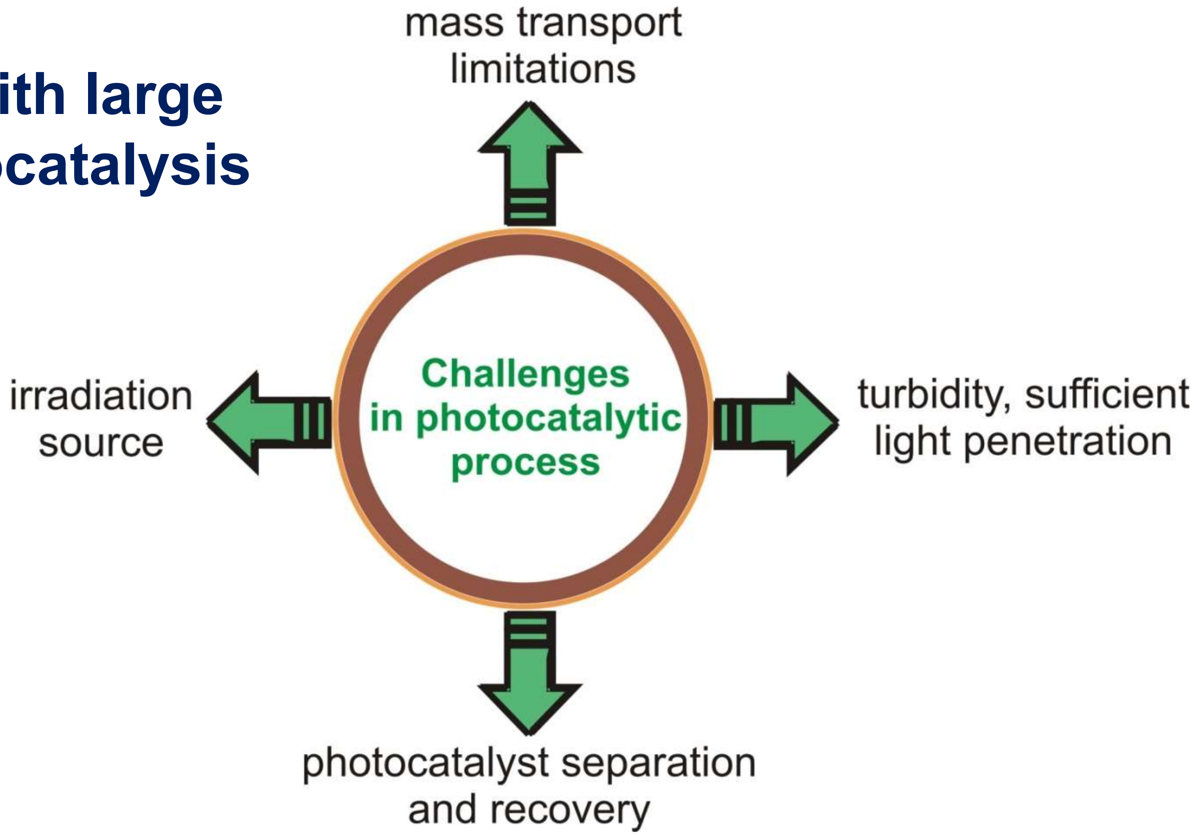


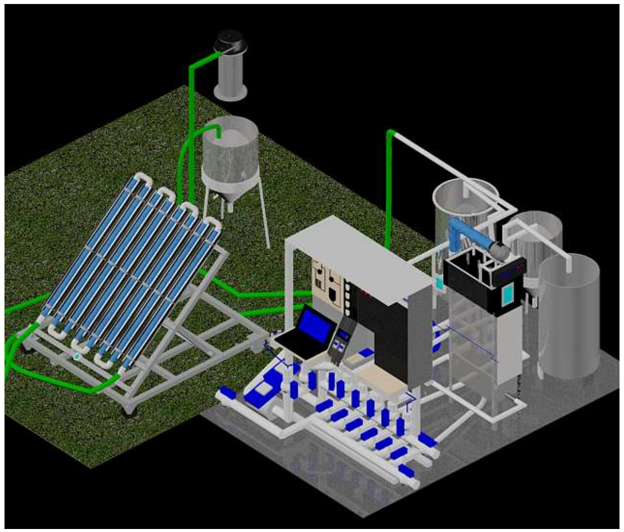
Peroxymonosulfate (PMS)

- PS and PMS assisted processes are efficient in degrading persistent organic pollutants, including pesticides, pharmaceuticals, and plasticizers, attributed to the generation of $SO4^{\bullet-}$ and/or $^{\bullet}OH$
- PMS may effectively produce sulphate radicals with strong oxidation ability.

