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NOWELTIES' FINAL CONFERENCE
New Materials and Inventive Waste Water Treatment Technologies.
Harnessing resources effectively through innovation

The effect of water matrix on photocatalytic degradation of bisphenols and pharmaceuticals

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Chemical Engineering Journal 388 (2020) 124184

Once through continuous flow removal of metronidazole by dual effect of photo-Fenton and photocatalysis in a compound parabolic concentrator at pilot plant scale

Steffi Talwar[a], Anoop Kumar Verma[b,*], Vikas Kumar Sangal[c], Urška Lavrenčič Štangar[d]

Environmental Research 197 (2021) 110982

Synergism in TiO_2 photocatalytic ozonation for the removal of dichloroacetic acid and thiacloprid

Andraž Šuligoj [a,b,*], Marko Kete [c,1], Urh Černigoj [d], Fernando Fresno [e], Urška Lavrenčič Štangar [a,c]

Materials **2020**, *13*, 1621; doi:10.3390/ma13071621

One-Pot Synthesis of Sulfur-Doped TiO_2/Reduced Graphene Oxide Composite (S-TiO_2/rGO) with Improved Photocatalytic Activity for the Removal of Diclofenac from Water

Marin Kovačić [1,*], Klara Perović [1], Josipa Papac [1], Antonija Tomić [1], Lev Matoh [2], Boštjan Žener [2], Tomislav Brodar [3], Ivana Capan [3], Angelja K. Surca [4], Hrvoje Kušić [1,*], Urška Lavrenčič Štangar [2] and Ana Lončarić Božić [1]

Journal of Environmental Chemical Engineering 9 (2021) 106025

Tailored $BiVO_4$ for enhanced visible-light photocatalytic performance

Tayebeh Sharifi [a,*], Dora Crmaric [a], Marin Kovacic [a], Marin Popovic [b], Marijana Kraljic Rokovic [a], Hrvoje Kusic [a,*], Dražan Jozić [c], Gabriela Ambrožić [d], Damir Kralj [e], Jasminka Kontrec [e], Bostjan Zener [f], Urska Lavrencic Stangar [f], Dionysios D. Dionysiou [g], Ana Loncaric Bozic [a]

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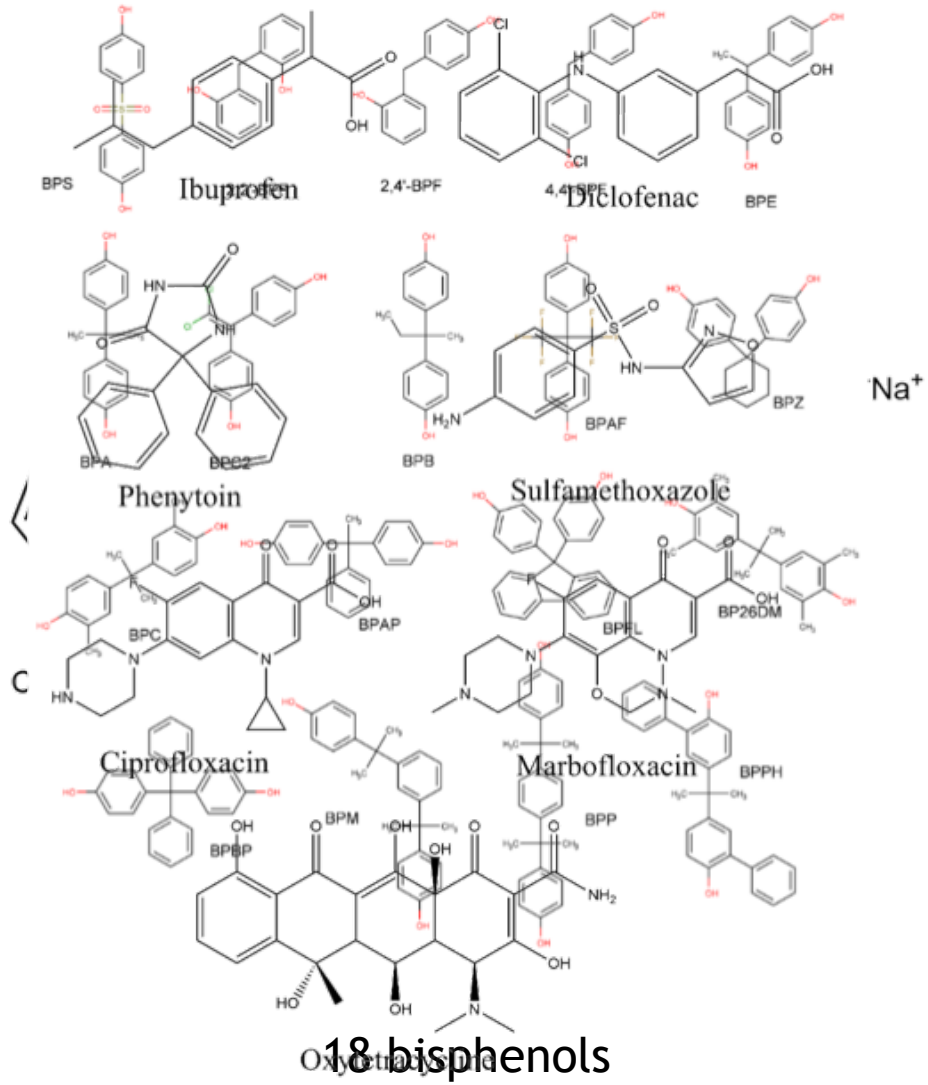
This study

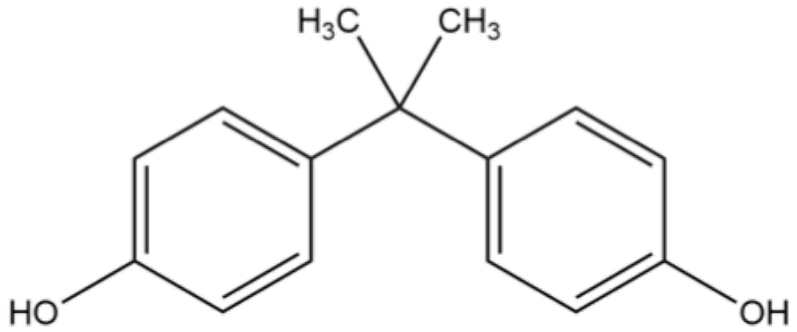
- Development of a packed bed photoreactor for treatment of contaminants in distilled water and wastewater
- Commercially available titanium dioxide was deposited onto glass beads
- We observed the photocatalytic degradation of:
  - **Plasmocorinth B** (organic dye),
  - **18 bisphenols** (co-dissolved in deionized water and bioreactor effluent),
  - **7 pharmaceuticals** (dissolved and co-dissolved in deionized water, bioreactor effluent and central wastewater treatment plant effluent)



18 bisphenols

Bisphenols

- Group of industrial chemicals containing two hydroxyphenyl functional groups
- Bisphenol A (BPA) is used as a hardener in the production of plastics
- BPA is an endocrine disrupting chemical (EDC)
- Important to find and effective method of removing these compounds from wastewater



BPA

Pharmaceuticals

- Among the most frequently detected contaminants in aquatic environment
- Lead to development of microorganisms, resistant to antibiotics
- High cell membrane penetration (bioaccumulation)
- Enter the environment through wastewater treatment plants via treated water

DEGRADATION OF BISPHENOLS

Removal of 18 bisphenols co-present in aqueous media by effectively immobilized titania photocatalyst

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[b] *Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[c] *Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[d] *Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia*

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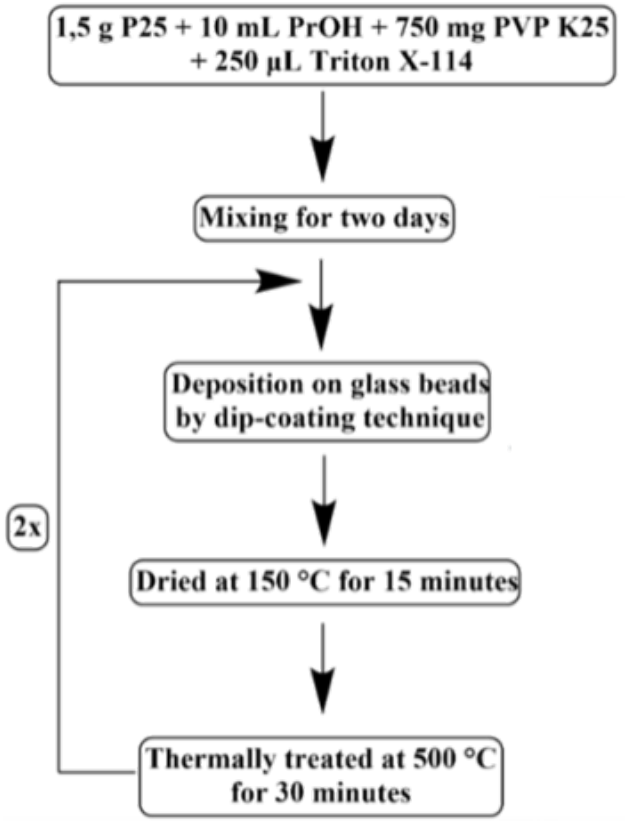
Preparation of the immobilized catalyst

- Photocatalytic coating was prepared by mixing **P25**, **1-propanol**, organic polymer **PVP K25** and surfactant **Triton X-114**
- The suspension was deposited onto glass beads (diameter ~3 mm)
- Glass beads were then packed in a PVC column (V=50 mL)



