Izazovi i novi pristupi tretmanu organskih mikropolutanata u vodi – primena ozona i unapređenih oksidacionih procesa

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Water Workshop 2024
safewat
SmartWaterTwin
Funded by the European Union
SmartWater Summer FORUM
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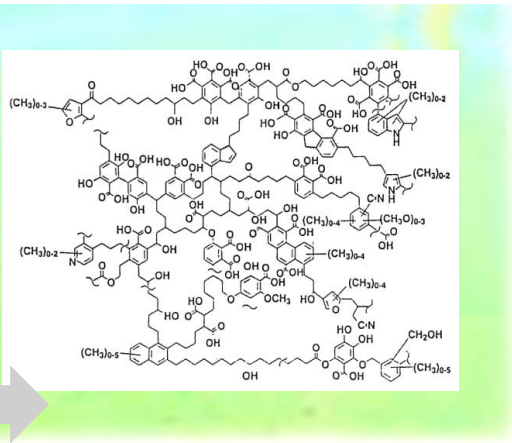
ORGANSKI MIKROPOLUTANTI U AKVATIČNIM EKOSISTEMIMA

Domaćinstva
Bolnice
Industrija
Vodosnabde-vanje
Prikupljanje i kanalisanje otpadnih voda
OZONIZACIJA/AOPs
UWWTP
Zemljište
DWTP
OZONIZACIJA/AOPs
Ispuštanje u recipijent
Ponovna upotreba
Poljoprivreda (navodnjavanje)
Prihranjivanje podzemnih voda
CECs i patogeni
Podzemna voda
Rizici?



~ 2,362 chemicals and TPs LC-HRMS (JDS4); 586 CECs detektovano

Emergentne supstance (*contaminants of emerging concern*)

- Toksini algi: npr. Mikrocistin-LR
- Biocidni TPs: npr. metIl triklosan
- Biocidi: npr. hloroksilenol, hlorofen
- Biloški/sabotažni agensi: npr. hloropikrin
- DBPs (voda za piće): npr. NDMA, HANs, HNMs
- Usporivači gorenja: npr. 1,2,5,6,9,10-heksabromociklododekan, tetrabromobisfenol A
- Droge: npr. kokain, heroin, morfin
- Aditivi hrani: npr. sukraloza, triacetin
- Aditivi goriva: npr. metil-terc-butil ethar

- Industrijske hemikalije: npr. 1,2,3-benzotriazol, hidrazin
- Antimikrobni agensi: npr. kamfor, izoborneol
- Perfluoroalkil supstance
- Proizvodi za ličnu negu/biocidi: npr. 4-metilbenziliden kamfor, etil paraben, tonalid, triklosan
- Farmaceutici: npr. 17-alfa-estradiol, azitromicin, diklofenak, ibuprofen, metformin
- Sredstva za zaštitu bilja/biocidi: npr. karbaril, linuron, mekoprop, cipermethrin
- Plastifikatori: npr. BPA
- Surfaktanti

NORMAN List of Emerging Substances

Trenutno nisu obuhvaćeni rutinskim monitoring programima na evropskom nivou; potencijalni kandidati za buduće regulative u oblasti voda

Prioritetne i prioritetne hazardne supstance

- Toksične
- Perzistentne
- Bioakumulativne

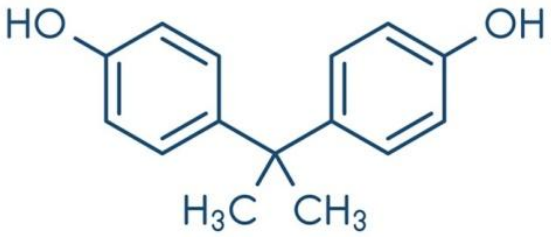
- Ftalati
- PAH
- Organofosforni insekticidi
- Organohlorni pesticidi i aromatična organohlorna jedinjenja
- Hlorovani rastvarači
- Dioksinis, PCB, BDE
- Metali
- Alkilfenoli
- Piretroidni insekticidi
- Perfluorovani surfaktanti
- Hinolinski herbicidi
- Hlorovani alkani
- HBCDD

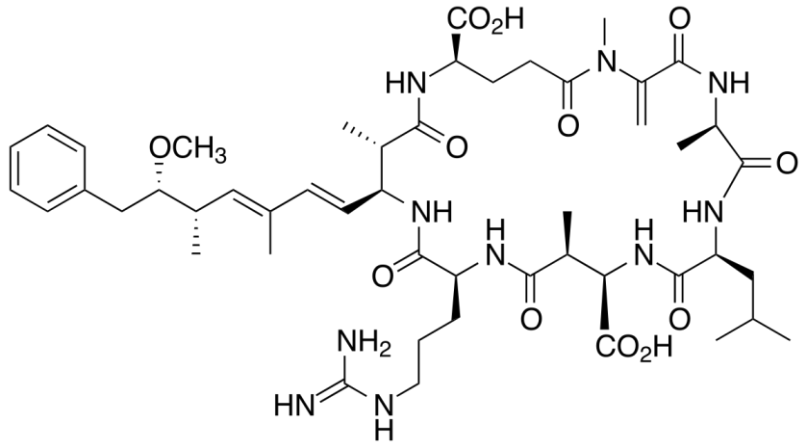
LISTA ZA PRAĆENJE (*Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC; DECISION EU 2022/1307*)

- Sulfametoksazol
- Trimethoprim
- Venlafaksin i O-desmetilvenlafaksin
- *Azolne komponente:* klotrimazol , flukonazol , imazalil, ipconazole, metkonazol, mikonazol, penkonazol, prohloraz, tebukonazol , tetrakonazol
- Dimoksistrobin; azoksistrobin
- Famoksadon
- Diflufenikan
- Fipronil
- Klindamicin
- Ofloksacin
- Metformin
- Guanilurea
- *Sunscreen agents:* Butil metoksidibenzoilmetane, oktokrilen, benzofenon-3

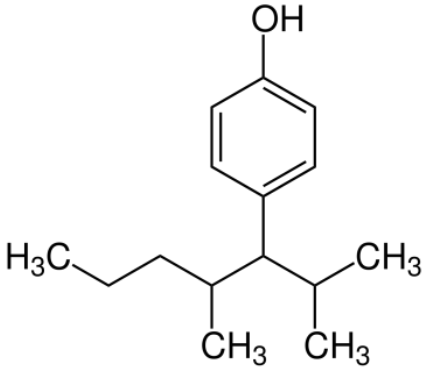
CECs i standardi kvaliteta vode za piće (Directive EU 2020/2184)

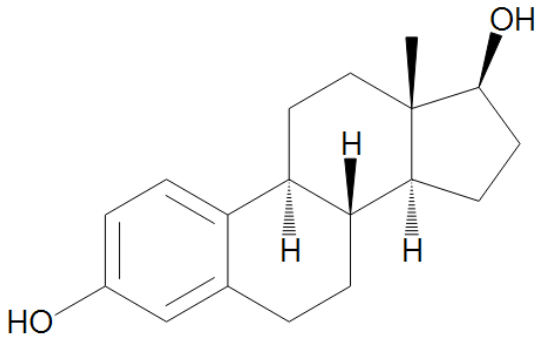
- Novi parametri: bisphenol A (2,5 µg/l); mikrocistin LP (1 µg/l), PFAS (0,5 µg/l), uran (30 µg/l).



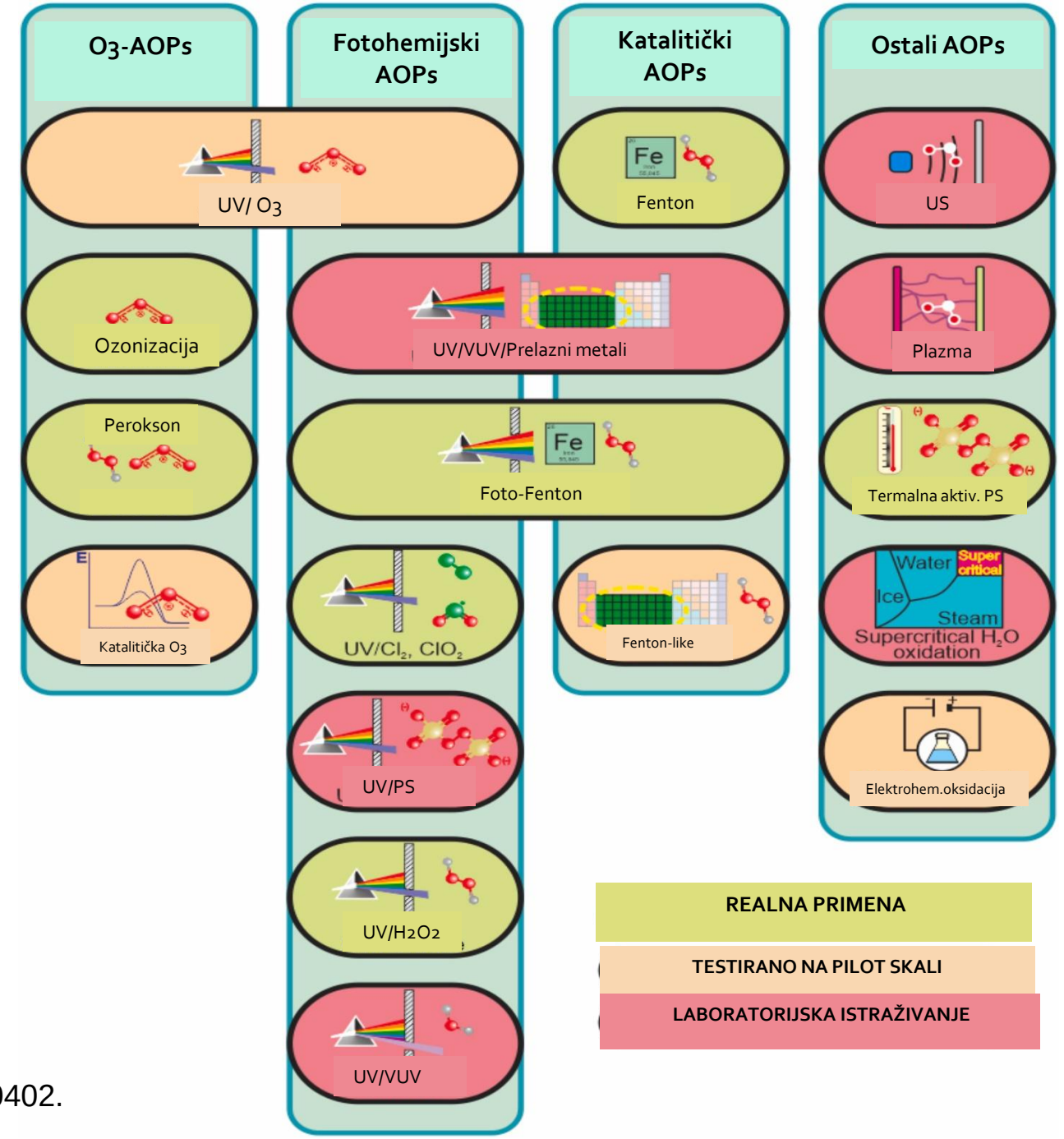


- "Watch list": nonilfenol (0,3 µg/l) i beta-estradiol (1 ng/l)



