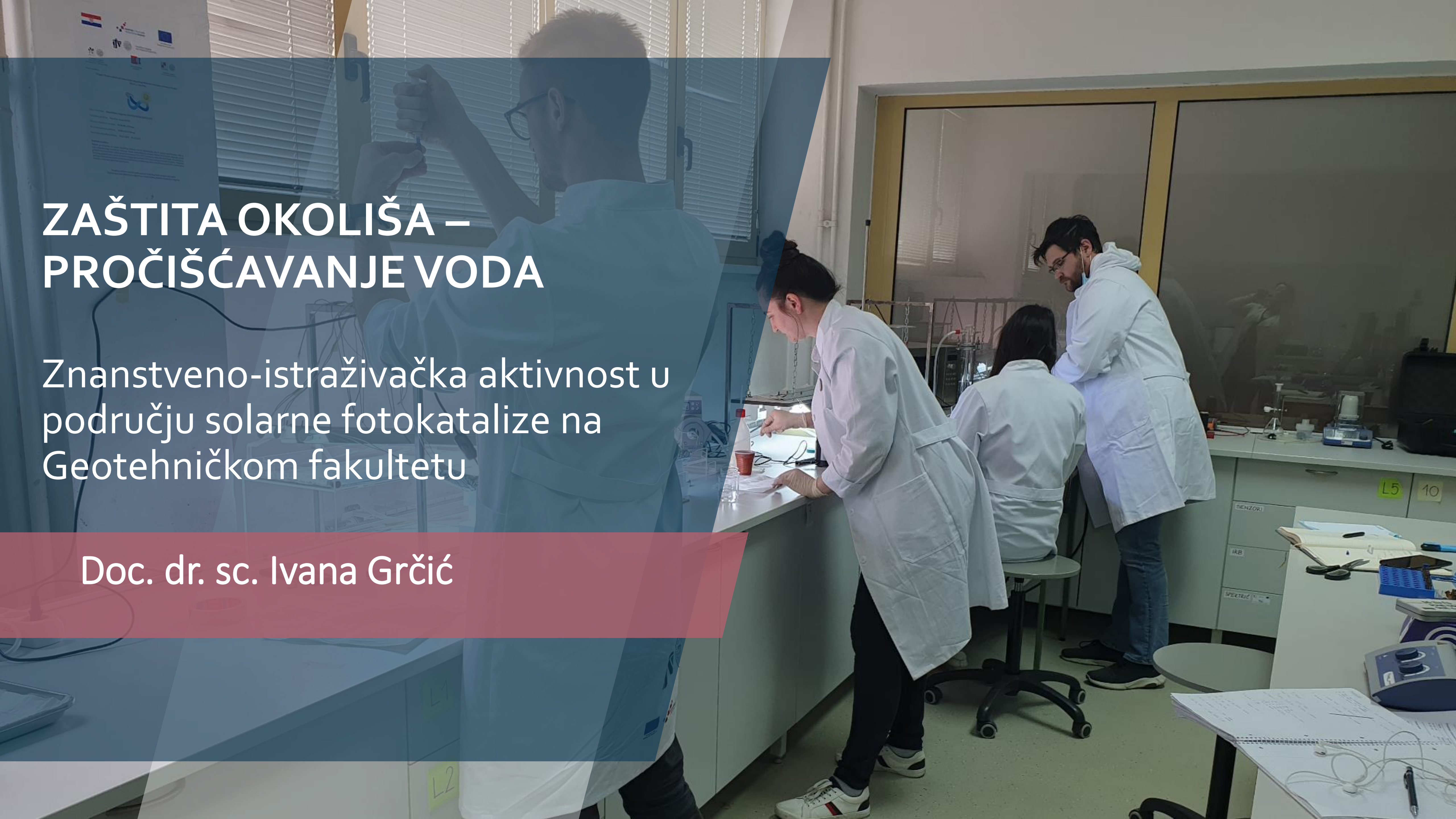


ZAŠTITA OKOLIŠA – PROČIŠĆAVANJE VODA

Znanstveno-istraživačka aktivnost u području solarne fotokatalize na Geotehničkom fakultetu

Doc. dr. sc. Ivana Grčić

CONTENTS

Trnava – prirodni prijemnik, Čakovec
Mjesto uzorkovanja blizu UPOV-a

Water Research 202 (2021) 117421

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

ELSEVIER

WATER RESEARCH

Review

Engineering and modeling perspectives on photocatalytic reactors for water treatment

Dawei Wang[a,*], Miguel Angel Mueses[b], José Angel Colina Márquez[b], Fiderman Machuca-Martínez[c], Ivana Grčić[d], Rodrigo Peralta Muniz Moreira[e], Gianluca Li Puma[e,*]

[a] Key Laboratory of Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China
[b] Photocatalysis & Solar Photoreactors Engineering, Modeling & Application of AOPs, Chemical Engineering Program, Universidad de Cartagena, Zip code 1382-Postal 195, Cartagena, Colombia
[c] GAOX, CENM, Escuela de Ingeniería Química, Universidad del Valle, Cali 760032, Colombia
[d] Faculty of Geotechnical Engineering, Department for Environmental Engineering, University of Zagreb, Hallerova aleja 7, Varaždin HR-42000, Croatia
[e] Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