B. Žener *et al.*
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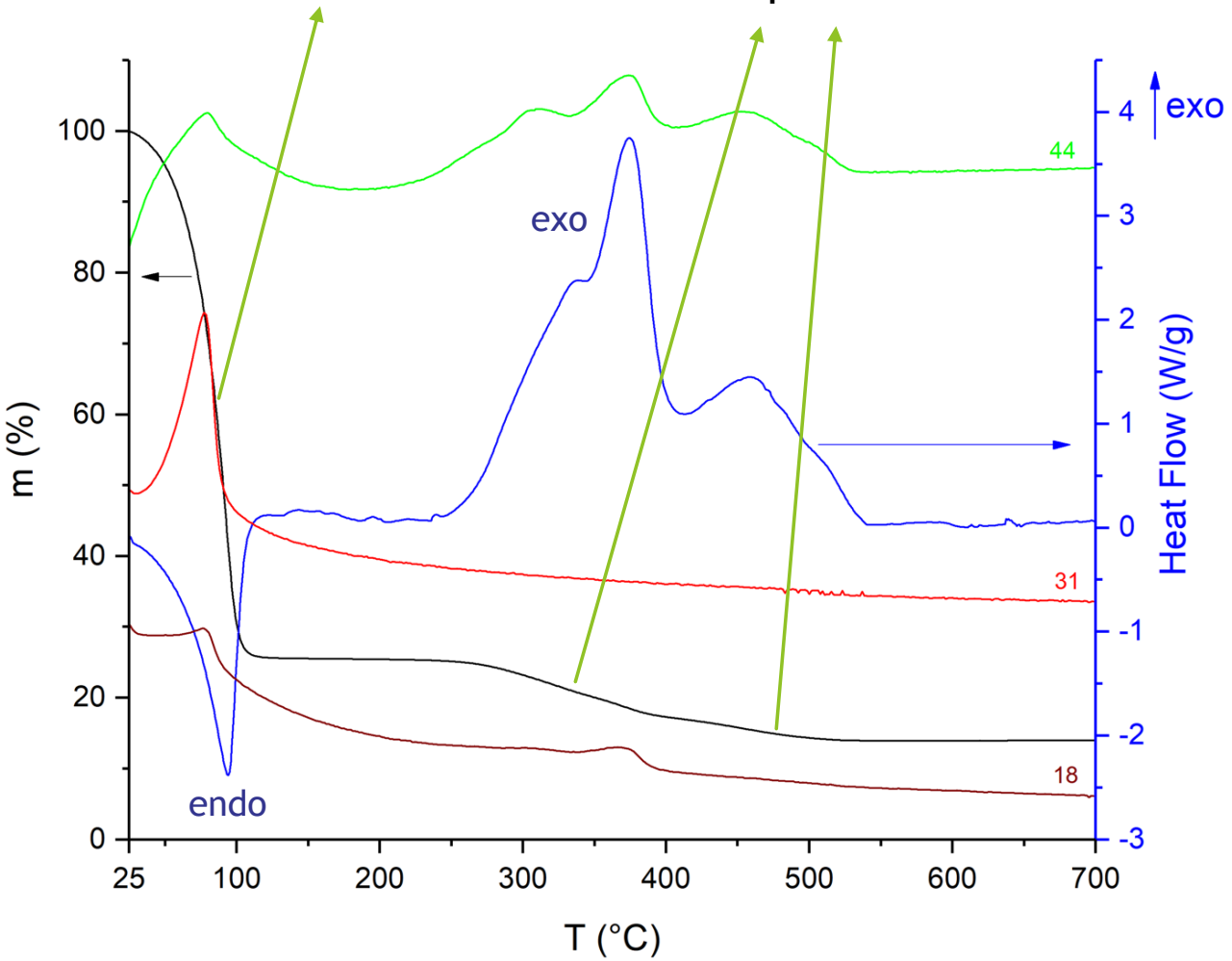
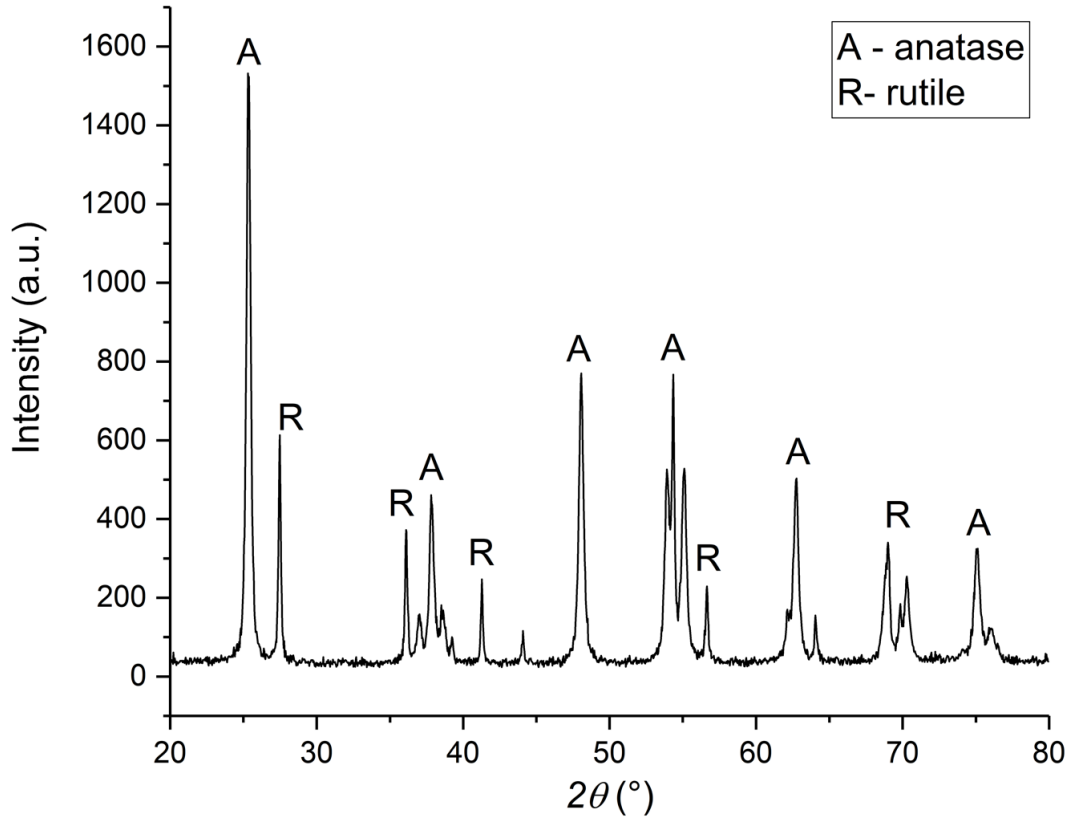
Thermal analysis (TG-DSC-MS)

Step 1: evolution of **propanol**

Step 2 and 3: evolution of **CO_2**



X-Ray Diffraction (XRD)



76% anatase (~ 34 nm), 24% rutile (~ 53 nm);

typical for P25 → not altered

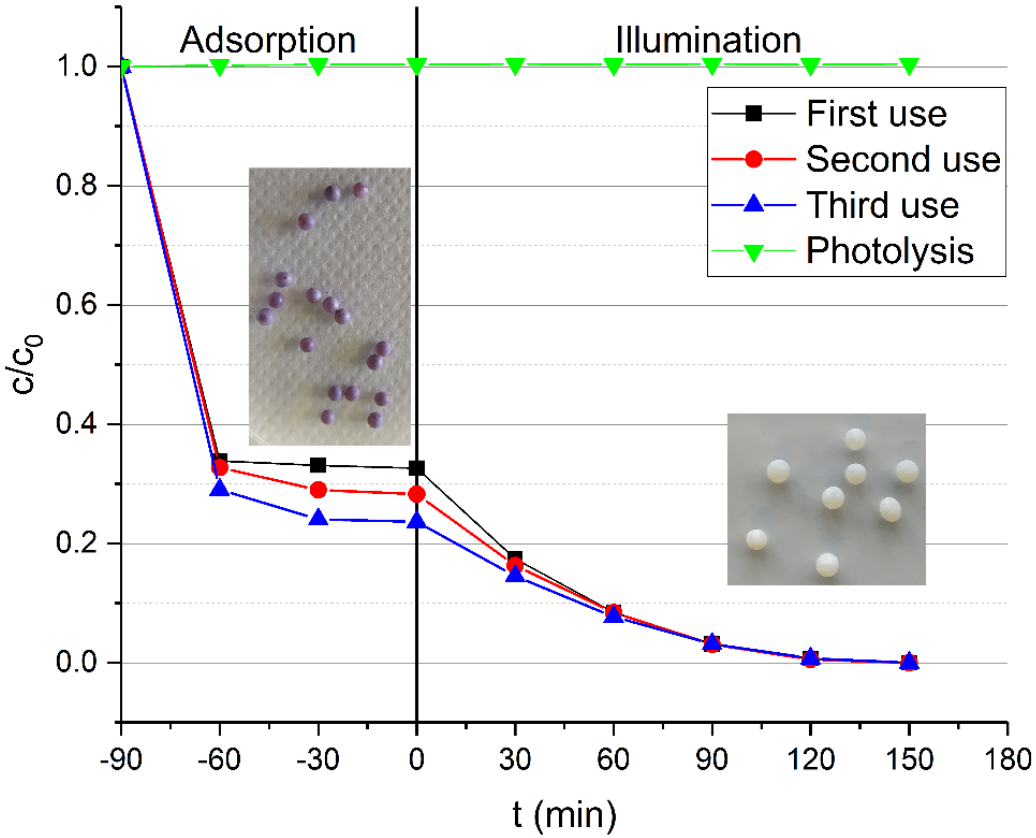
Tests of the photocatalyst

- Degradation of Plasmocorinth B

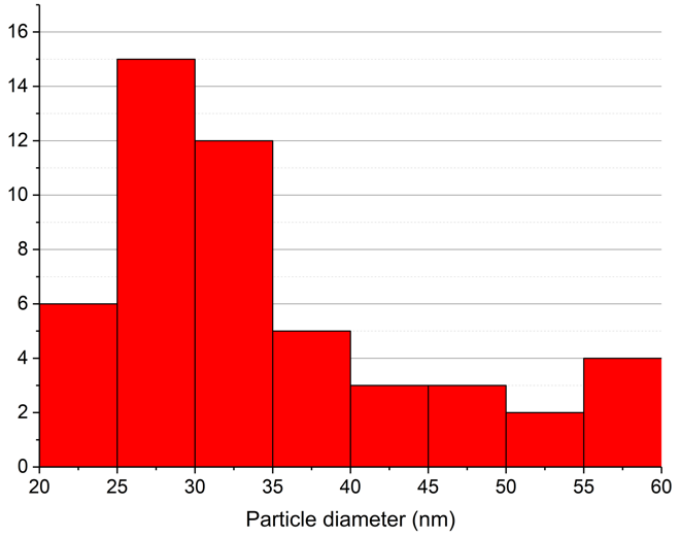
  ($V_{solution}$ = 500 mL, γ = 12 mg/L)

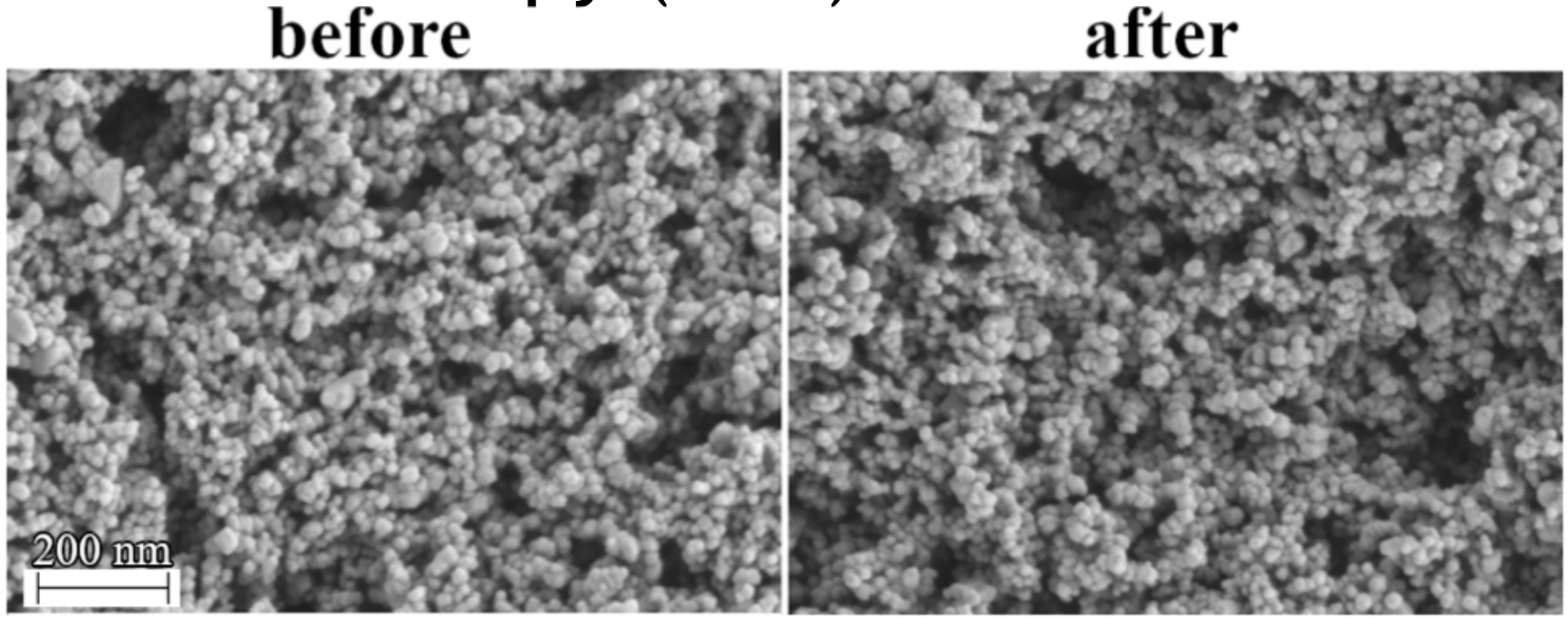
- Stability of the deposit was tested by performing multiple tests