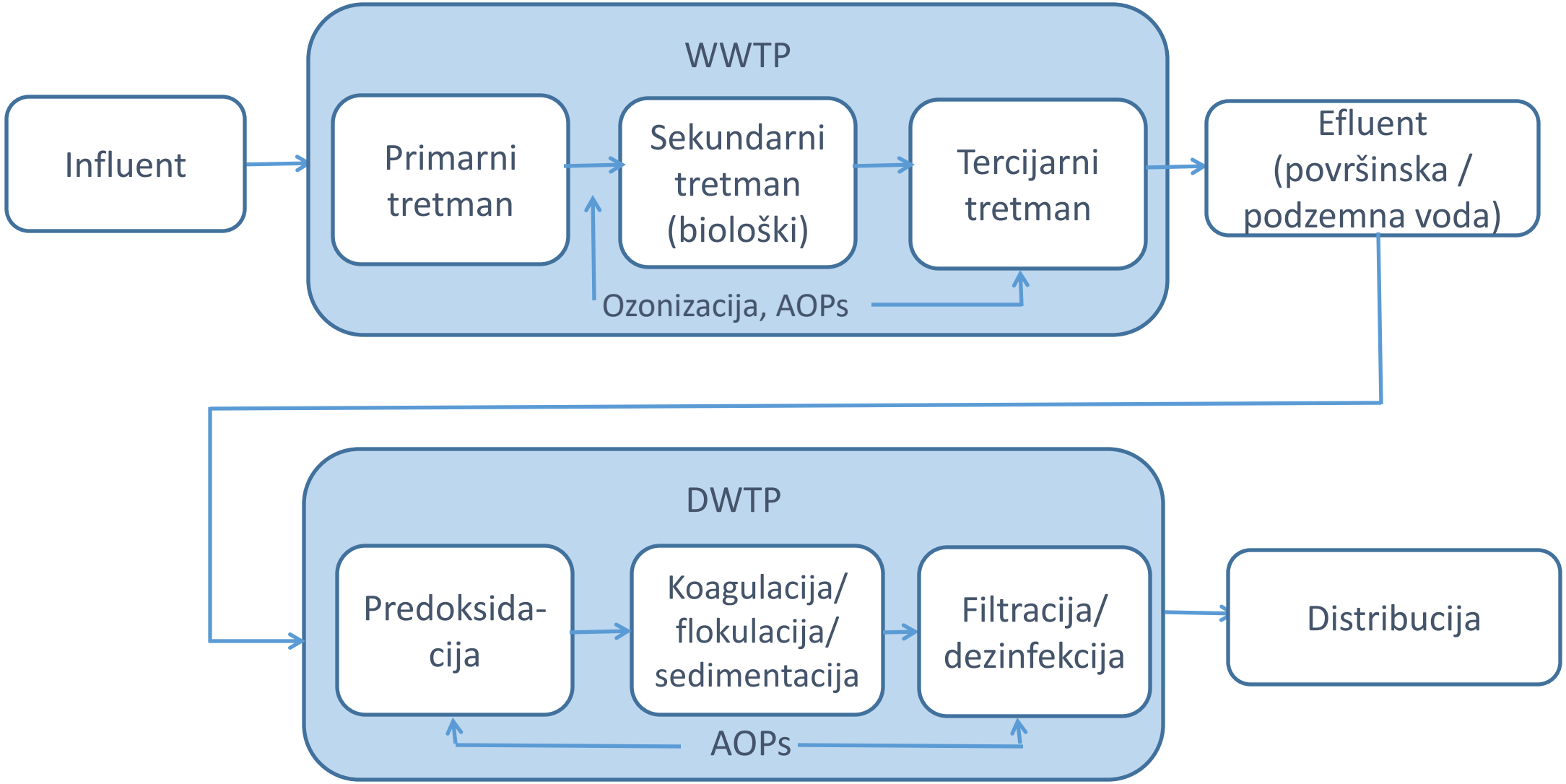


Klasifikacija i nivoi tehnološke primene AOPa

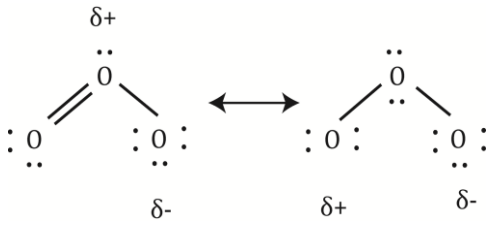


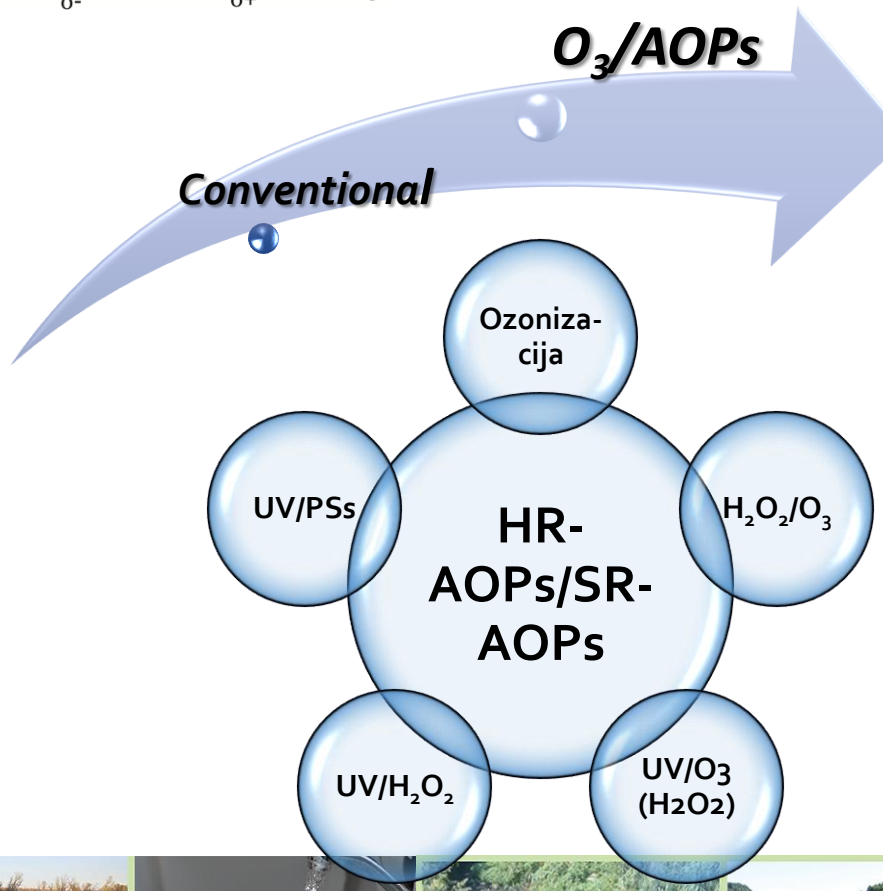
Hübner et al. (2024) Heliyon10, e30402.

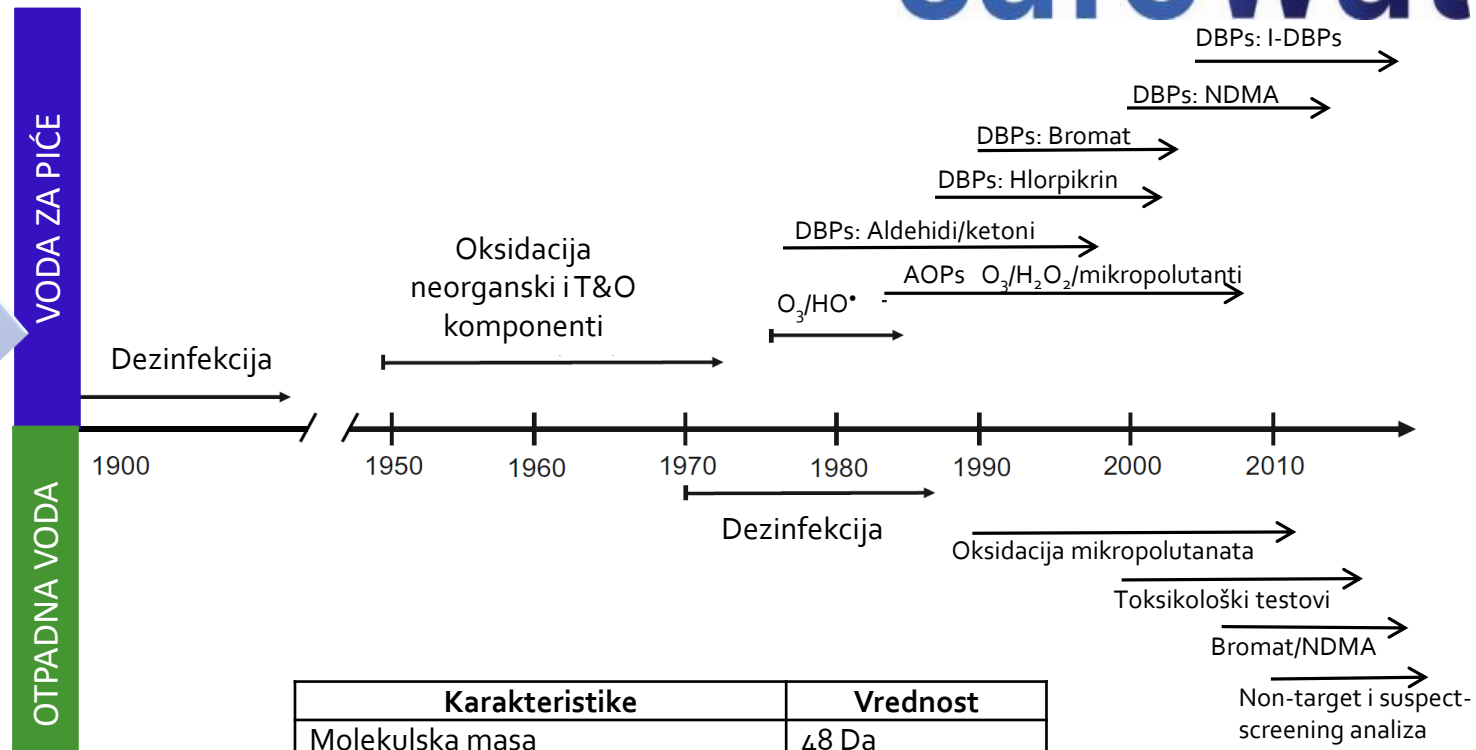
Primena ozonizacije i AOPs u tretmanu voda