ARTICLE INFO

Keywords:
Design
Modeling
Radiation transport
Reaction kinetics
Pilot plant
Process economics

ABSTRACT

The debate on whether photocatalysis can reach full maturity at commercial level as an effective and economical process for treatment and purification of water and wastewater has recently intensified. Despite a bloom of scientific investigations in the last 30 years, particularly with regards to innovative photocatalytic materials, photocatalysis has so far seen a few industrial applications. Regardless of the points of view, it has been realized that research on reactor design and modeling are now equally urgent to match the extensive research carried out on innovative photocatalytic materials. In reality, the development of photocatalytic reactors has advanced steadily in terms of modeling and reactor design over the last two decades, though this topic has captured a smaller specialized audience. In this critical review, we introduce the latest developments on photocatalytic reactors for water treatment from an engineering perspective. The focus is on the modeling and design of photocatalytic reactors for water treatment at pilot- or at greater scale. Photocatalytic reactors utilizing both natural sunlight and UV irradiation sources are comprehensively discussed. The most promising photoreactor designs and models are examined giving key design guidelines. Other engineering considerations, such as operation, cost analysis, patents, and several industrial applications of photocatalytic reactors for water treatment are also presented. The dissemination of key photocatalytic reactor design principles among the scientific community and the water industry is currently one of the greatest obstacles in translating PWT research into widespread real-world application.

TRENUTNO STANJE TEHNIKE

- Značajan razvoj fotokatalitičkih reaktora
- Ključni parametri za dizajn
- Složeni modeli
- Poneka industrijska primjena
- Pregršt publikacija i patenata vezanih uz razvoj materijala

....

Solarna fotokataliza kao odgovor na velika pitanja u zaštiti okoliša

⇨

Podizanje osviještenosti

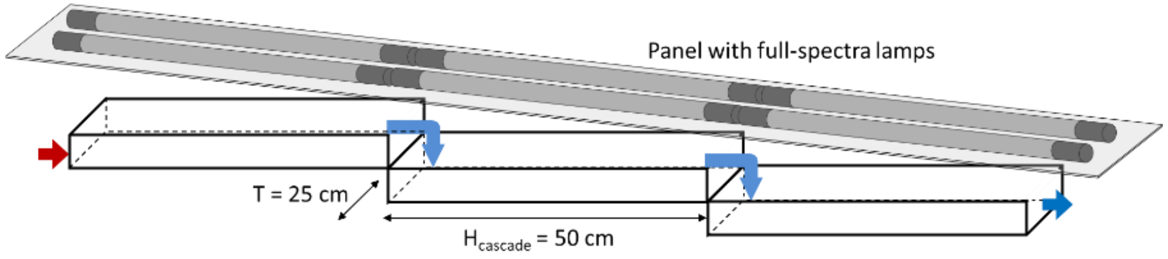
Edukacija novih generacija inženjera okoliša

Reaktorski sustavi

Pločasti reaktori - *Semi-pilot scale flat-plate cascade reactor (FPCR)*

Cijevni reactor s koncentrirajućim zračenjem pomoću paraboličnih zrcala - *Compound parabolic collector reactor (CPC)*

FPCR sustav



Konfiguracija reaktora

Laminarni do prijelazni tok vode

Rad u recirkulaciji

Hidrodinamika pravokutnog otvorenog kanala

Debljina sloja vodee ≈ 0.7 – 1.0 cm

Izvori zračenja s punim spektrom i različitim omjerima UVB:UVA

Fotokatalitički materijali

TiO_2 P25/TEOS premaz na staklenim vlaknima

Uvođenje ugljikovih nanocijevi (MWCNT)

Cijevni reactor s koncentrirajućim zračenjem (CPC sustav)

Osnovne karakteristike

Indoor / outdoor primjena

Modularni reaktor

Do 20 m duljine (lako za skaliranje!)

Podesiv nagib ovisno o upadnom kutu Sunčevog zračenja

Primjenjiv i za vode i za zrak!!

Mikroonečišćivala u površinskim vodama

Glavne grupe i tvari s Drugog popisa praćenja (Izvještaj Hrvatskih voda, 2020)

LC-MS-QTOF

1H-benzotriazol

karbamazepin

Imidakloprid

17β-estradiol

ibuprofen

Groups	Substances	Maximum acceptable detection limit (µg/L)	Monitoring results of substances (µg/L)	Expected results after solar photocatalysis (µg/L)
Hormones	17-β-Estradiol (E2)	0,0004	<0,000053 – 0,000093	0
	Estrone (E1)	0,0004	<0,000995	0
	17-α-Ethinyl Estradiol (EE2)	0,000035	<0,000012 – 0,000099	0
Pesticides	Methiocarb	0,002	<0,00239 – 0,003118	0
	Imidacloprid	0,0083	<0,00179	0
	Thiacloprid	0,0083	<0,0009	0
	Thiamethoxam	0,0083	<0,00188 – 0,004701	0
	Clothianidin	0,0083	<0,00181	0
	Acetamiprid	0,0083	<0,00056	0
Macrolide antibiotics	Erythromycin	0,019	<0,00323	0
	Clarithromycin	0,019	<0,00259 – <0,00931	0
	Azithromycin	0,019	<0,00309 – <0,00623	0
Insecticides	Metaflumizone	0,065	<0,00118	0
Antibiotics	Amoxicillin	0,078	<0,00442 – 0,004729	0
	Ciprofloxacin	0,089	0,0345925 – 0,1416513	0