- After 120 minutes of illumination (UV 365 nm, 20 W/m^2) the dye is degraded



Scanning electron microscopy (SEM)





- SEM images of the deposit before and after use
- Particle sizes from 20 to 60 nm
- Deposition is porous with a wide distribution of pore sizes

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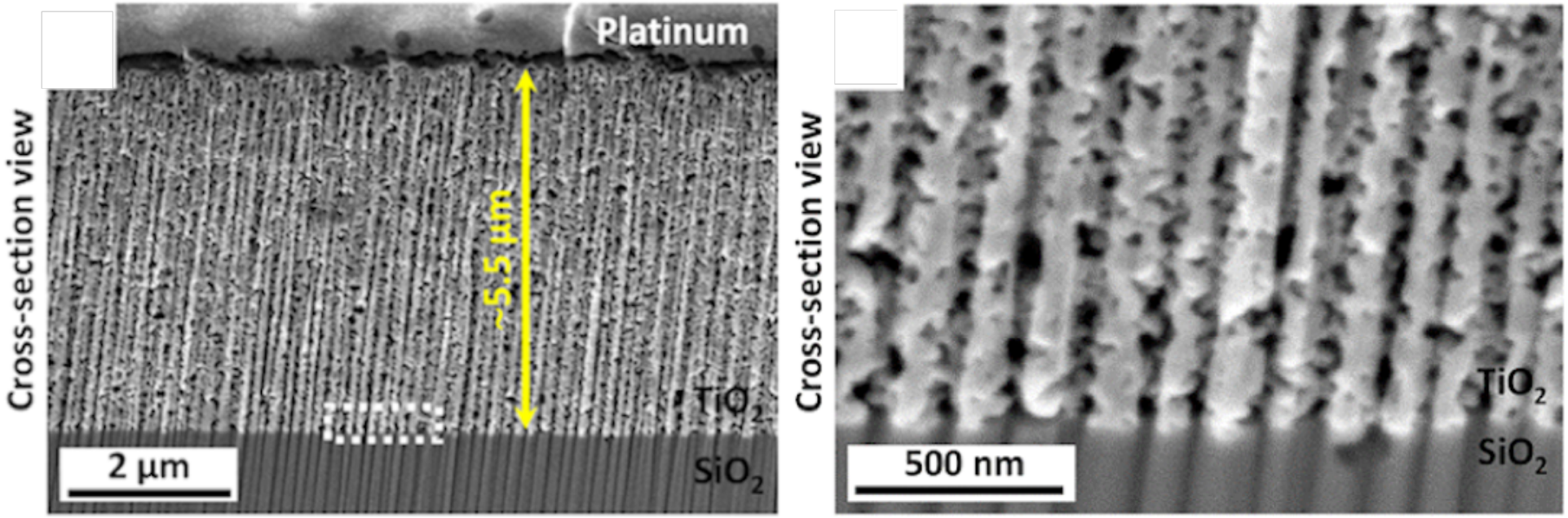
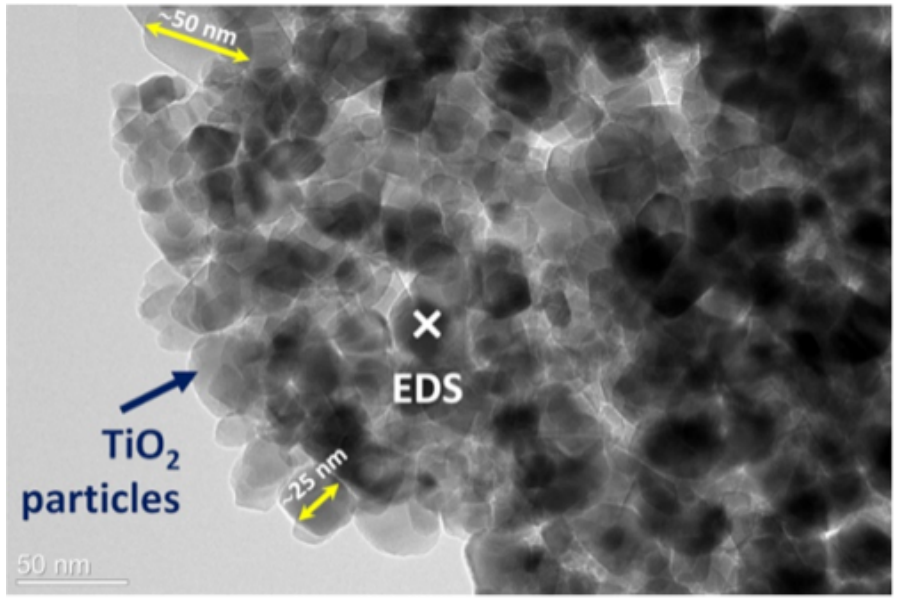
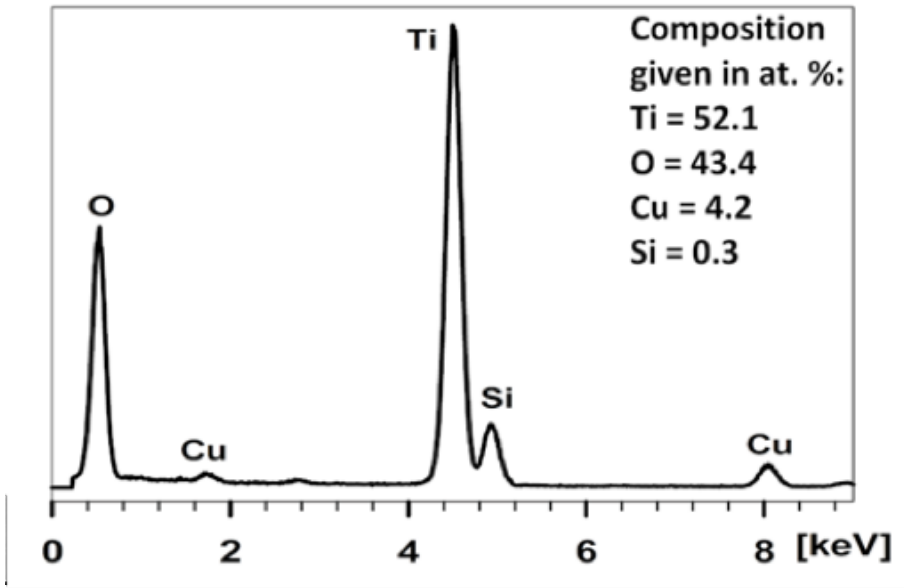
Cross-section of the deposit (FIB/SEM)



- Uniform coating without any boundary layers (although 3-step deposition)
- Good adhesion to the glass beads,nanopores

Transmission electron microscopy (TEM)





- Particle sizes from 20 to 60 nm, close-packed domains
- HRTEM shows lattice spacings in the nanocrystals
- TEM of the initial P25 is the same (no change in structure during preparation, immobilization)
- EDS analysis: the deposition consists of Ti and O

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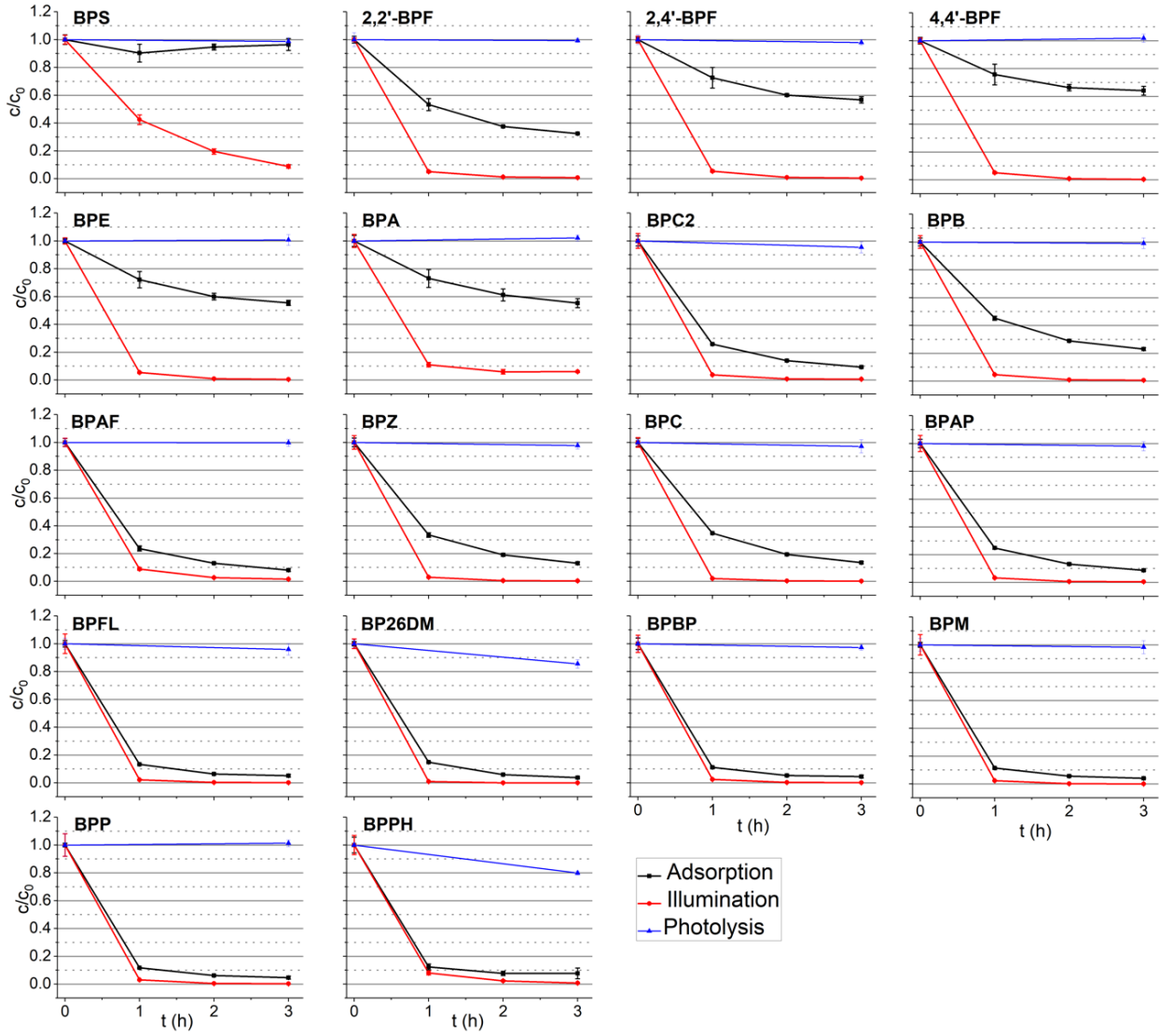
Photocatalytic degradation of bisphenols

- Degradation of 18 bisphenols, co-dissolved in deionized water (with the same beads)
- $V_{solution}$ = 500 mL; concentration of each bisphenol = 1 µg/L; GC-MS/MS analysis
- 95% removal after 1 hour, except BPS (most polar)
- Polar bisphenols show lower adsorption