Primena ozona i AOPs u tretmanu voda



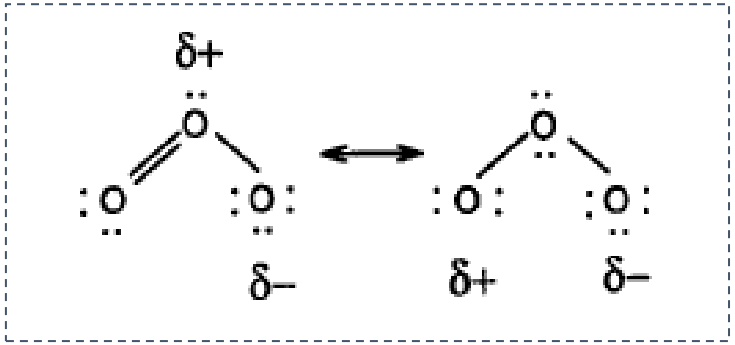


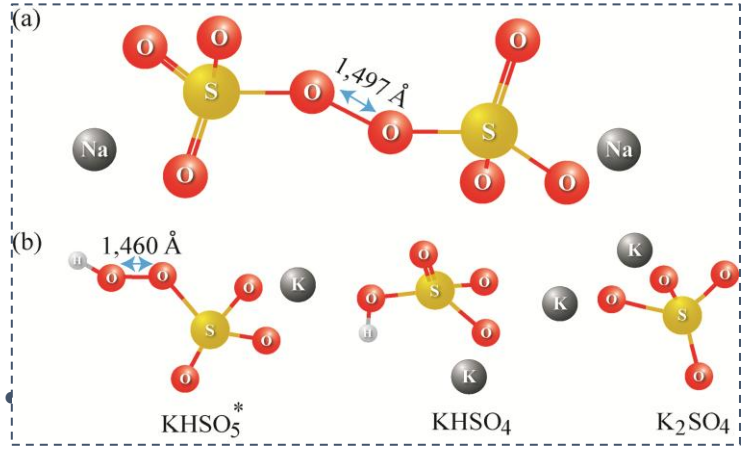


Karakteristike	Vrednost
Molekulska masa	48 Da
Dipolni momenat	0,537 debaj
Dužina veze	1,28 Å
Ugao veze	117°
Tačka topljenja	-192,7 °C
Tačka ključanja	-110,5 °C
Rastvorljivost u vodi na 0°C	$2,2 \times 10^{-2}$ M
Rastvorljivost u vodi na 20°C	$1,19 \times 10^{-2}$ M
Henrijeva konstanta na 0°C	35 atm M^{-1}
Henrijeva konstanta na 20°C	100 atm M^{-1}
Prag pri kojem dolazi do eksplozije	10% ozon

Lim, et al. (2022) Water Research 213, 118053

HR-AOPs/SR-AOPs





- $HO^{\bullet}$ i druge ROS: $HO_2^{\bullet}$; $3O_2$; $ROO^{\bullet}$
- $SO_4^{\bullet-}$

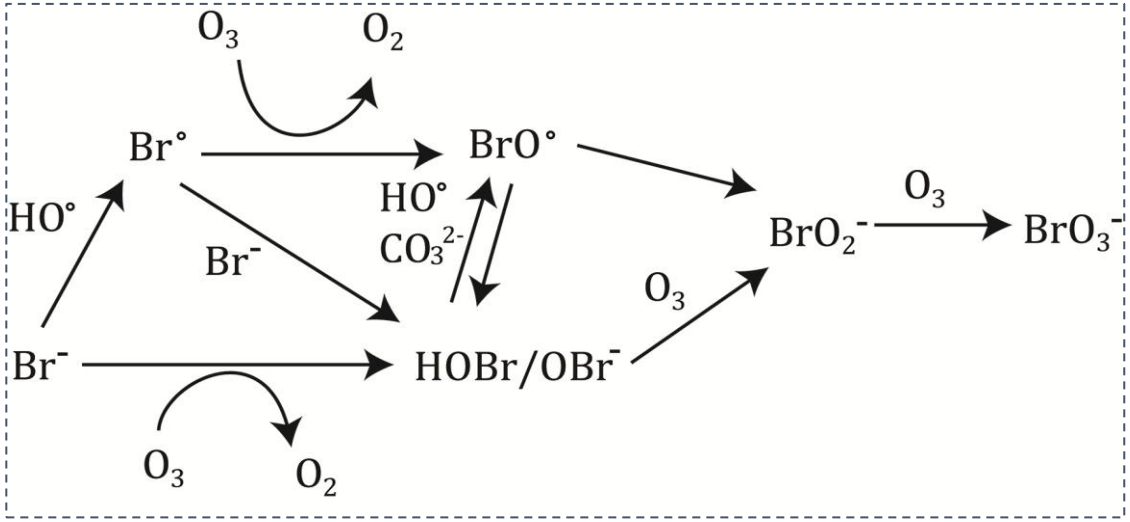
- **$HO^{\bullet}$**
  - snažni,
  - neselektivni hemijski oksidansi
  - Kompleksne radikalske reakcije

- **$SO_4^{\bullet-}$**
  - snažni,
  - selektivniji u odnosu na $HO^{\bullet}$ (reakcije transfera elektrona)
  - Efikasni u širokom opsegu pH (2-8)
  - Duže vreme poluživota u odnosu na $HO^{\bullet}$

Oksidacione vrste	Oksidacioni potencijal (V)
Fluor	3.03
Hidroksil radikali	**2.80**
$SO_4^{\bullet-}$	**2.5-3.1**
Atomski kiseonik	2.42
Ozon	2.07
Vodonik-peroksid	1.78
Hidroperoksil radikal	1.70
Permanganat	1.68
Hipobromna kiselina	1.59
Hlor-dioksid	1.57
Hipohloritna kiselina	1.49
Hlor	1.36
Kiseonik	1.20

Oksidacija bromida ozonom i hidroksil radikalima

- **Kontrola:**
  - Doze ozona,
  - Kontaktnog vremena,
  - Doziranje H_2O_2,
- smanjenje pH



Prekursor organskih DBPs + Prekursor neorganskih DBPs + Dezinfe-ktant = **Regulisani i emergentni DBPs**

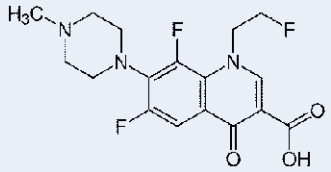
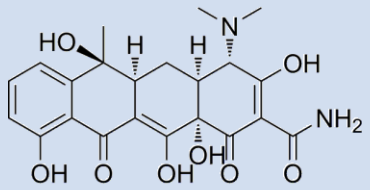
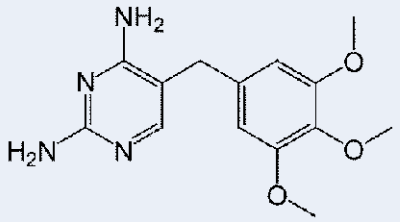
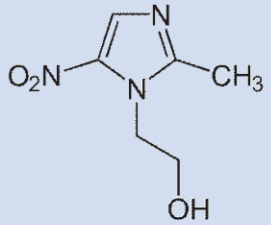
NOM
Algal organic matter
Wastewater effluent organic matter

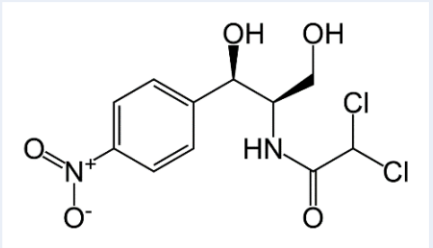
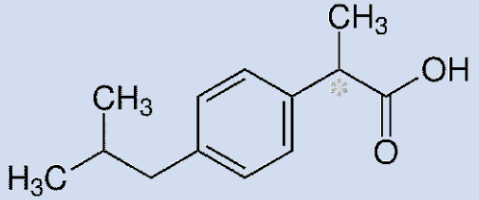
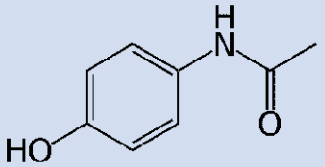
Bromide
Iodide

Ozone
Ozone/hlorine
UV-based tretatments

Aldehydes, ketoacids, ketones, carboxylic acids
Bromoform, monobromoacetic acid, dibromoacetic acid, dibromoacetone, cyanogen bromide

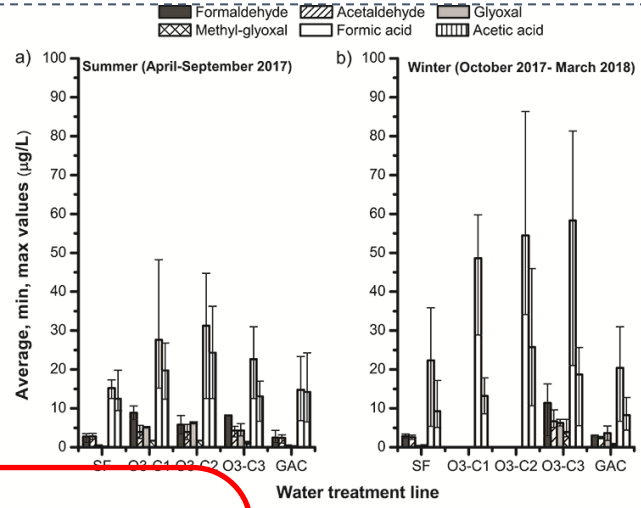
FARMACEUTICI KAO PREKURSORI EMERGENTNIH DBPs U PROCESIMA SA HLOROM

FARMACEUTICI	HEMIJSKA STRUKTURA	DEZINFE-KTANT	POTENCI-JALNI DBP
Enoksacin		ClO_2	HAA, HAN, THM, HK, HAL
Fleroksacin		hlor ili ClO_2	THM, HAA, HAN
Tetraciklini		hlor ili hloramin	TCM, DCAcAm, DCAN, TCM
Trimetoprim		UV/hlor	TCM, CH, DCAN, TCNM
Metronidazol		hloramin	TCM, DCAcAm, TCAcAm, DCAN