Predviđajući modeli

Konceptualni dijagram za određivanje **stvarnih kinetičkih konstanti** u procesu fotokatalize

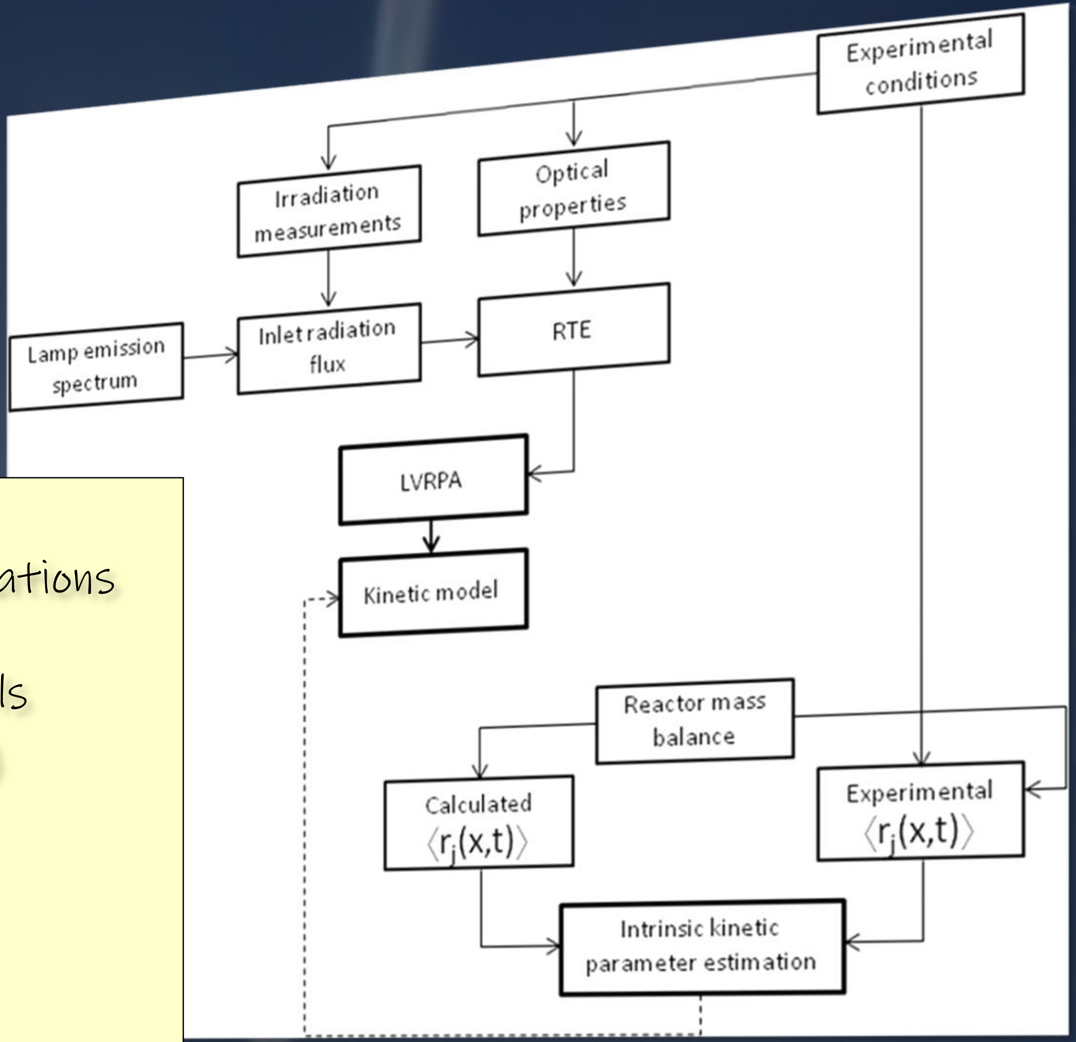
Irradiation emission models
→ Find the appropriate equations

Irradiation absorption models
→ Absorption vs. scattering

Kinetic models
→ Reaction mechanisms
→ Adsorption

Hydrodynamics

Mass balance
→ Reactor type



J. Marugan, et al., *Appl. Cat.B* **85** (2008) 48-60

Modeliranje solarne fotokatalize

Incident irradiation intensity (W m^{-2})

I_e, I_0 Irradiation emission (LSSE, ESSDE models)

Local volumetric rate of photon absorption (LVRPA, W m^{-3})

e_a Light absorption and scattering

Velocity field

Re, v_z Hydrodinamics

Intrinsic degradation rate constant (mol^{1-n} $dm^{3m-3n-3}$ s^{-1} W^{-m})