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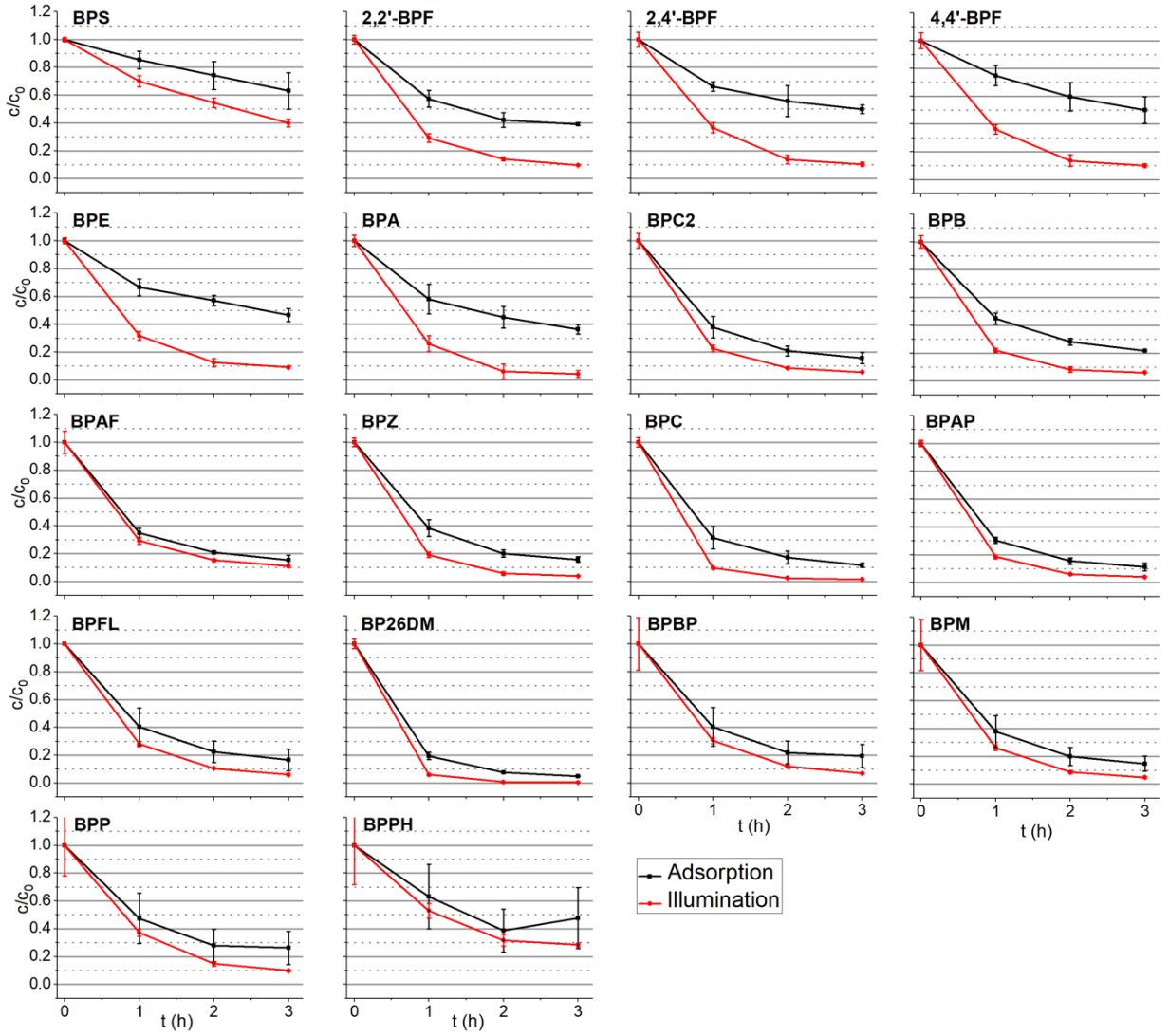
- Degradation of 18 bisphenols, co-dissolved in bioreactor effluent (same conditions as in distilled water)
- Degradation and adsorption rates are expectedly lower
- 90 % removal for most bisphenols after 2 hours

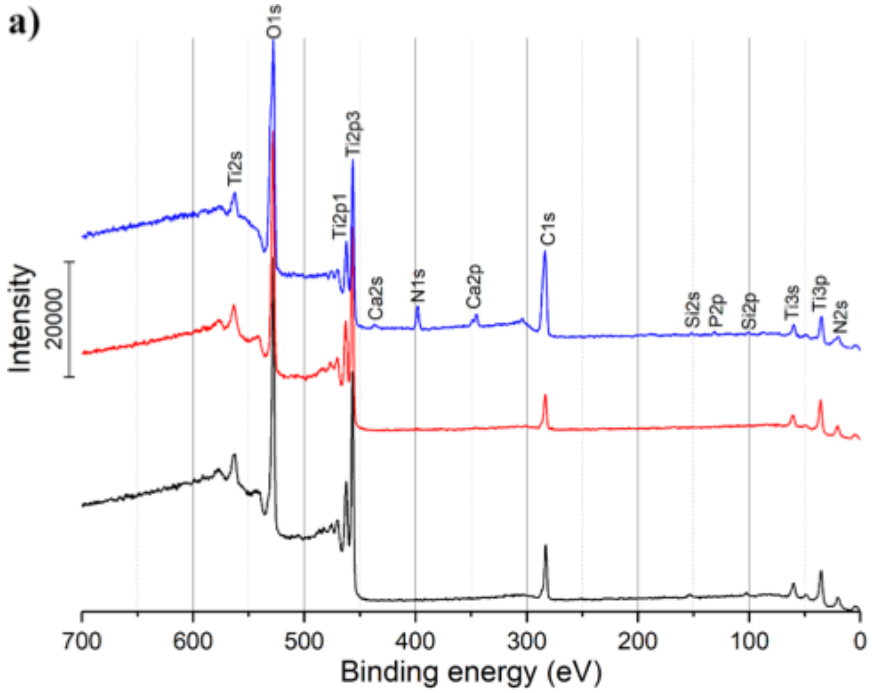


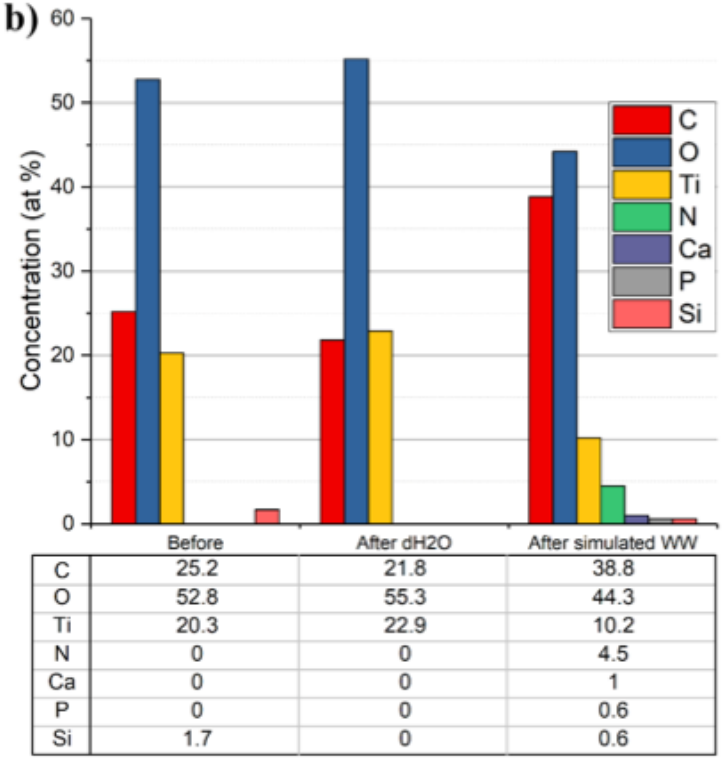
X-Ray photoelectron spectroscopy (XPS)

- All of the samples show Ti and O peaks, typical for TiO_2

- Sample after **degradation in bioreactor effluent:**

presence of Ca, P and N can be attributed to the adsorbed species from wastewater





	Before	After dH2O	After simulated WW
C	25.2	21.8	38.8
O	52.8	55.3	44.3
Ti	20.3	22.9	10.2
N	0	0	4.5
Ca	0	0	1
P	0	0	0.6
Si	1.7	0	0.6

DEGRADATION OF PHARMACEUTICALS

Photocatalytic degradation of 7 selected pharmaceuticals in (waste)water

Lev Matoh[1], Boštjan Žener[1], Marin Kovačić[2], Hrvoje Kušić[2], Iztok Arčon[3,4], Marjetka Levstek[5], Urška Lavrenčič Štangar[1]

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not yet published

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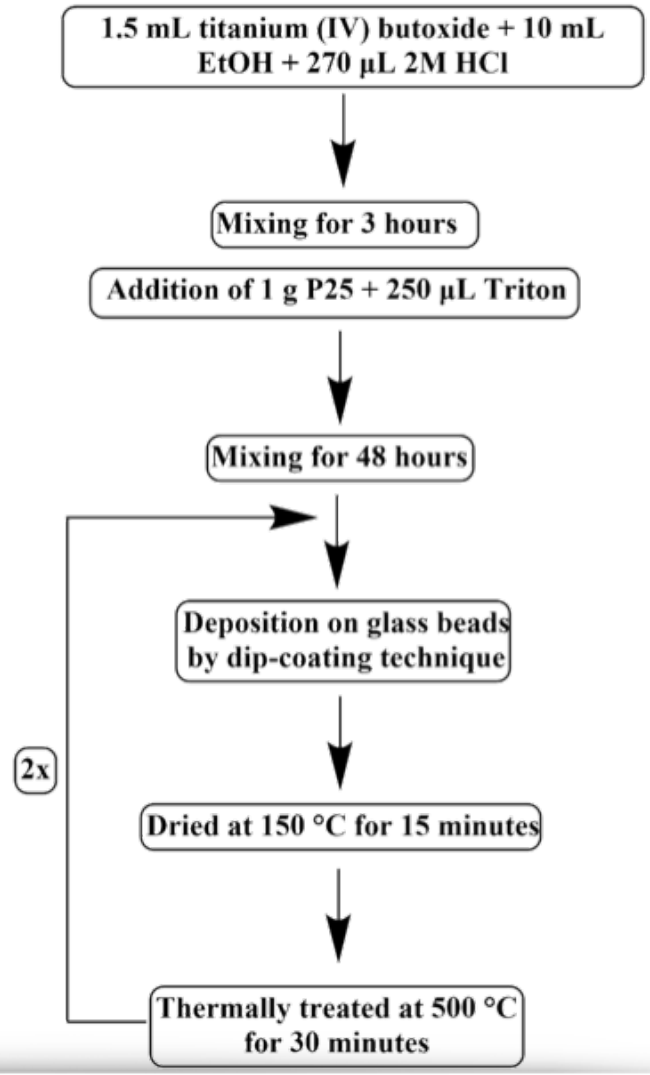
Preparation of the hybrid catalyst