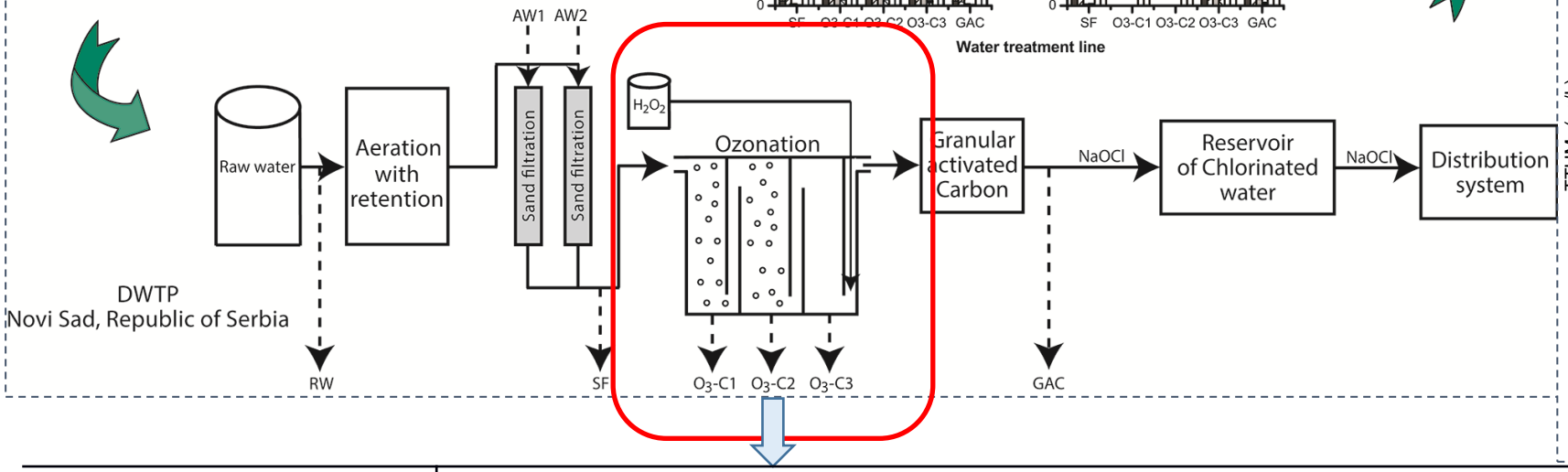
FARMACEUTICI	HEMIJSKA STRUKTURA	DEZINFE-KTANT	POTENCI-JALNI DBP
Hloramfenikol		UV/hlor	MCNM, DCNM, TCNM
Ibuprofen		UV/hlor	TCM, CH, 1,1,1-TCP, 1,1-DCP, DCAA, TCAA
Paracetamol		hloramin	TCM, DCAN, DCAcAm, TCAcAm
Karbamazepin		UV/hlor	TCM, DCAA, TCAA, DCAN, TCNM

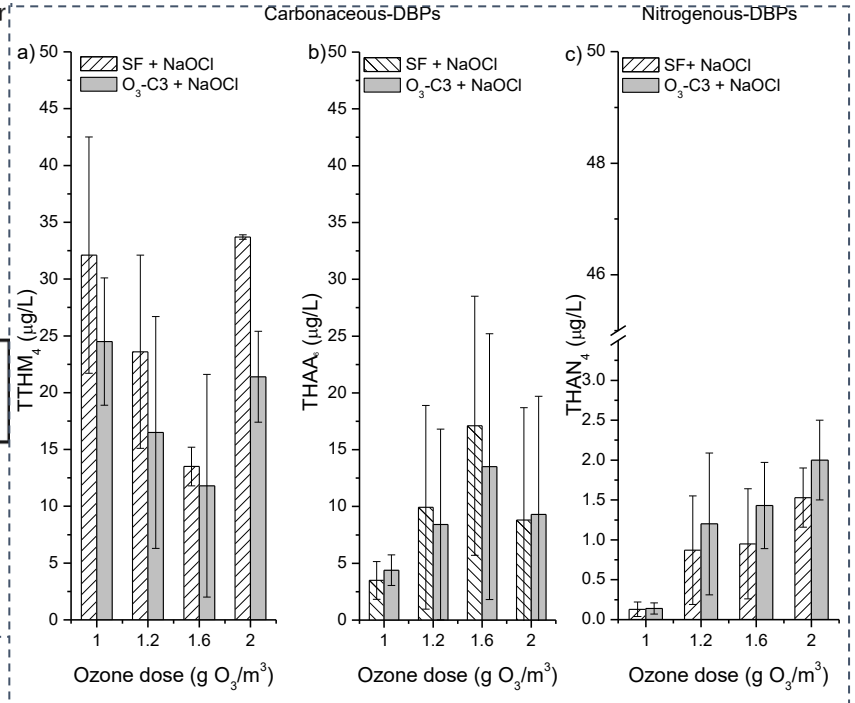
HAL-haloacetamidi; HAN-halonitrometani; TCM-hloroform; DCAcAm-dihloracetamid; TCAcAm-trihloracetamid

Primena ozona u tretmanu vode za piće



Fate of organic matter during DWTP





Ozone Catalytic decomposition of residual ozone with H_2O_2	Volume 900 m^3, two lines with three ozonation chambers each (first and second are for ozone dosing, third is for stabilisation), hydraulic retention time 15 min per line. Ozone dose 1-2 mg/l, gas phase distribution I chamber 60%, II chamber 40%. Ozone produced from LOX, and dosing as 10% gas phase. The equipment is produced by WEDECO (Germany).

ENVIRONMENTAL TECHNOLOGY
https://doi.org/10.1080/09593330.2020.1732474
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Fate of natural organic matter and oxidation/disinfection by-products formation at a full-scale drinking water treatment plant

Mladen Popov[a], Marijana Kragulj Isakovski[b], Jelena Molnar Jazić[b], Aleksandra Tubić[b], Malcolm Watson[b], Marina Šćiban[c] and Jasmina Agbaba[b]

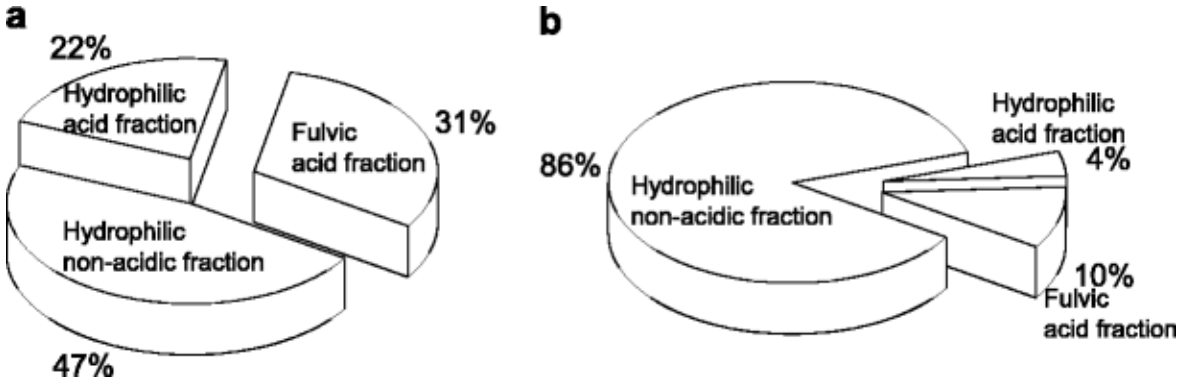
UTICAJ OZONIZACIJE NA STRUKTURU POM I FORMIRANJE EMERGENTNIH N-DBPs

Environ Sci Pollut Res (2012) 19:3079–3086
DOI 10.1007/s11356-012-0896-y
INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT IN ZURICH – ICCE 2011

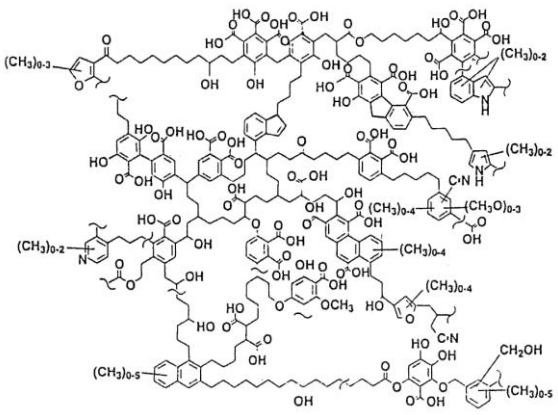
Influence of pH and ozone dose on the content and structure of haloacetic acid precursors in groundwater

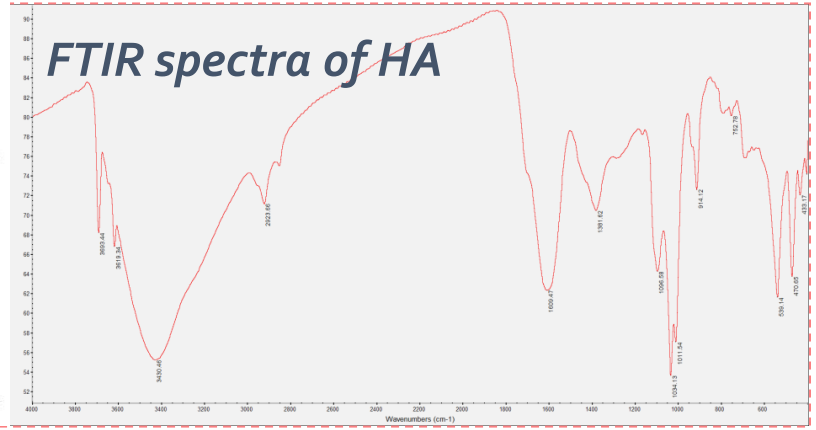
Jelena Molnar · Jasmina Agbaba · Božo Dalmacija · Srđan Rončević · Miljana Prica · Aleksandra Tubić

Raw groundwater: 9.85 ± 0.18 mg/L DOC (65% FAF, 14% HAF, hydrophilic NOM 21%)



Distribution of DOC in the natural organic matter fractions from the ozonated water at pH 7.5 (a) and pH 10 (b) (3 mg O_3/mg DOC)

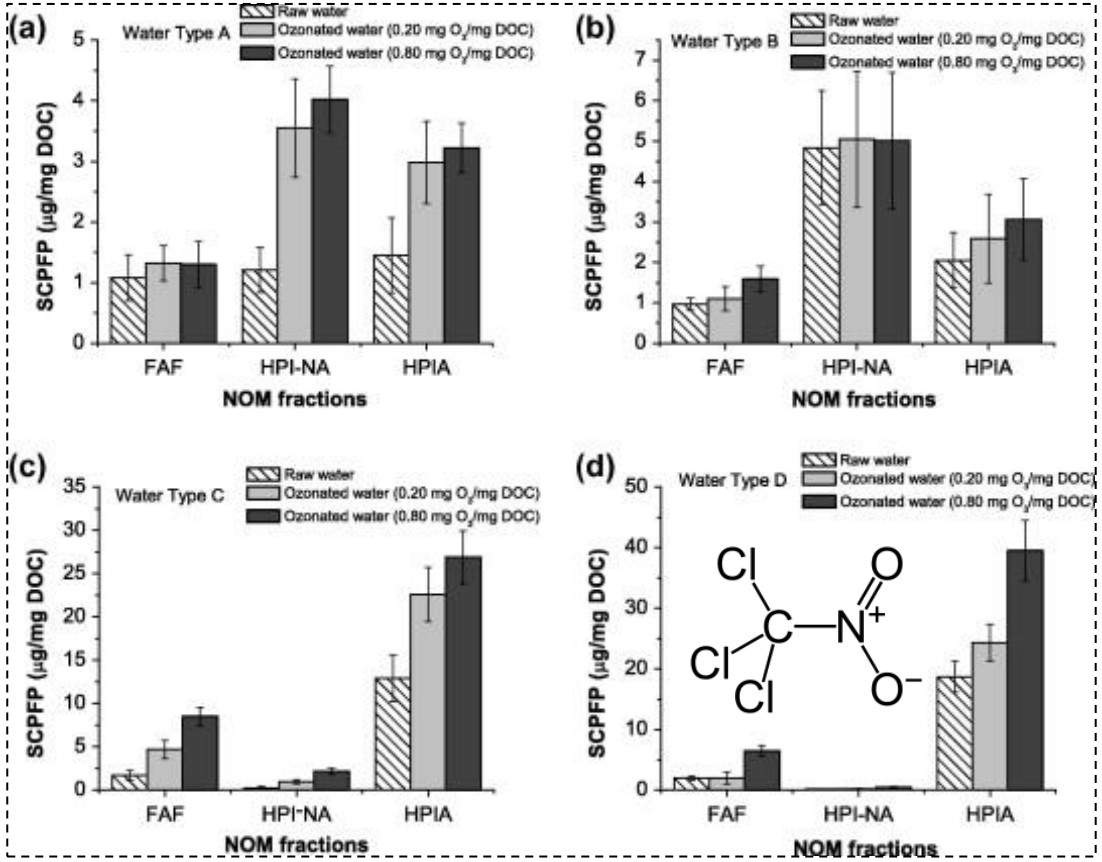




Chemical Engineering Journal 232 (2013) 435–443
Contents lists available at SciVerse ScienceDirect
Chemical Engineering Journal
journal homepage: www.elsevier.com/locate/cej