$k_{intrinsic}$ Kinetic models

$$r_i = \frac{d[X_i]}{dt} = -k_i\left(e^a(T,H)_{UVB} + e^a(T,H)_{UVA}\right)^m [X_i]^n$$

→ SFM, scattering albedo/optical properties

$$e^a_{h,T,z} = \frac{\tau_{app} I_0(T)}{\omega_{corr}(1-\gamma)}\left[\left(\omega_{corr} - 1 + \sqrt{1-\omega_{corr}^2}\right)\exp(-\tau_{app}h*) + \gamma\left(\omega_{corr} - 1 - \sqrt{1-\omega_{corr}^2}\right)\exp(-\tau_{app}h*)\right]$$

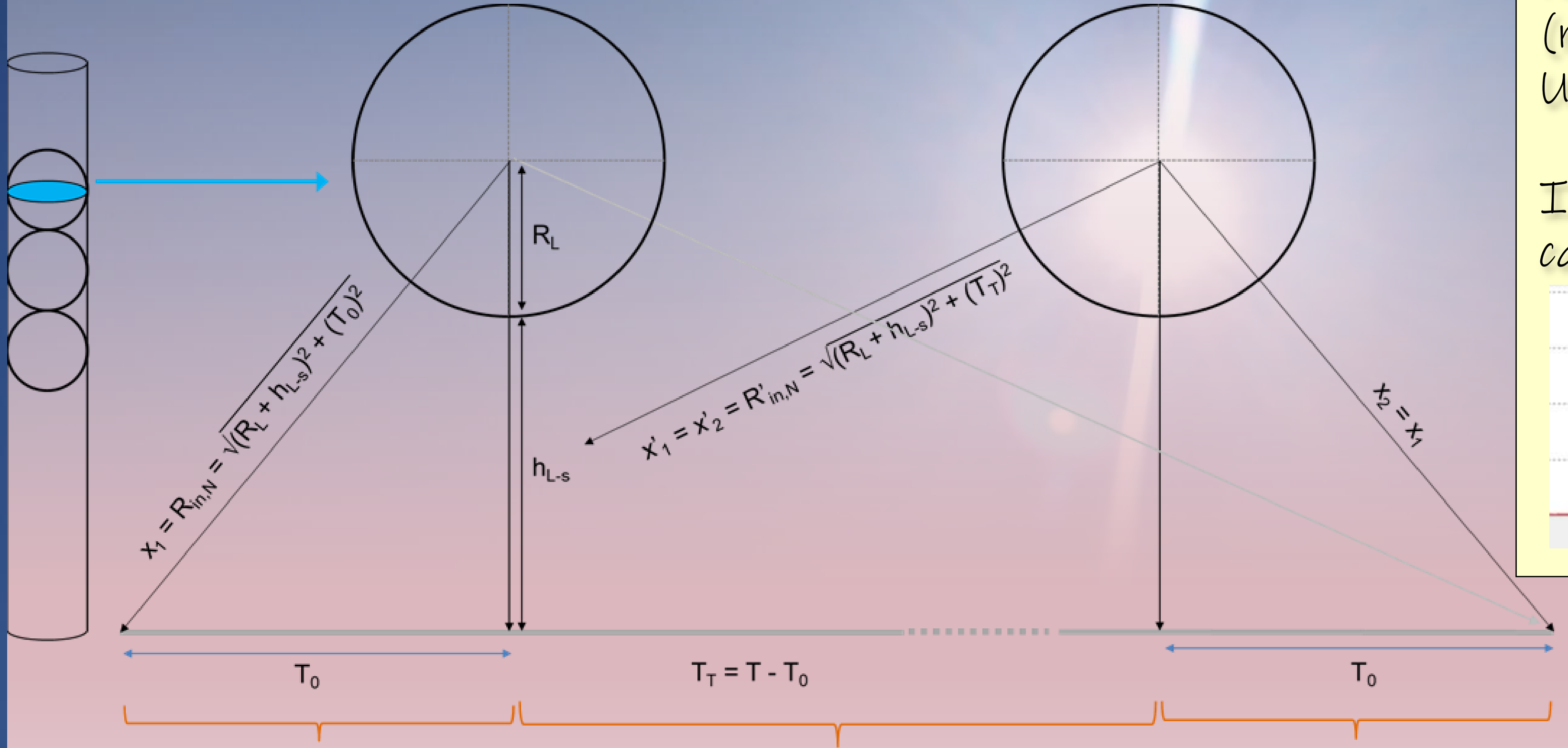
→ (Incident photon flux*absorption coefficient) introduced in case of films

$$r_i = \frac{d[X_i]}{dt} = -k_i\left((\mu I_0(T,H))_{UVB} + (\mu I_0(T,H))_{UVA}\right)^m [X_i]^n$$

→ Visible part of spectra?