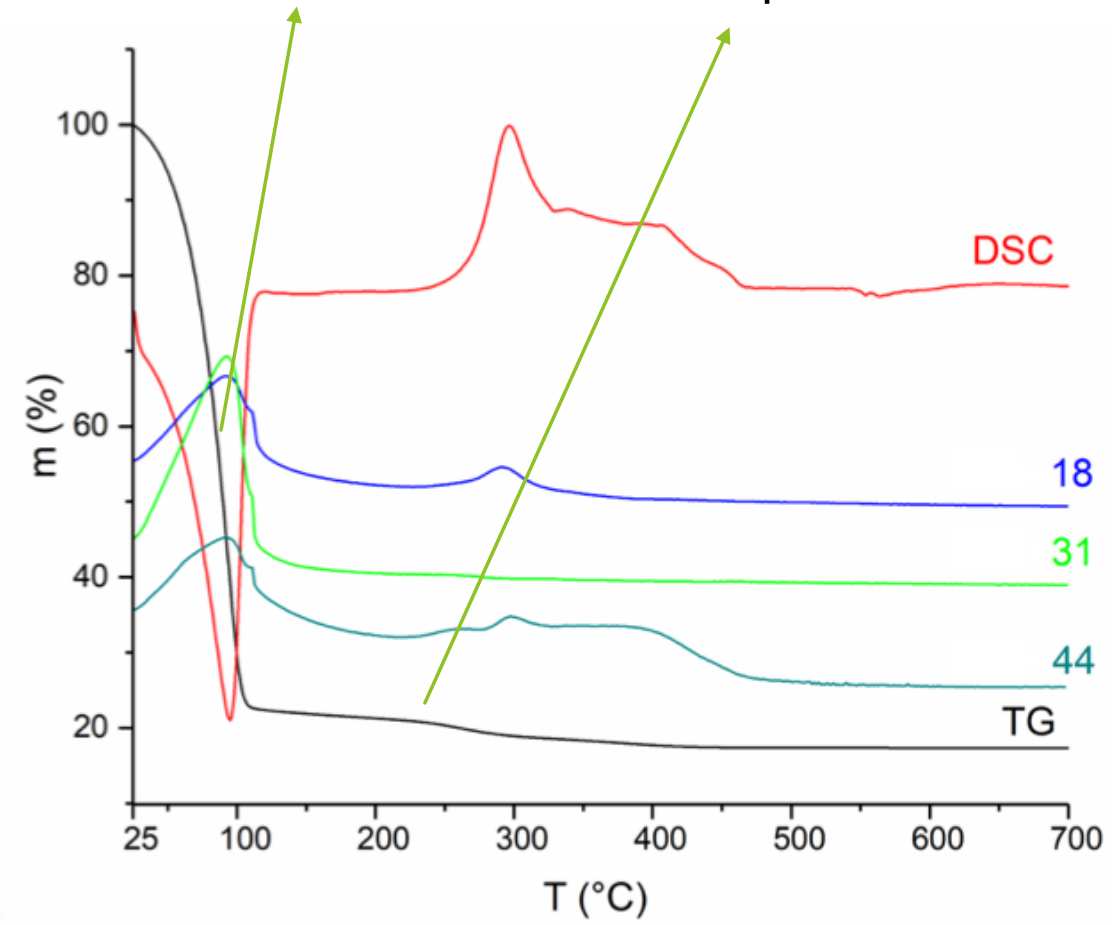
- Suspension of **P25** in TiO_2 sól, which acted both as a photocatalyst and as a binder
- Sól: **titanium(IV) butoxide, ethanol, 2 M HCl**
- Similarly, the coating was deposited on glass beads and packed in a column



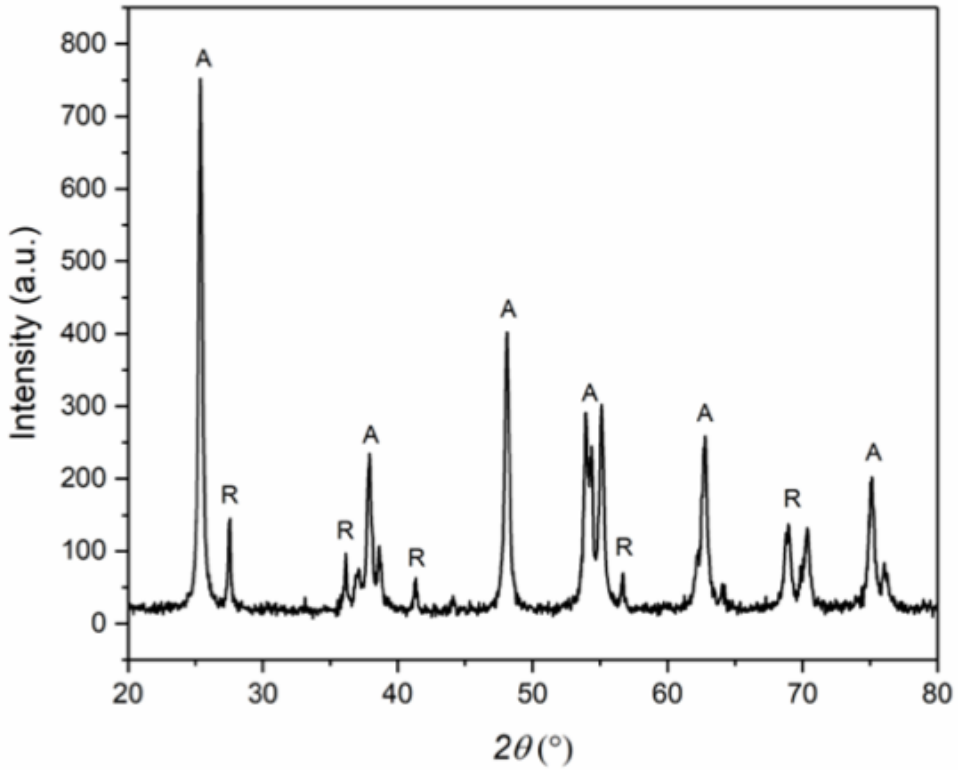
Thermal analysis (TG-DSC-MS)

Step 1: evolution of **ethanol**

Step 2: evolution of **CO_2**



X-Ray Diffraction (XRD)



80% anatase (~ 25 nm), 20% rutile (~ 50 nm);

higher % of anatase attributed to sól

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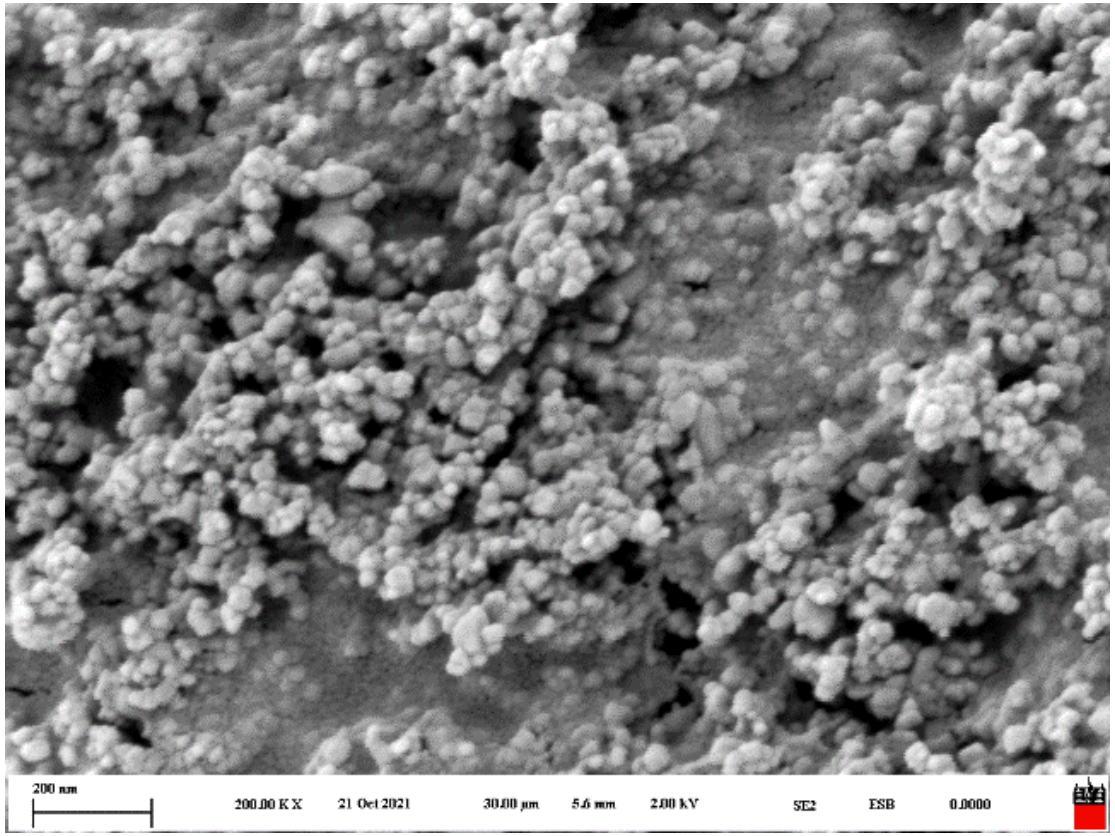
Scanning electron microscopy (SEM)



- Deposition is uniform with small cracks
- Larger P25 particles bound together by a compact layer from TiO_2 sól
- Compact layer contains small pores -> increased activity

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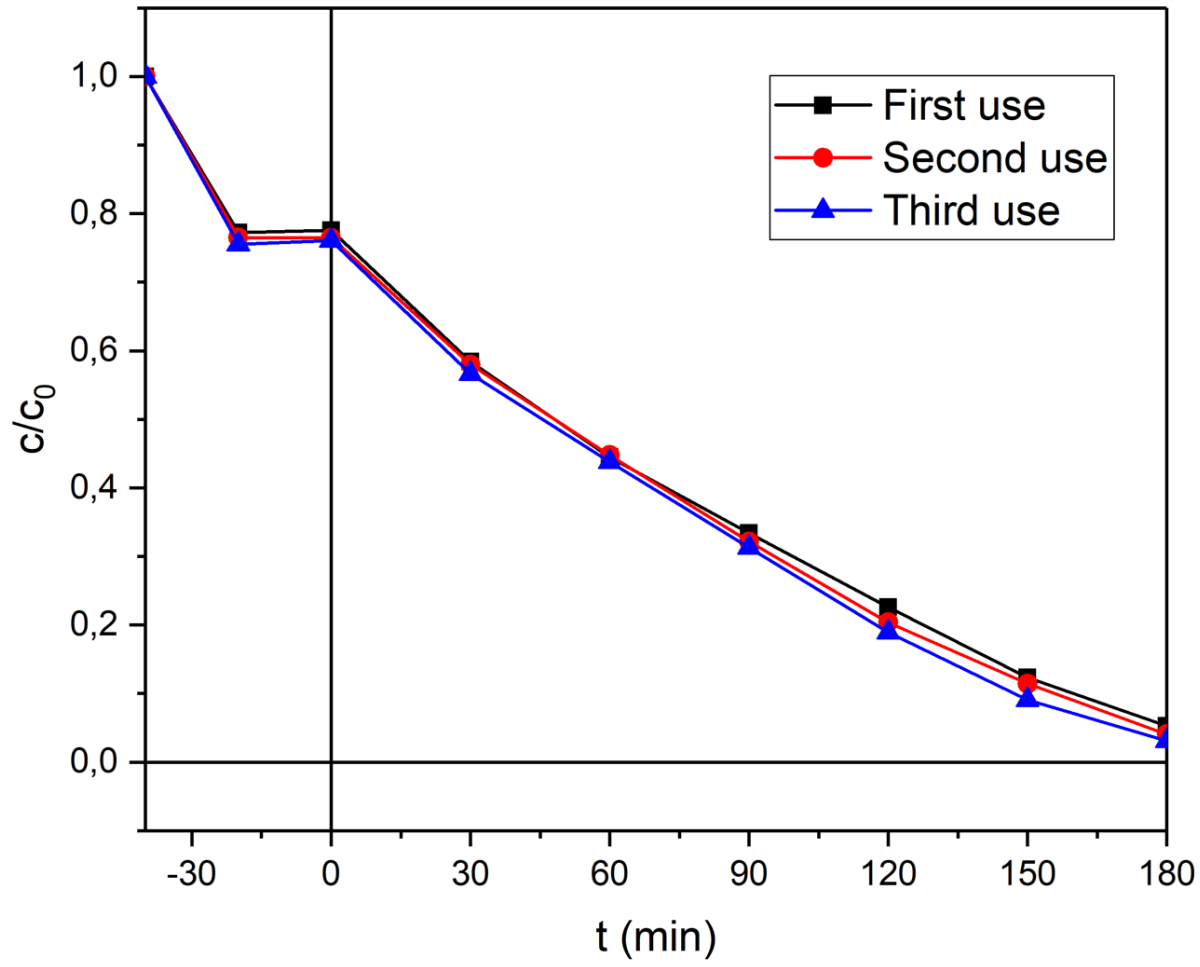
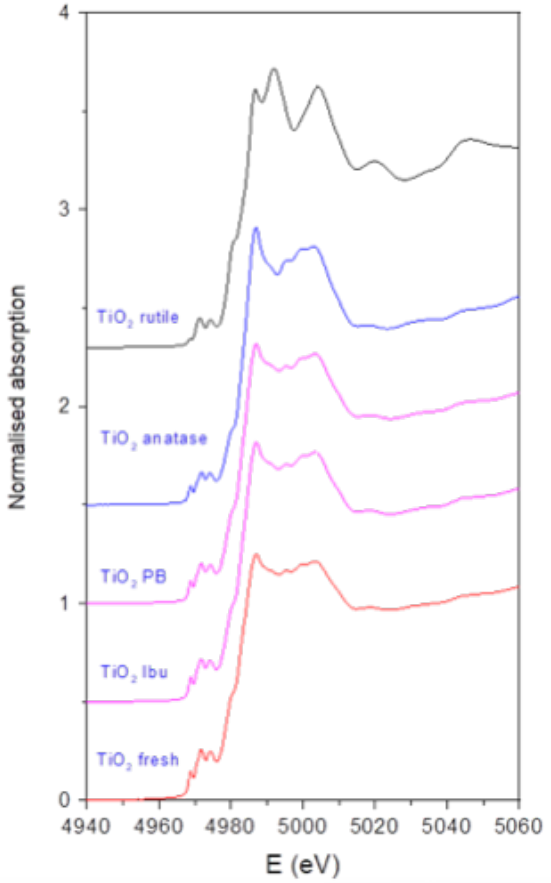
Tests of the photocatalyst