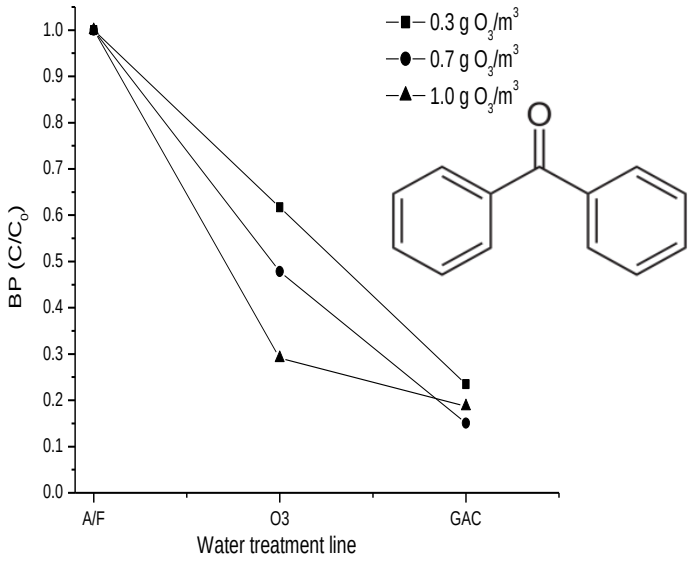
The effects of matrices and ozone dose on changes in the characteristics of natural organic matter

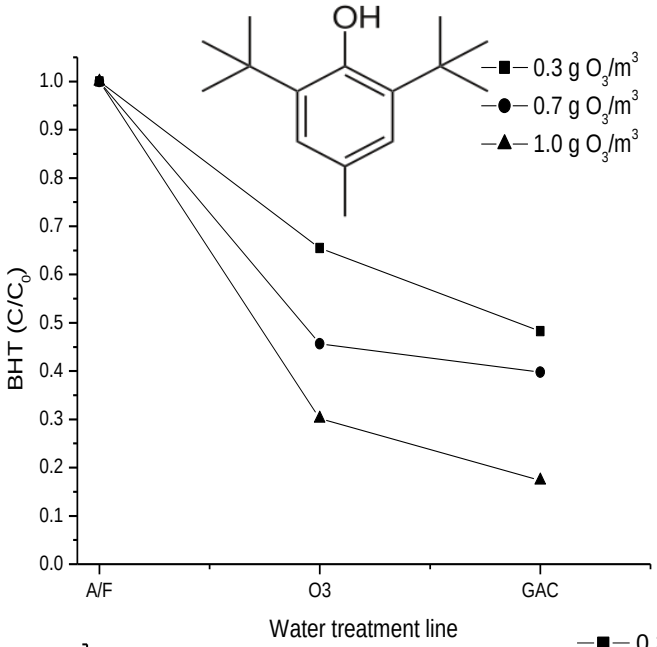
Jelena Molnar *, Jasmina Agbaba, Božo Dalmacija, Aleksandra Tubić, Dejan Krčmar, Snežana Maletić, Dragana Tomašević

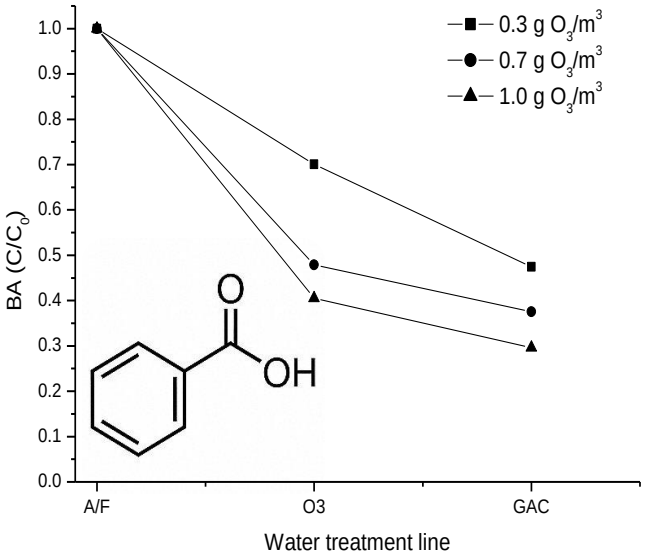


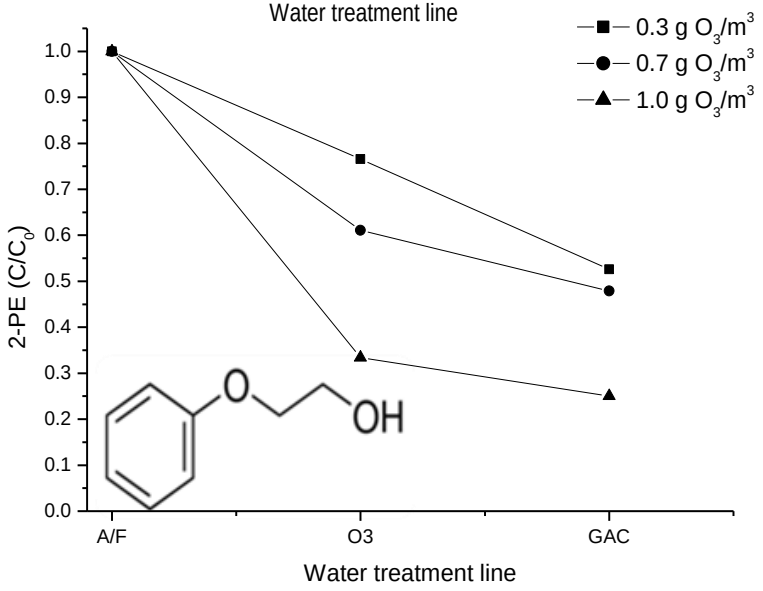
Chloropicrin precursors distribution in the NOM fractions of the raw and ozonated waters with different matrices

UKLANJANJE CECs IZ PODZEMNE VODE PRIMENOM OZONIZACIJE I GAU FILTRACIJE – ISTRAŽIVANJA NA PILOT POSTROJENJU









APTEFF, 51, 1-206 (2020)
DOI: https://doi.org/10.2298/APT2051009M
UDC: 582.998.2+581.48]:544.77.054.6:621.928
BIBLID: 1450-7188 (2020) 51, 9-15

Original scientific paper

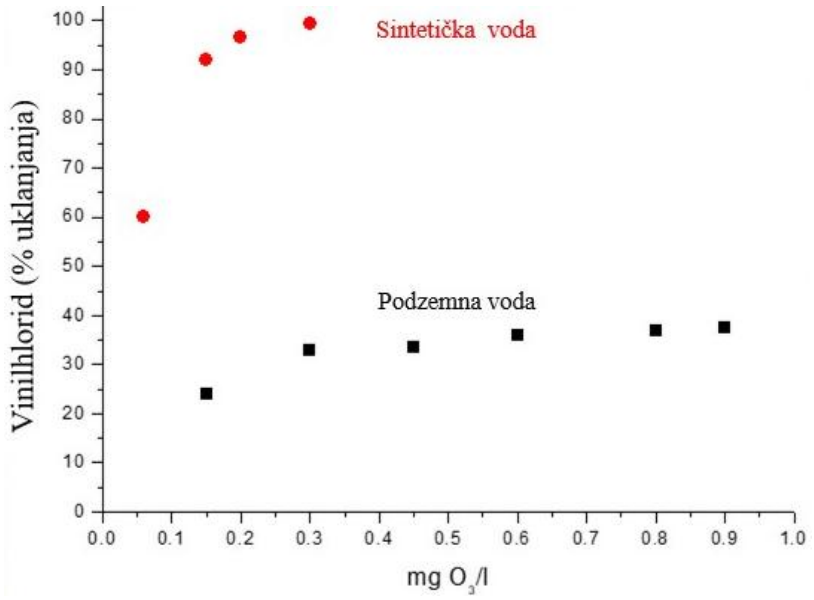
REMOVAL OF NATURAL ORGANIC MATTER AND EMERGING CONTAMINANTS FROM GROUNDWATER USING OZONATION AND GAC FILTRATION

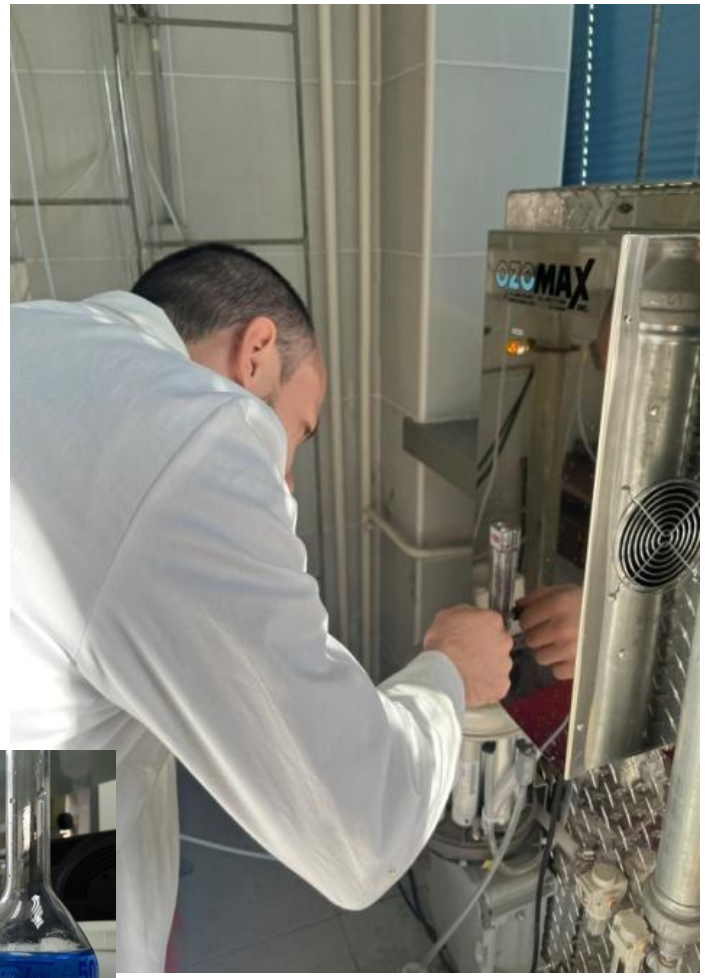
*Jelena J. Molnar Jazić, Marijana M. Kragulj Isakovski, Aleksandra M. Tubić, Tamara B. Apostolović, Malcolm A. Watson, Snežana P. Maletić, Jasmina R. Agbaba**