Procjena upadnog zračenja po cijeloj površini fotokatalitičkih materijala

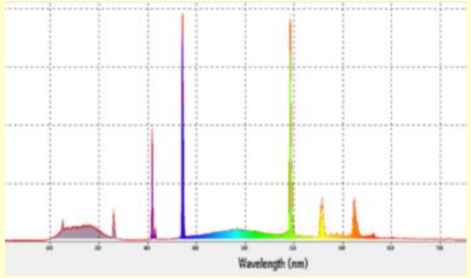
$$I_{R_{in,0}\to T/2} = I_w R_L^2 \sum_{k=1}^{k=11} \frac{R_{in}(T)}{\left[R_{in}(T)^2 + \left(z-2(k-1)R_L\right)^2\right]^{3/2}}$$



$I_{0,T} = I_{0,x1(T)} + I_{0,x'2(T)}$ $\quad$ $I_{0,T} = I_{0,x'1(T)} + I_{0,x'2(T)}$ $\quad$ $I_{0,T} = I_{0,x'1(T)} + I_{0,x2(T)}$

The UVB and UVA intensities on the lamp wall (I_w) were determined radiometrically using midrange UVB (range 280–340 nm) and longwave UVA sensor (range 335-385 nm)

If needed, whole emission spectrum can be taken



$\Sigma\,(\mu_\lambda I_{0,\lambda})$

Materijali za solarnu fotokatalizu

TiO_2 premaz na staklenim vlaknima (uz silane)
TiO_2 na poliesteru i vuni (uz kitozan)
TiO_2 na gumi (zaštita zraka, projekt KK.01.1.1.07.0058)

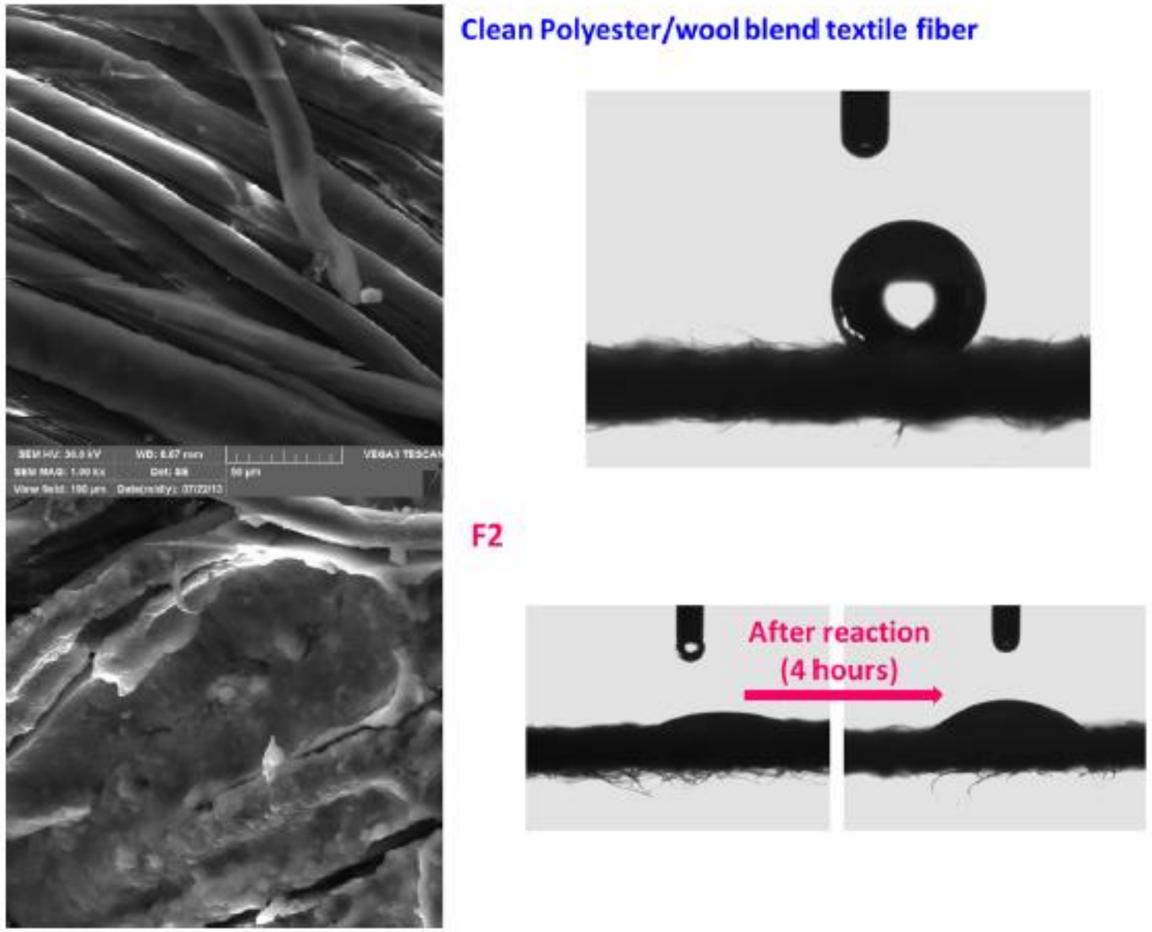
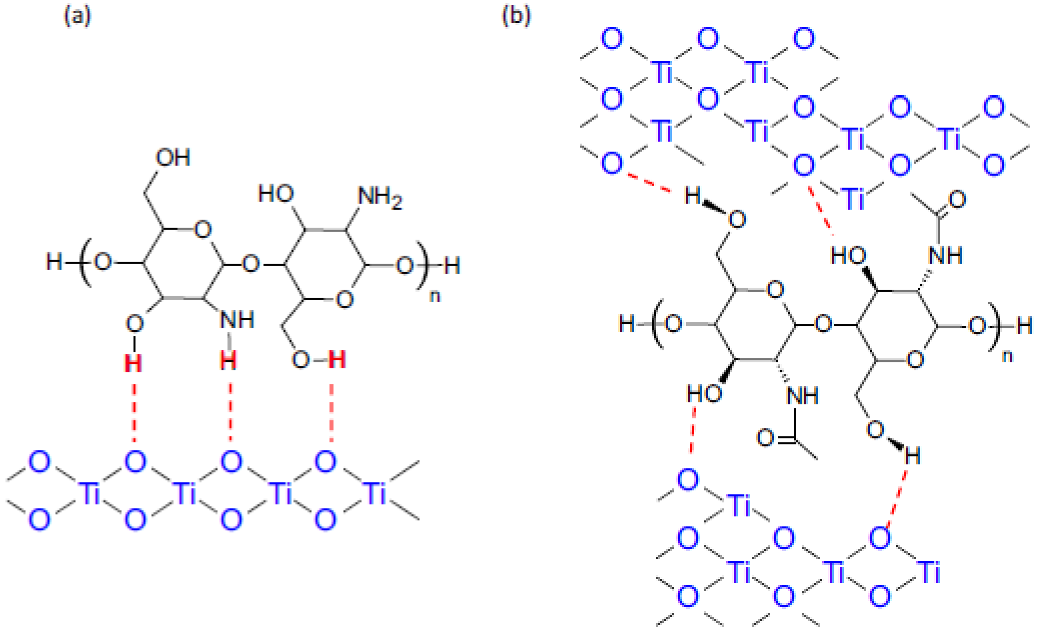
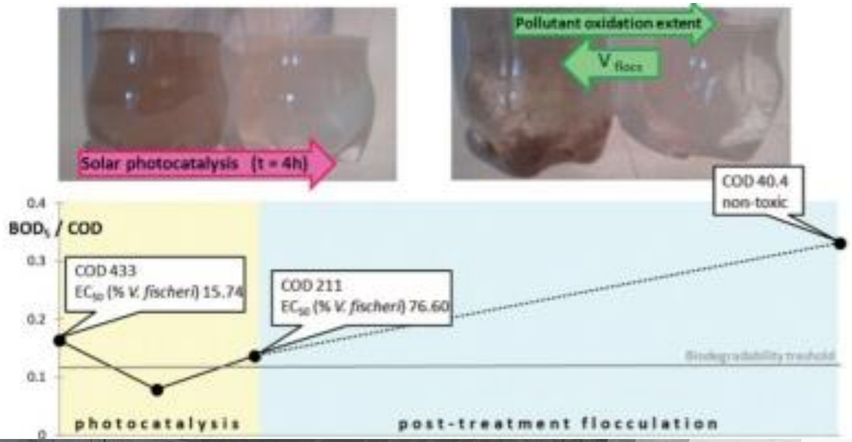