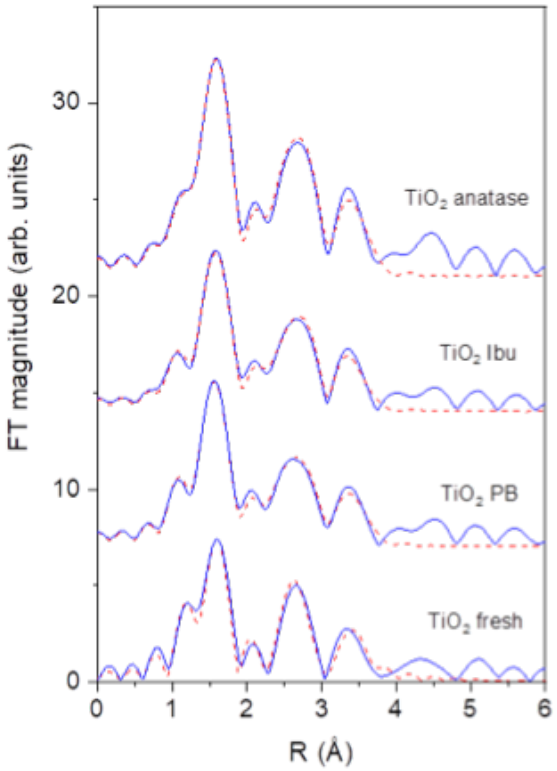
- Reusability tests of the deposited photocatalyst
- Degradation of Plasmocorinth B
- Results show no loss in activity and adsorption in subsequent tests



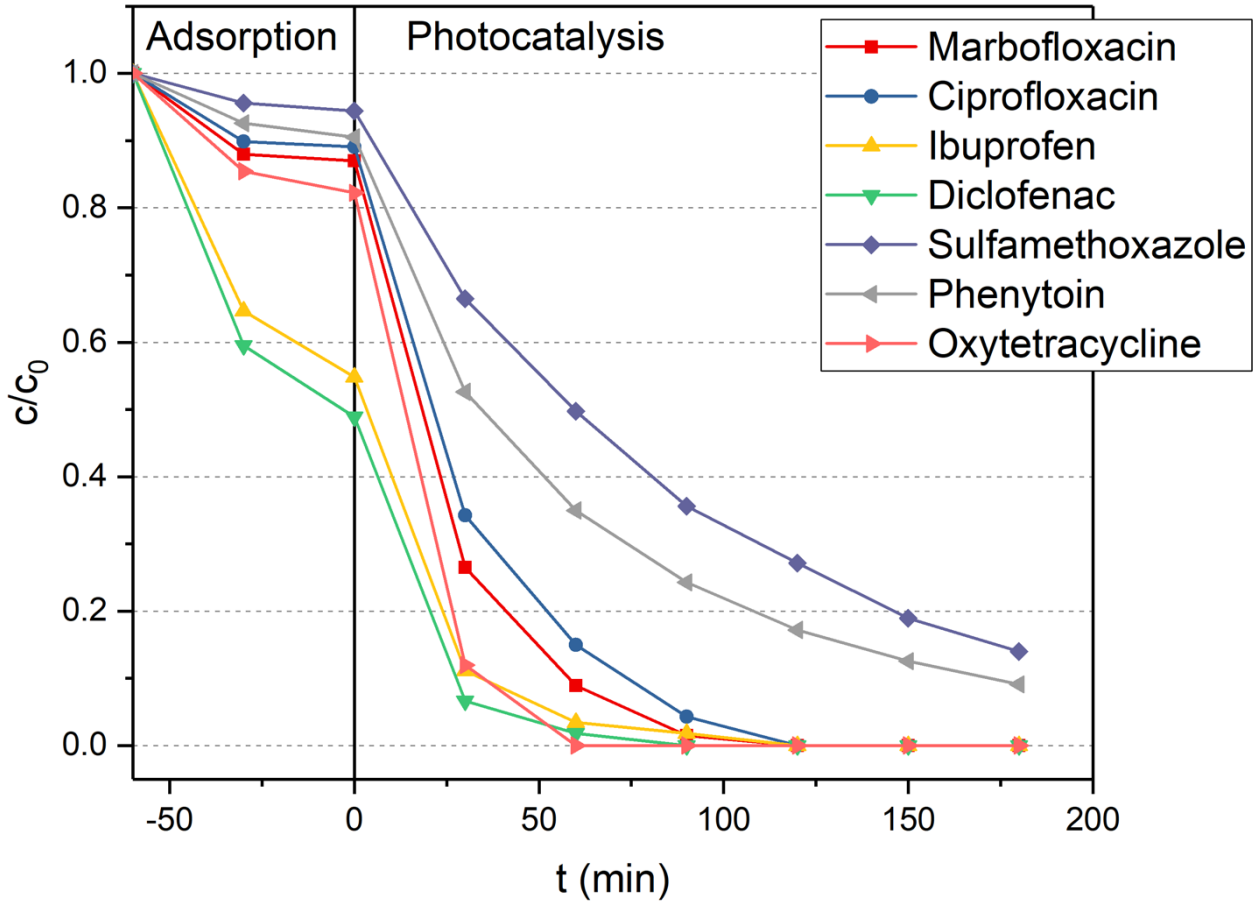
X-ray absorption spectroscopy

- Fresh catalyst and used samples in photocatalytic treatment of dye and ibuprofen
- No rutile observed, its proportion less than 10% (smaller fraction of rutile than in XRD due to too small anatase particles (2 nm) to be detected by XRD)
- During photocatalytic degradation relative amount of ordered crystalline TiO_2 rutile and anatase phases without defects increases in the mixture





Photocatalytic degradation of pharmaceuticals in deionized water



- Degradation for each individual compound

  (V = 500 mL, γ = 10 mg/L (4 mg/L for DCF), HPLC-DAD analysis)

- Most compounds removed after 120 minutes

- Lower degradation rates for phenytoin and sulfamethoxazole

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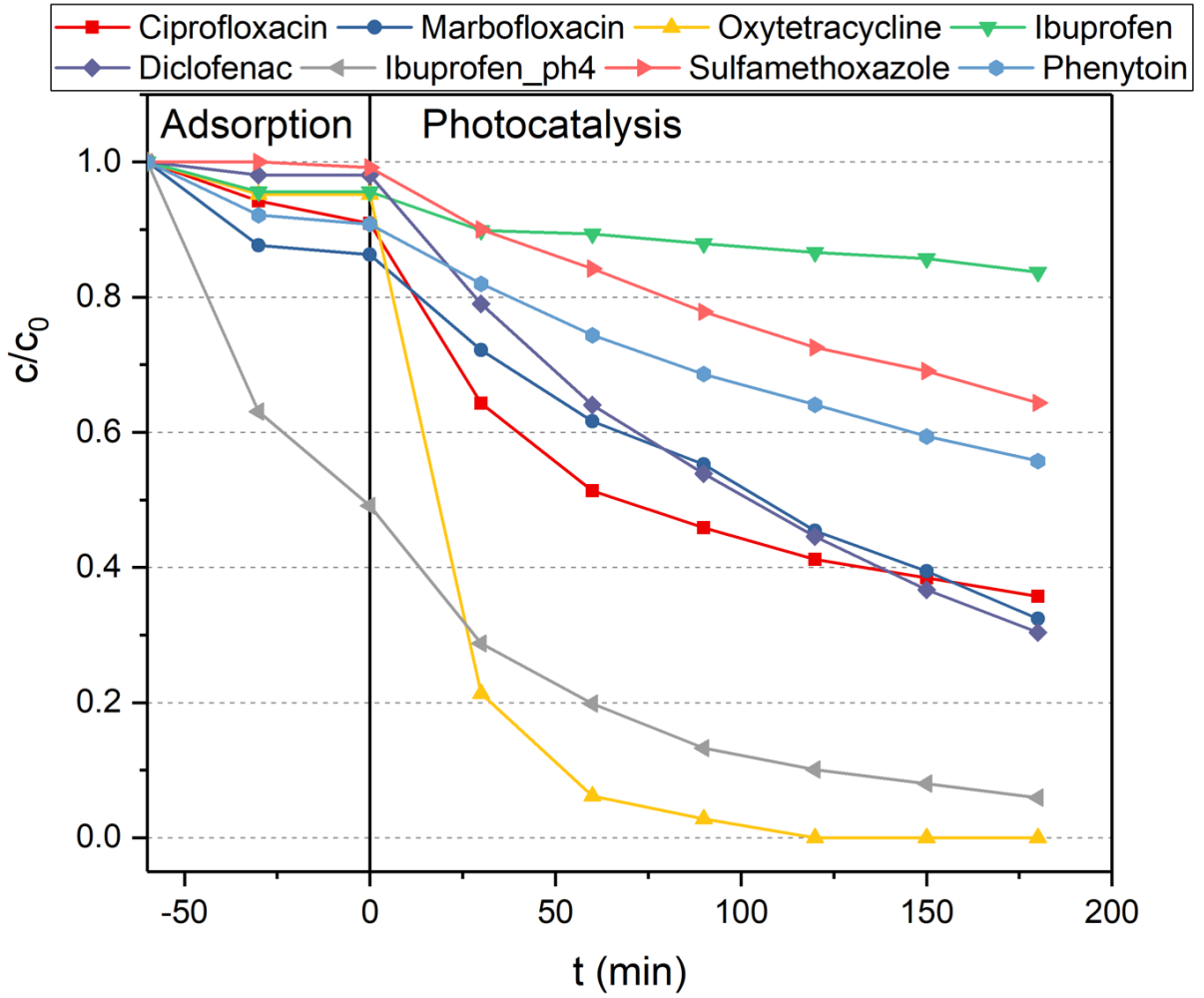
Photocatalytic degradation in bioreactor effluent