- The sulphate radical ($\bullet SO_4^-$) possesses a close or even higher redox potential of 2.5–3.1 V (vs. NHE) compared to hydroxyl radical (E_0=1.8-2.8 V). Moreover, sulphate radicals have higher selectivity, longer half-life (30–40 μs), and could be activated in the broader pH range from 2 to 8 than •OH radicals.

Technical challenges with large scale utilization of photocatalysis



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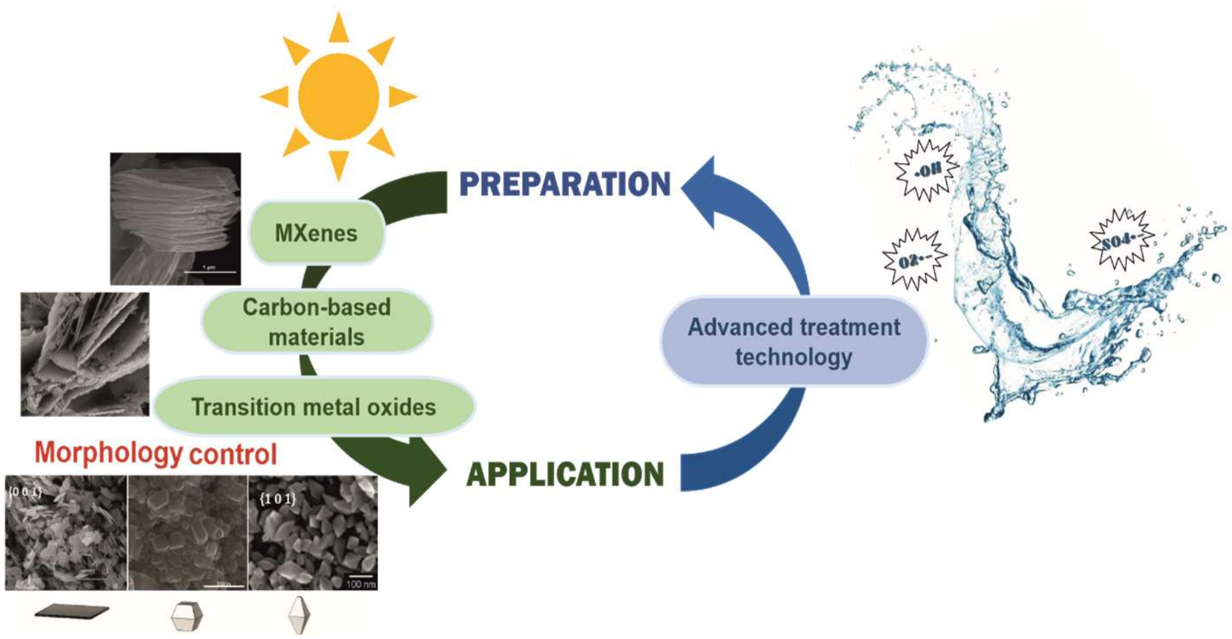
Summarizing



- ✓ The surface chemistry and controlled growth of semiconductor nanocrystals
- ✓ The electron-donor cocatalyst loading on the crystal facets with the preference of holes accumulation
- ✓ The electron-acceptor cocatalyst for reductive facets

- ✓ The hybridization of semiconductor with graphene-related material and combining photocatalytic reaction with transition metal-based PMS acceleration

Acknowledgments

Project granted by the European Union within Interreg Baltic Sea Region Programme.
„Improving quality of BSR waters by advanced treatment processes", AdvIQwater (2022-2025)

The AdvIQwater project aims to the development of solar-driven photocatalysis, biofilms, and fungal treatment for efficient removal of pharmaceuticals from water.