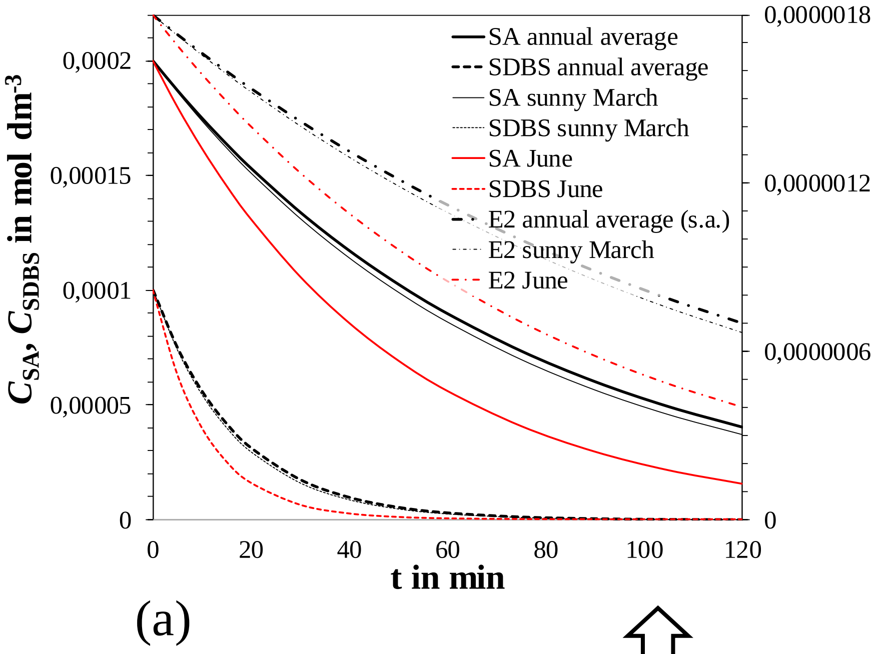
Fig. 3. Micrographs (left) and water contact angle (right) at the surface of clean textile fiber and coated textile (F2).