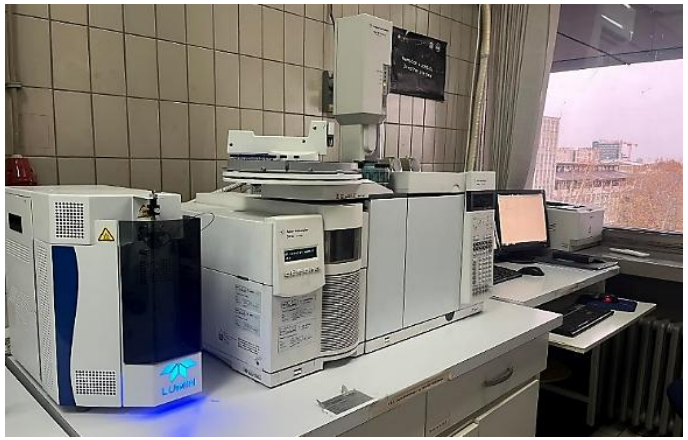
- 2 m^3/h; water flow through the ozonation column ~ 1300 L/h
- Electric ozone generator - 10 g/h
- 0.3-1.0 g O_3/m^3
- *Off*-ozone underwent destruction via AC
- Water flowing from the retention column was fed to the GAC adsorber

UKLANJANJE ISPARLJIVIH ORGANSKIH MATERIJA IZ PODZEMNE VODE PRIMENOM OZONIZACIJE

safewat

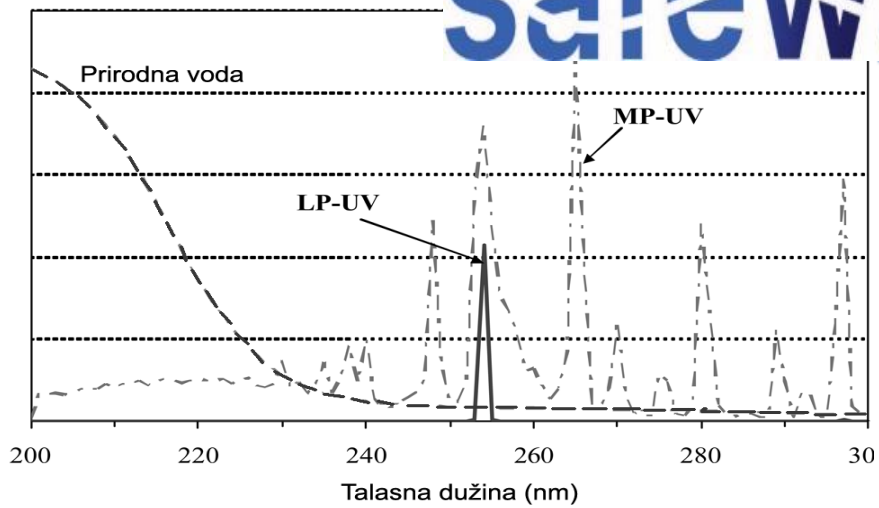




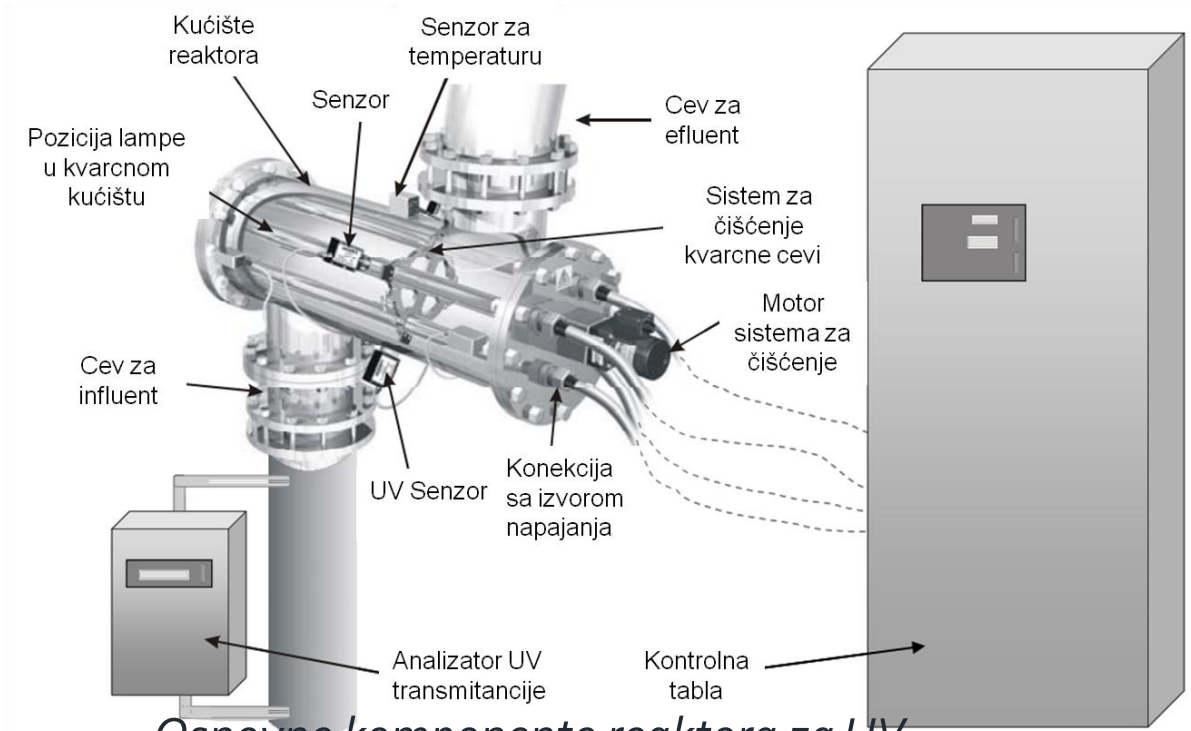


FOTOHEMIJSKI AOPS - UV TRETMAN VODE

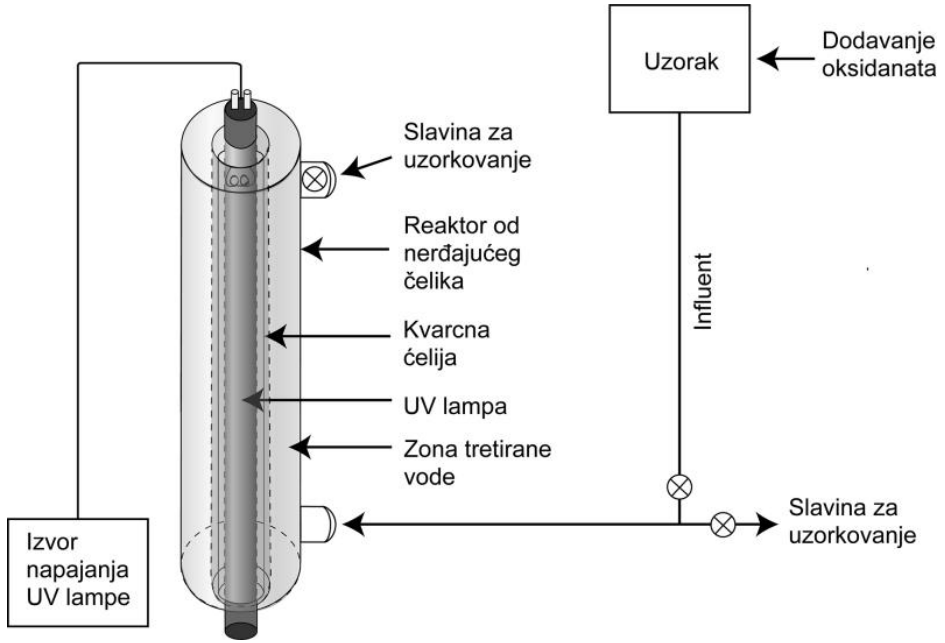
- Jednostavne i "čiste" tehnologije,
- isplative za brojne aplikacije,
- dezinfekcija vode;
- Monohromatski
- Polihromatski izvor zračenja



Emisioni spektar UV lampi niskog i srednjeg pritiska i apsorbancija prirodne vode (prevashodno prouzrokovana prisustvom POM i nitrata)