- Degradation of individual compounds - same conditions as in distilled water
- Reactions and adsorption rates are slower due to other organic matter present in the solution
- IBU: very low degradation, significantly increased with decreasing pH from native 7-8 to 4



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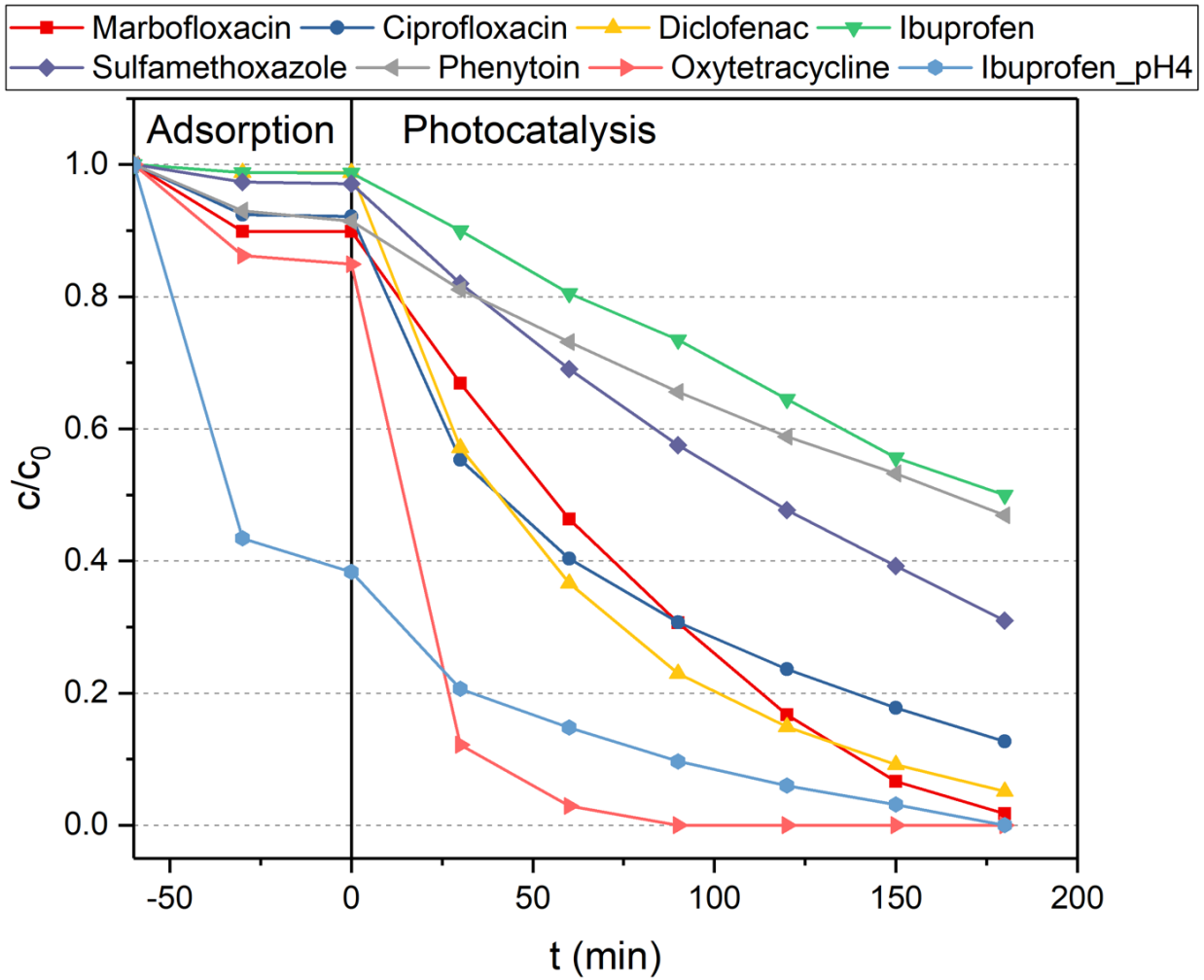
Photocatalytic degradation in wastewater treatment plant effluent

- Wastewater was collected from Domžale-Kamnik central wastewater treatment plant (WWTP)
- Reaction rates are higher compared to bioreactor effluent – lower amount of dissolved organic matter
- Lowering the pH to 4 (ibuprofen) increases the degradation rates



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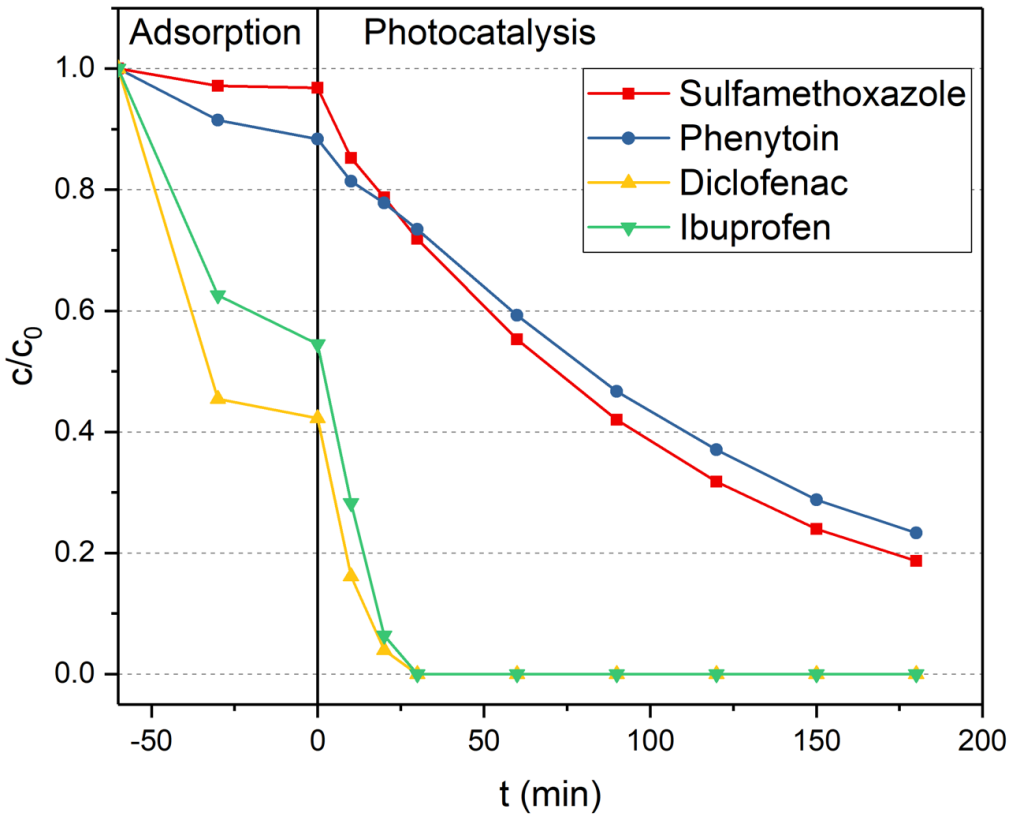
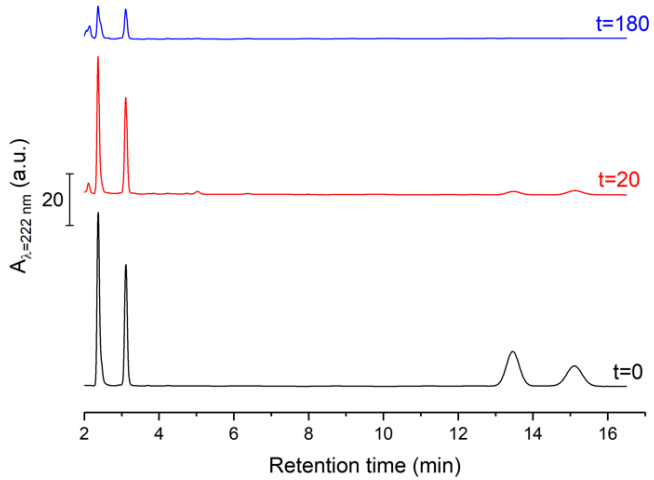
Degradation of a combination of pharmaceuticals in different matrices



- Degradation in deionized water ($\gamma_{\text{each pharmaceutical}}$ = 4 mg/L)
- Degradation profiles are comparable to those for individual compounds - no interacting or preferential reactions
- Chromatograms:



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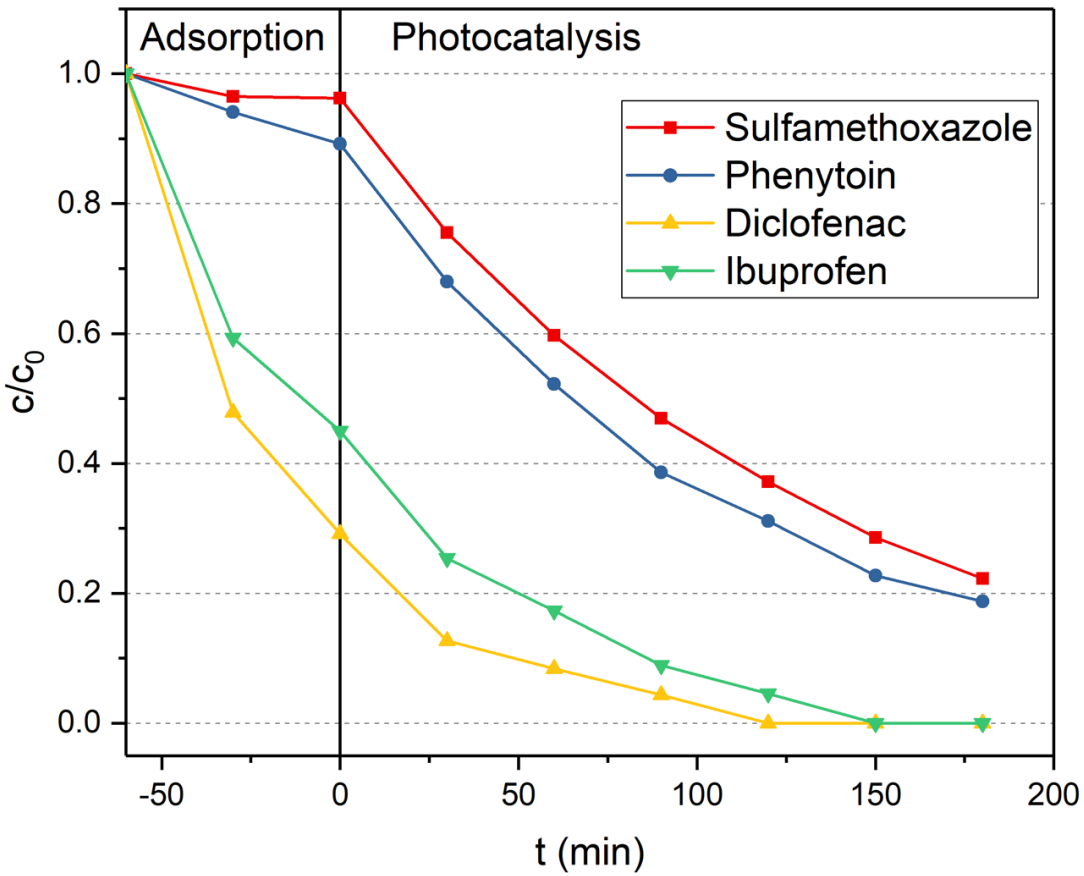
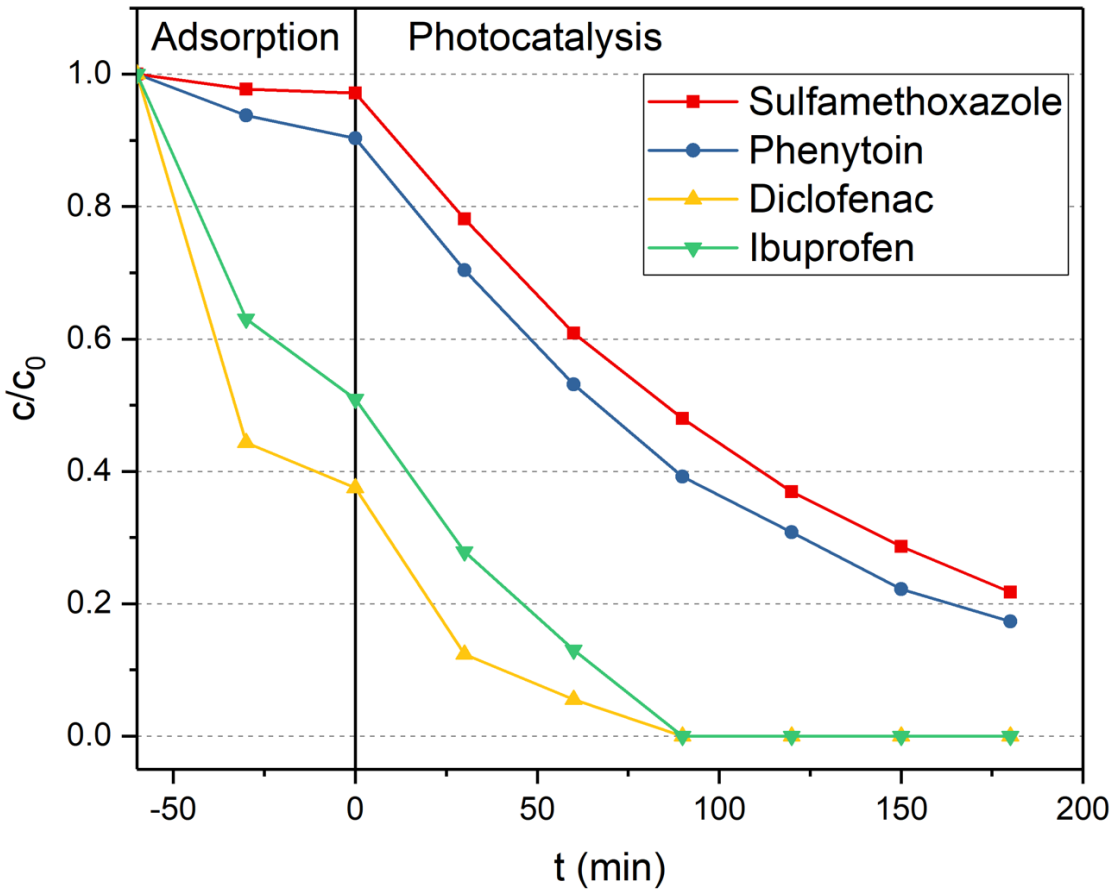
Bioreactor effluent (pH=4)