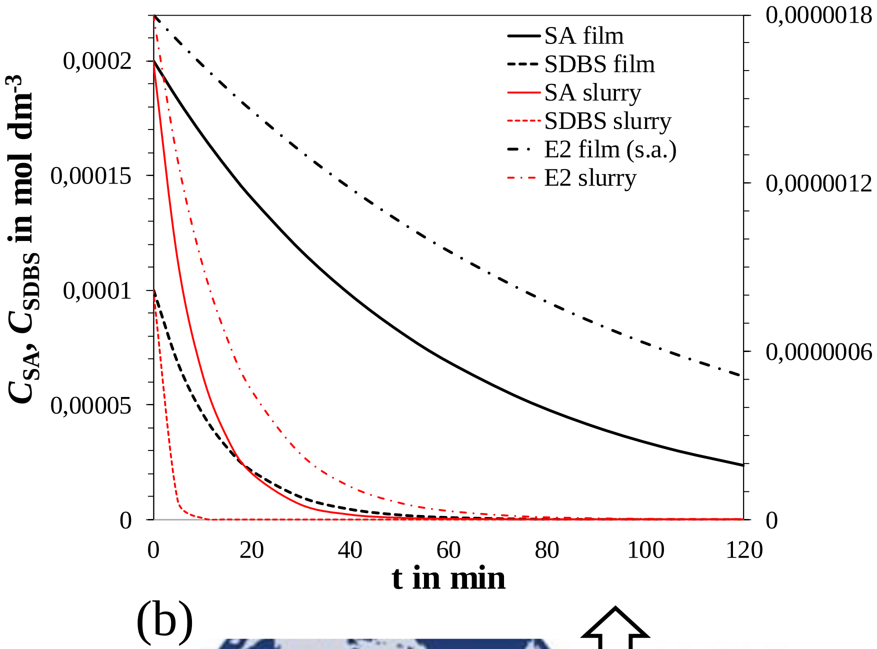




3. Materijali

Projekcije uklanjanja mikroonečišćivala u površinskim vodama (na temelju rezultata iz FPCR sustava)





Zagreb (45°N)

Imobilizirani TiO_2 na staklenim vlaknima

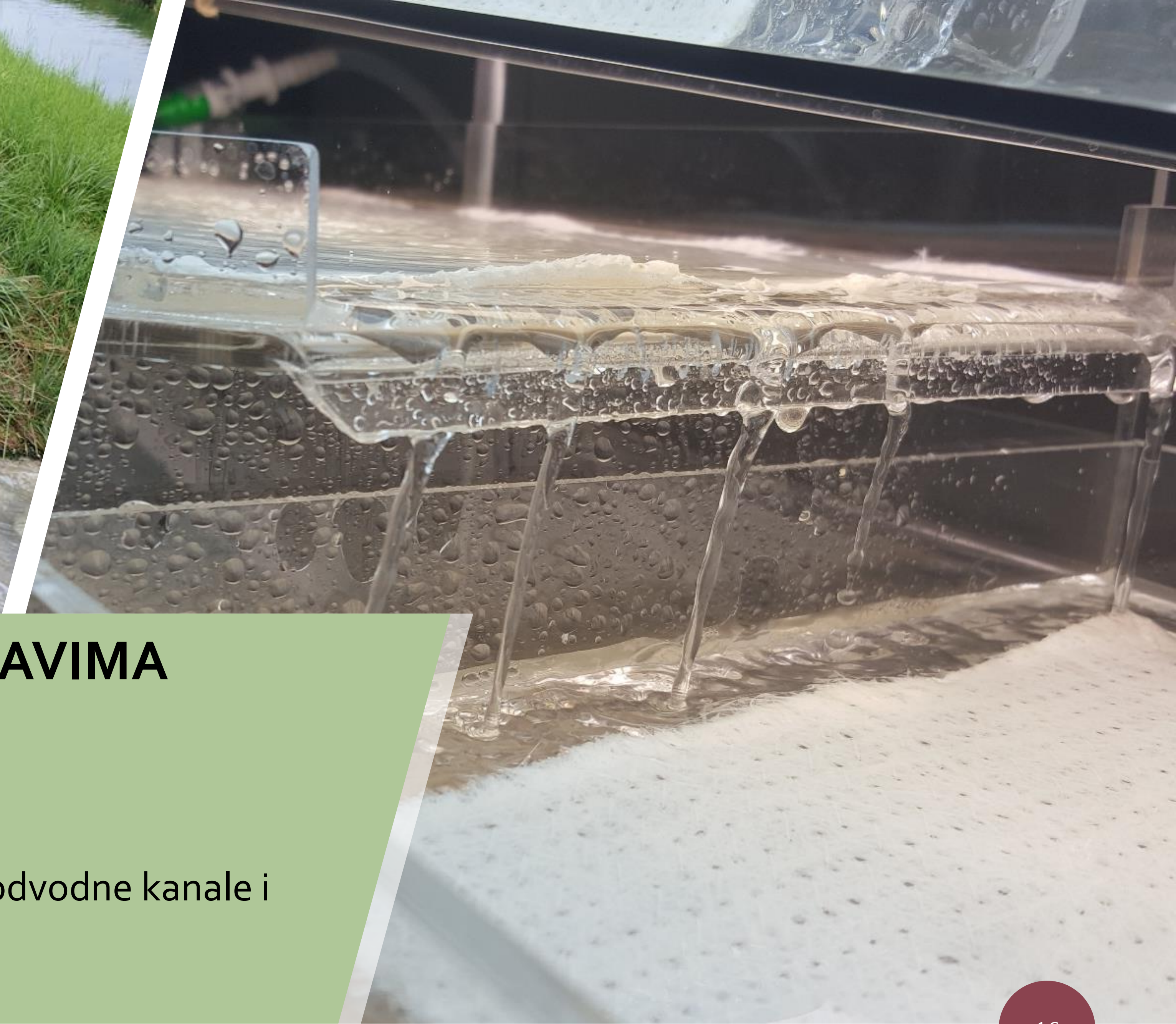
Predviđanja modela na temelju srednjih vrijednosti intenziteta UV zračenja oko ekvatora