Osnovne komponente reaktora za UV tretman



PRIMENA UV AOPs U TRETMANU VODA – UKLANJANJE PESTICIDA ALAHLORA

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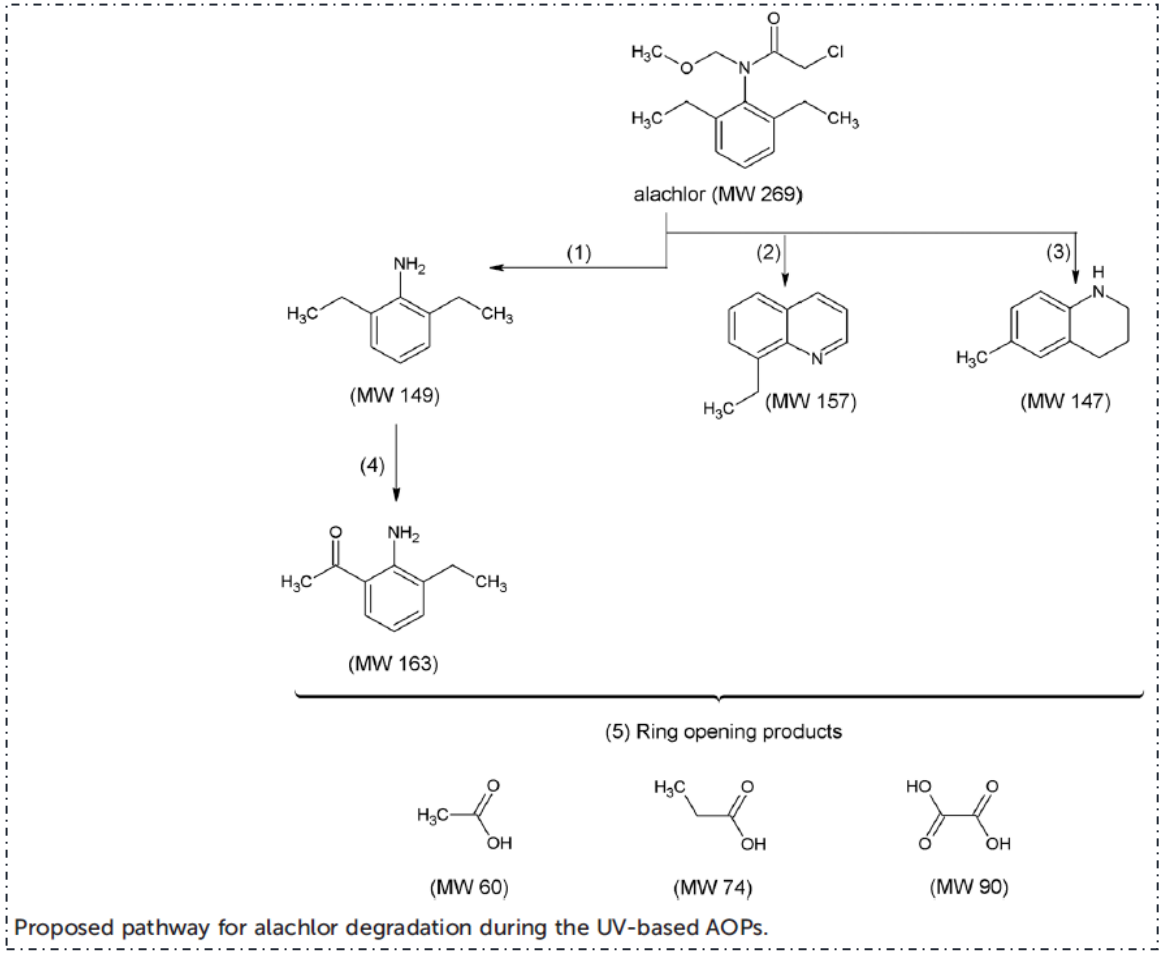
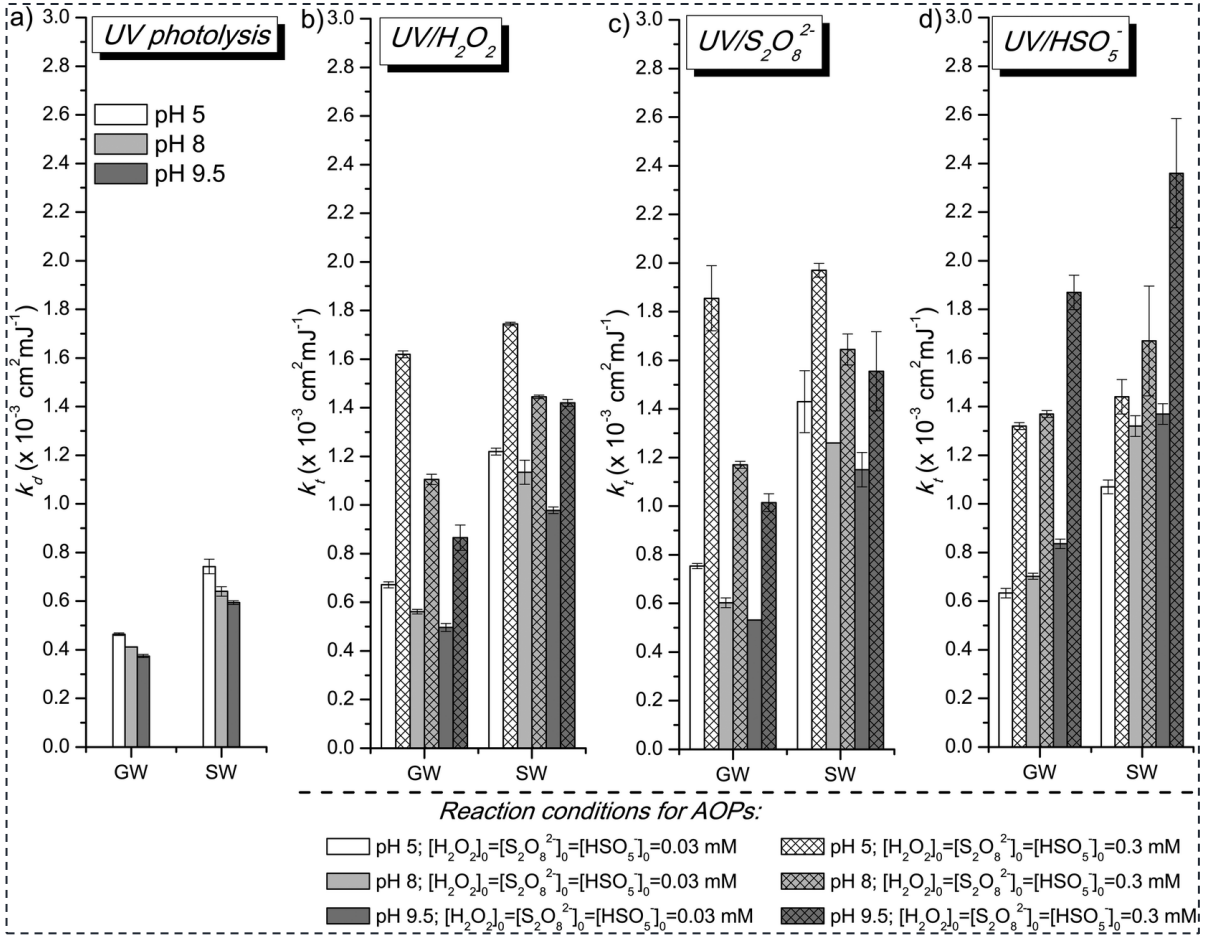
Degradation of a chloroacetanilide herbicide in natural waters using UV activated hydrogen peroxide, persulfate and peroxymonosulfate processes†

Jelena Molnar Jazić, *[a] Tajana Đurkić,*[a] Bojan Bašić,[b] Malcolm Watson,[a] Tamara Apostolović,[a] Aleksandra Tubić[a] and Jasmina Agbaba[a]



Proposed pathway for alachlor degradation during the UV-based AOPs.



Fluence-based pseudo first-order rate constants for alachlor degradation in groundwater and surface water using: (a) UV photolysis alone, and the (b) UV/H_2O_2, (c) UV/$S_2O_8^{2-}$ and (d) UV/HSO_5^- processes.

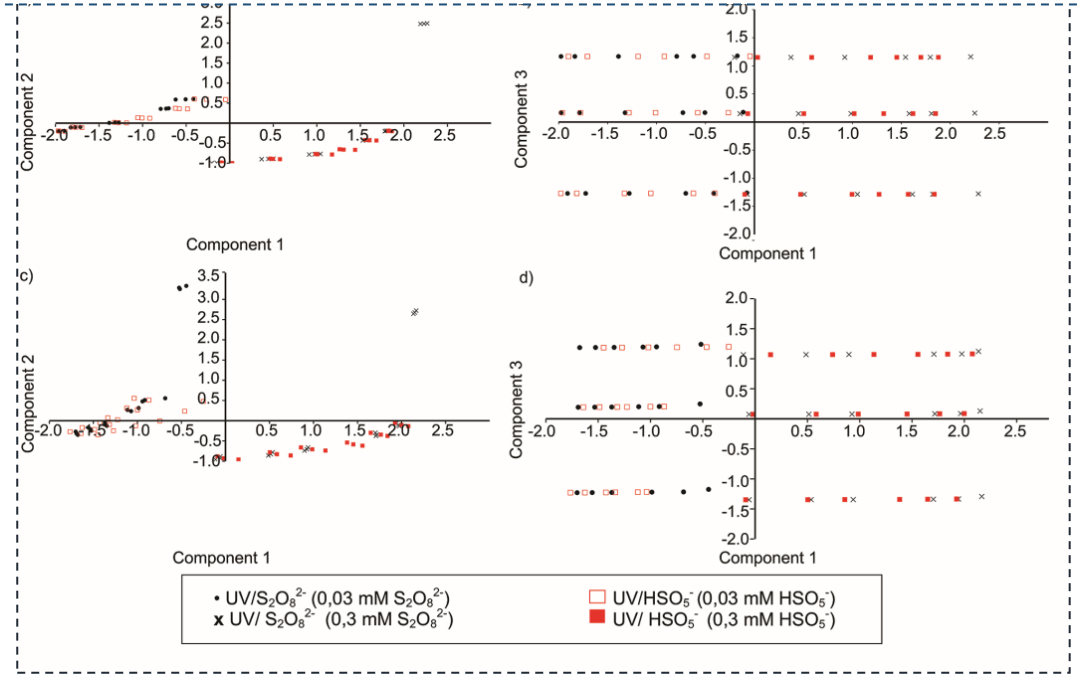
PRIMENA UV AOPs U TRETMANU VODA – UKLANJANJE INDUSTRIJSKIH HEMIKALIJA (1,2,3-TRIHLORBENZEN)

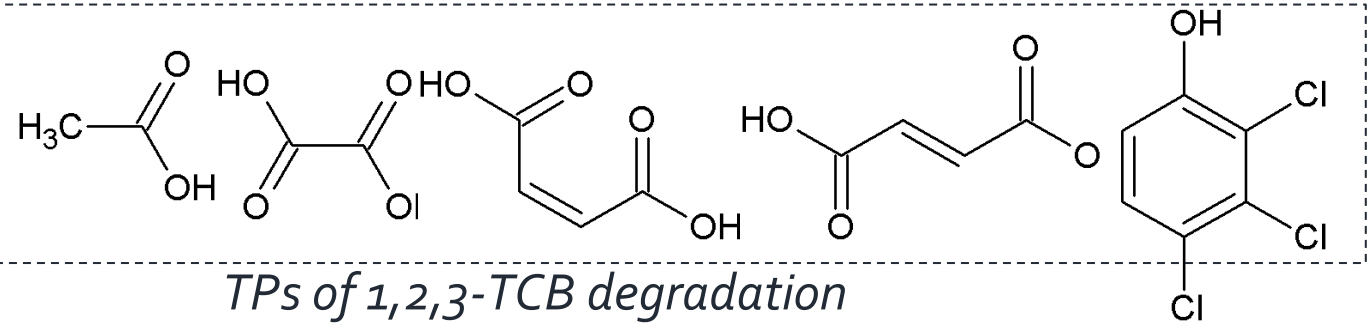
Environmental Science and Pollution Research (2021) 28:59165–59179
https://doi.org/10.1007/s11356-020-09787-w