Wastewater treatment plant (WWTP) effluent (pH=4)



- Reaction rates lower than in deionized water
- Higher degradation rates in WWTP effluent -> similar to the results for individual compounds
- Lowering the pH to 4 also increases the degradation rates

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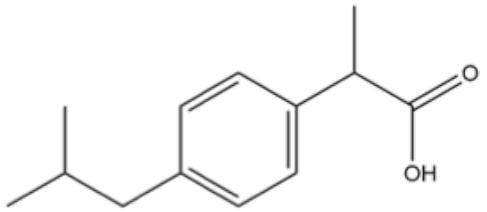
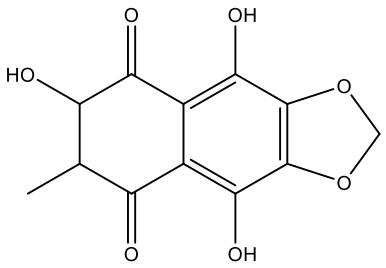
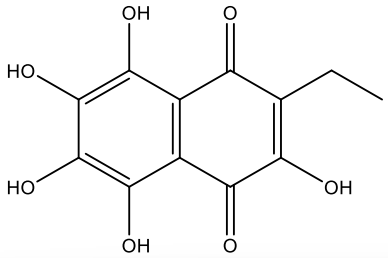
Degradation byproducts (in deionized water)

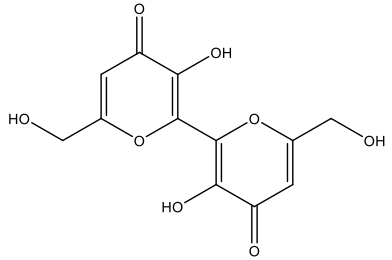
Ibuprofen degradation intermediates

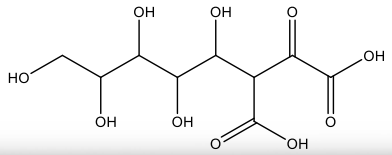


Tandem liquid chromatography triple-quadrupole mass spectrometry analysis
(FKIT, University of Zagreb)

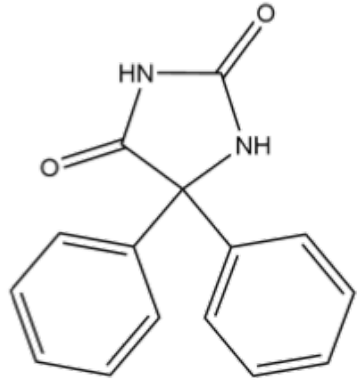


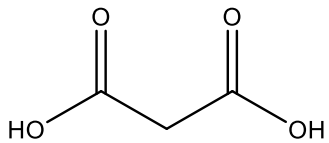


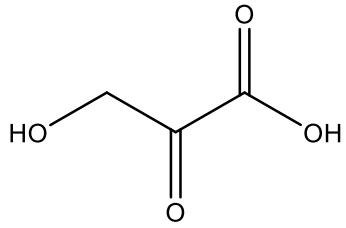




Phenytoin degradation intermediates







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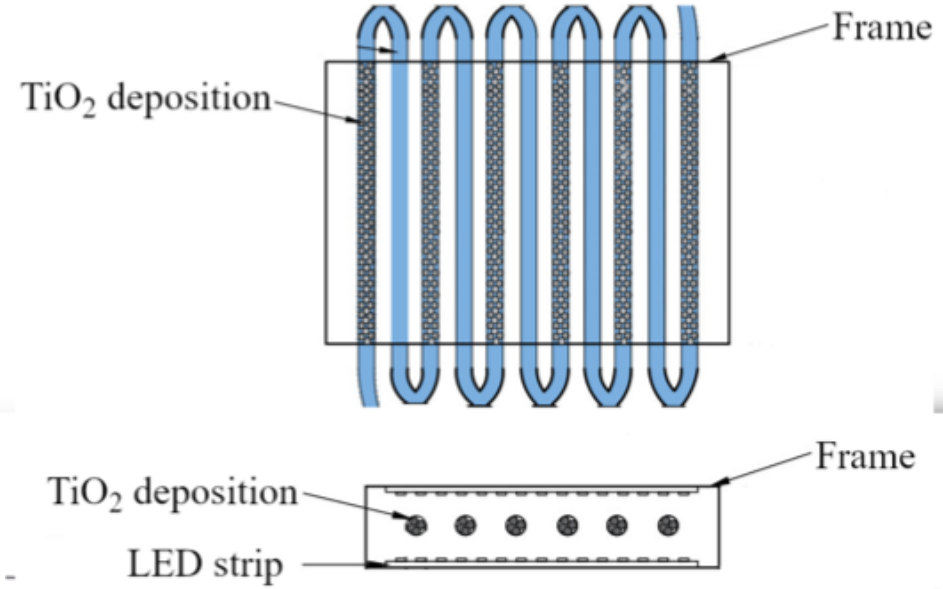
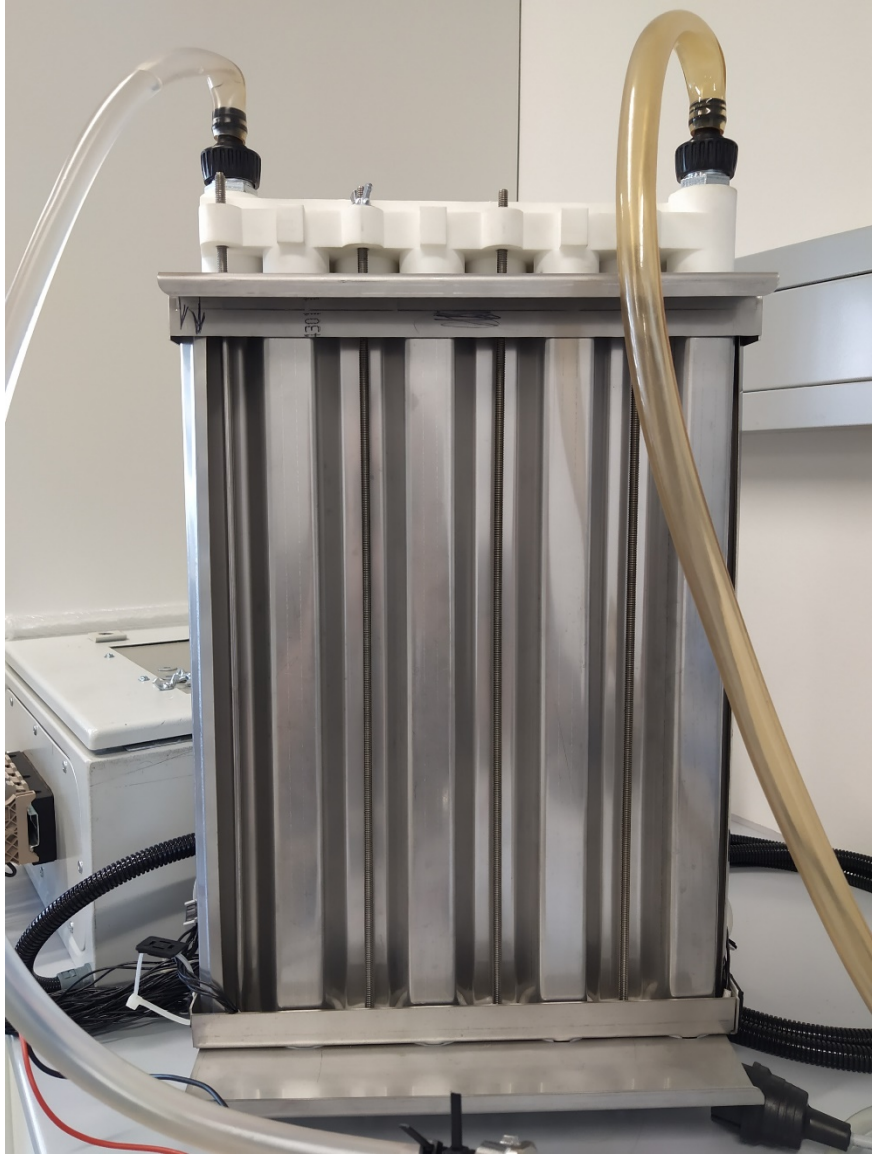
Future work

- Scaling-up the photoreactor unit to ~ 2 L (tubes with volume of 150 mL)

- Use of photoreactor units for practical wastewater treatment applications





Conclusions

- We developed two effective and cost-efficient methods of depositing P25 onto glass beads
- Photocatalyst is stable during the degradation process
- High activity for the removal of Plasmocorinth B, bisphenols and pharmaceuticals in deionized water
- Reaction rates are lower in wastewater matrices
- Nevertheless, it is still possible to remove problematic substances

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Thank you for your attention!

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