4. Projekcije

Analiza mikroonečišćivala u površinskim vodama SZ RH

Analiza uzoraka na LC-MS/Q-TOF sustavu

- Ibuprofen u SVIM uzorcima, uz kortizon, citostatike i sl. supstance
- Početna ukupna koncentracija procjenjena na 5 $\mu g\ L^{-1}$
- Model razgradnje u CPC sustavu ukazuje na potpunu razgradnju većine detektiranih spojave unutar 60 min



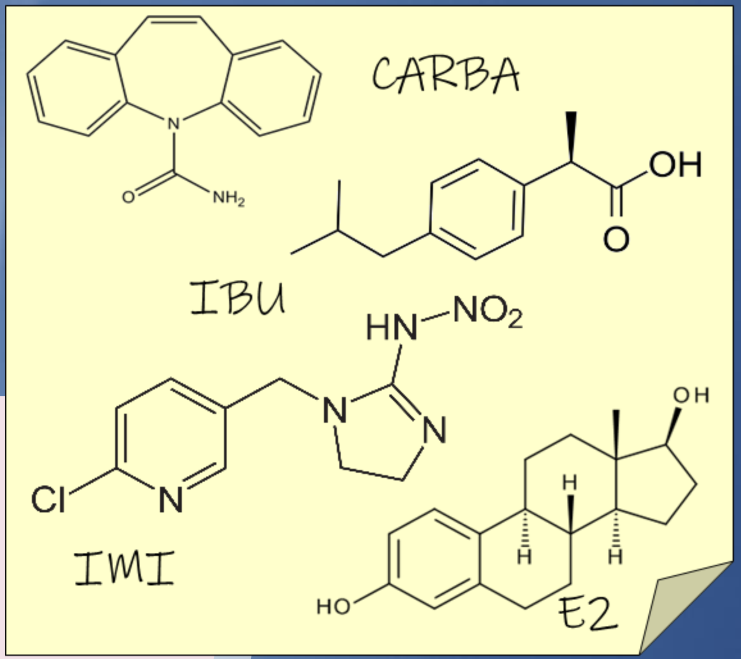
PRIMJENA U REALNIM SUSTAVIMA

FPCR sustav u prirodi:

→ Pročišćavanje površinskih voda

→ Umetanje fotokatalitičkih materijala u odvodne kanale i prirodne prijemnike / plitka korita

→ No, je li stvarno tako jednostavno?



Rezultat projekcija za odabrane lokacije

Zagreb, Sevilla and Lapsista (Grčka):

→ 99% uklanjanjanja CARBA, IBU, IMI, E2 i BT tijekom cijele godine

→ **Potrebna duljina FPCR-u sličnog sustava u odvodnom kanalu (širina 5-10 m):**

→ 300 m (Zagreb)

→ 160 m (Sevilla)

→ 80 m (Lapsista)

→ Nedovoljno istraživanja

→ Najranija primjena: 2030.

Solarna fotokataliza u parku ☺

Krenimo dječjim koracima:
→ ispitivanje novih katalizatora,
utjecaj na okoliš i ponašanje materijala u stvarnom mjerilu
→ validacija predviđajućih modela

Varaždin ⇨ umjetni potočić u parku iza fakulteta

5. Primjena u realnim sustavima?

Ljubljana ?

5. Primjena u realnim sustavima?

Hvala na pažnji

....

Assist. Prof. Ivana Grčić, PhD

+385 (42) 408 900

ivana.grcic@gfv.unizg.hr

https://www.gfv.unizg.hr/static/projekti

https://www.os-mi.eu

Istraživanje je financirano iz ESI fondova
Projekt KK.01.1.1.04.0006
"Otpad & Sunce u službi fotokatalitičke razgradnje Mikroonečišćivala u vodama" (OS-Mi)
1.13 M Euros