RECENT DEVELOPMENTS AND INNOVATIVE STRATEGIES IN ENVIRONMENTAL SCIENCES IN EUROPE

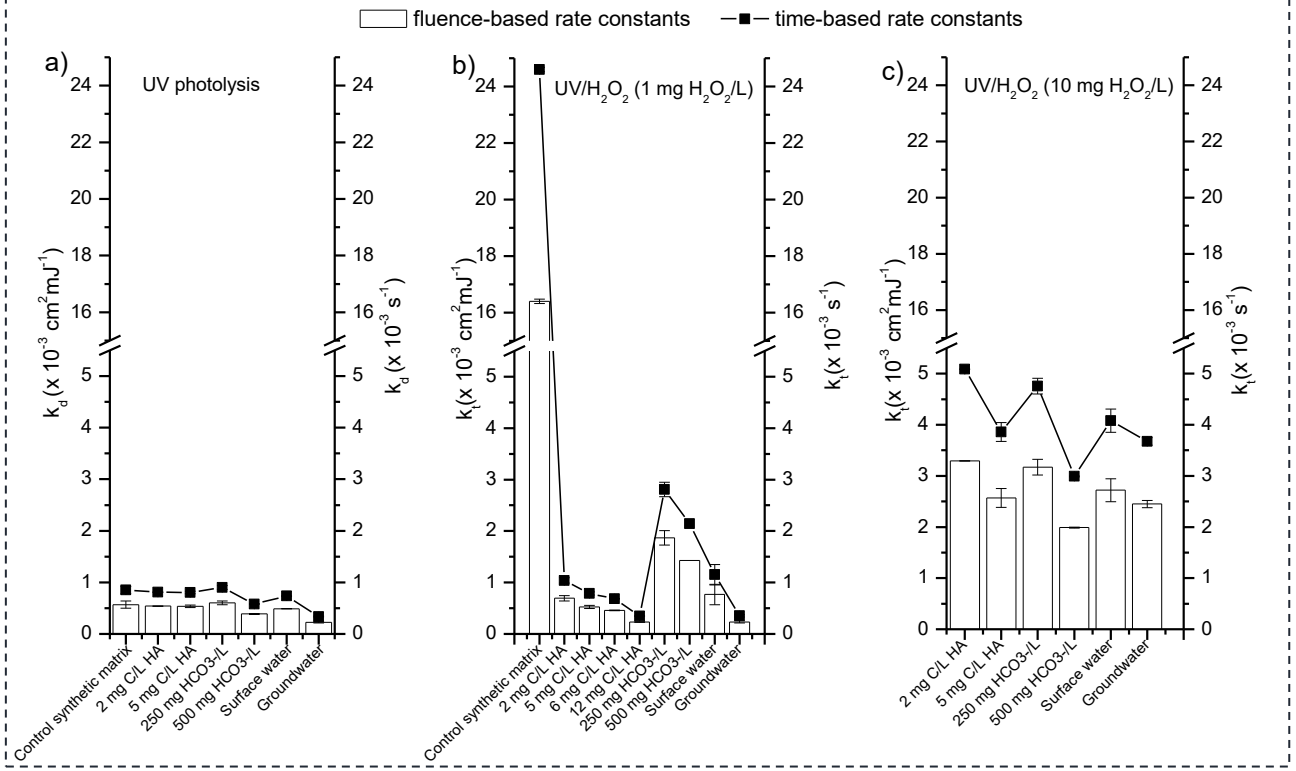
Application of UV-activated persulfate and peroxymonosulfate processes for the degradation of 1,2,3-trichlorobenzene in different water matrices

Tajana Đurkić[1] · Jelena Molnar Jazić[1] · Malcolm Watson[1] · Bojan Bašić[2] · Miljana Prica[3] · Aleksandra Tubić[1] · Snežana Maletić[1] · Jasmina Agbaba[1]





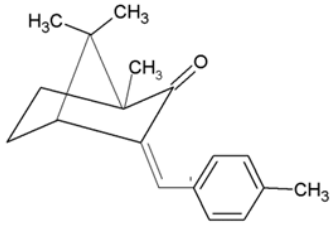
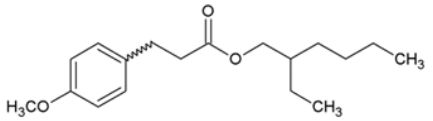
TPs of 1,2,3-TCB degradation



Fluence-based and time-based pseudo first-order rate constants for TCB degradation in synthetic and natural water matrices using: (a) UV photolysis, (b) UV/H2O2 (1 mg H2O2/L), and (c) UV/H2O2 (10 mg H2O2/L).

Đurkić, T., Molnar Jazić, J., Kragulj Isakovski, M., Maletić, S., Tubić, A., Dalmacija, B., Agbaba, J. (2019) Ultraviolet/Hydrogen Peroxide Oxidative Degradation of 1,2,3-Trichlorobenzene: Influence of Water Matrix and Toxicity Assessment. Environmental Engineering Science, 36(8), 947-957.

PRIMENA UV AOPs U TRETMANU VODA – UKLANJANJE SASTOJAKA KREMA ZA SUNČANJE – UV FILTERI

Compound	Information		Chemical Structure *
4-MBC [1]	Molecular formula:	$C_{18}H_{22}O$	
	Molecular weight:	254.37 g/mol	
	Density:	1.064 ± 0.06 g/cm³	
	logK$_{OTW}$:	5.92	
	Boiling point:	357 °C	
	Solubility in water:	1.3 mg/L at 20 °C	
	Vapor pressure:	1.0×10^{-3} Pa at 25 °C	
EHMC [2]	Molecular formula:	$C_{18}H_{26}O_3$	
	Molecular weight:	290.40 g/mol	
	Density:	1.005 ± 0.07 g/cm³	
	logK$_{OTW}$:	6.01	
	Boiling point:	193 °C	
	Solubility in water:	0.2 mg/L at 20 °C	
	Vapor pressure:	1.38×10^{-5} Pa at 25 °C	

* Data from ACD/ChemSketch; [1] reference [48]; [2] reference [49].

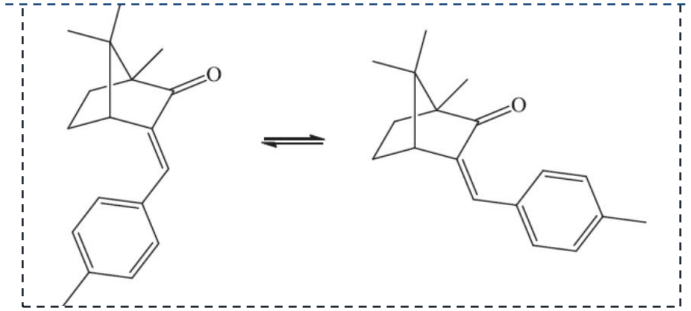
processes

MDPI

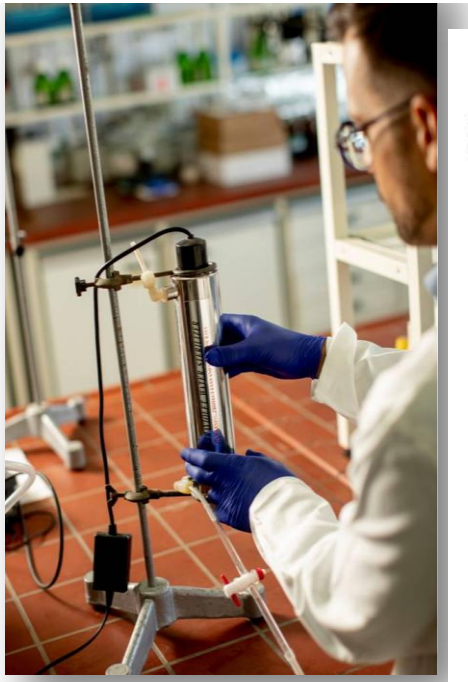
Article

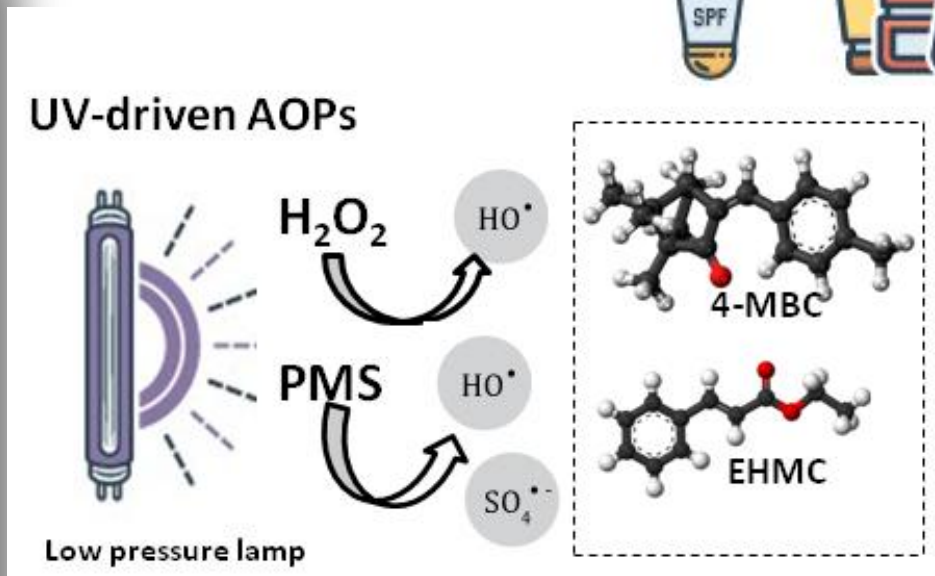
New Insight into the Degradation of Sunscreen Agents in Water Treatment Using UV-Driven Advanced Oxidation Processes

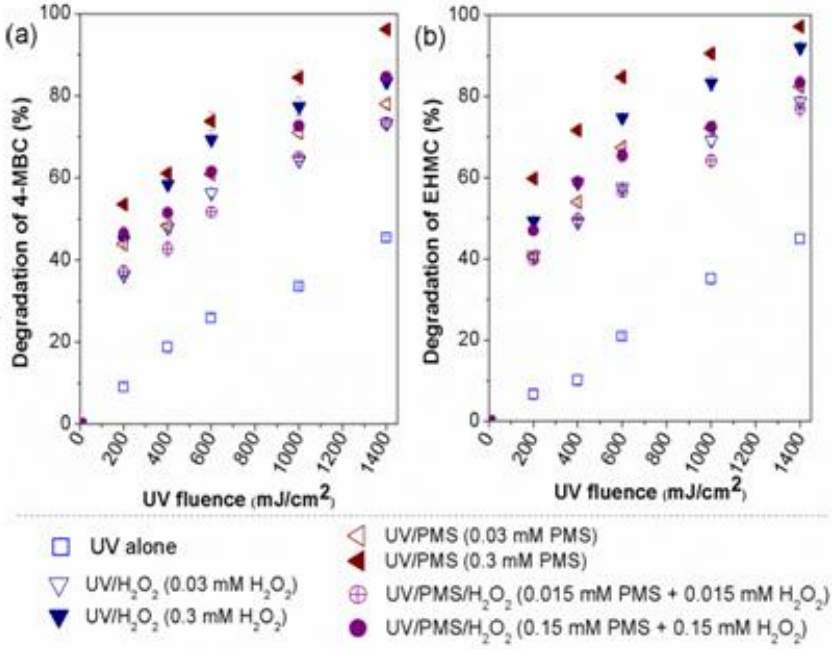
Tajana Simetić, Jasmina Nikić, Marija Kuč, Dragana Tamindžija, Aleksandra Tubić, Jasmina Agbaba and Jelena Molnar Jazić *



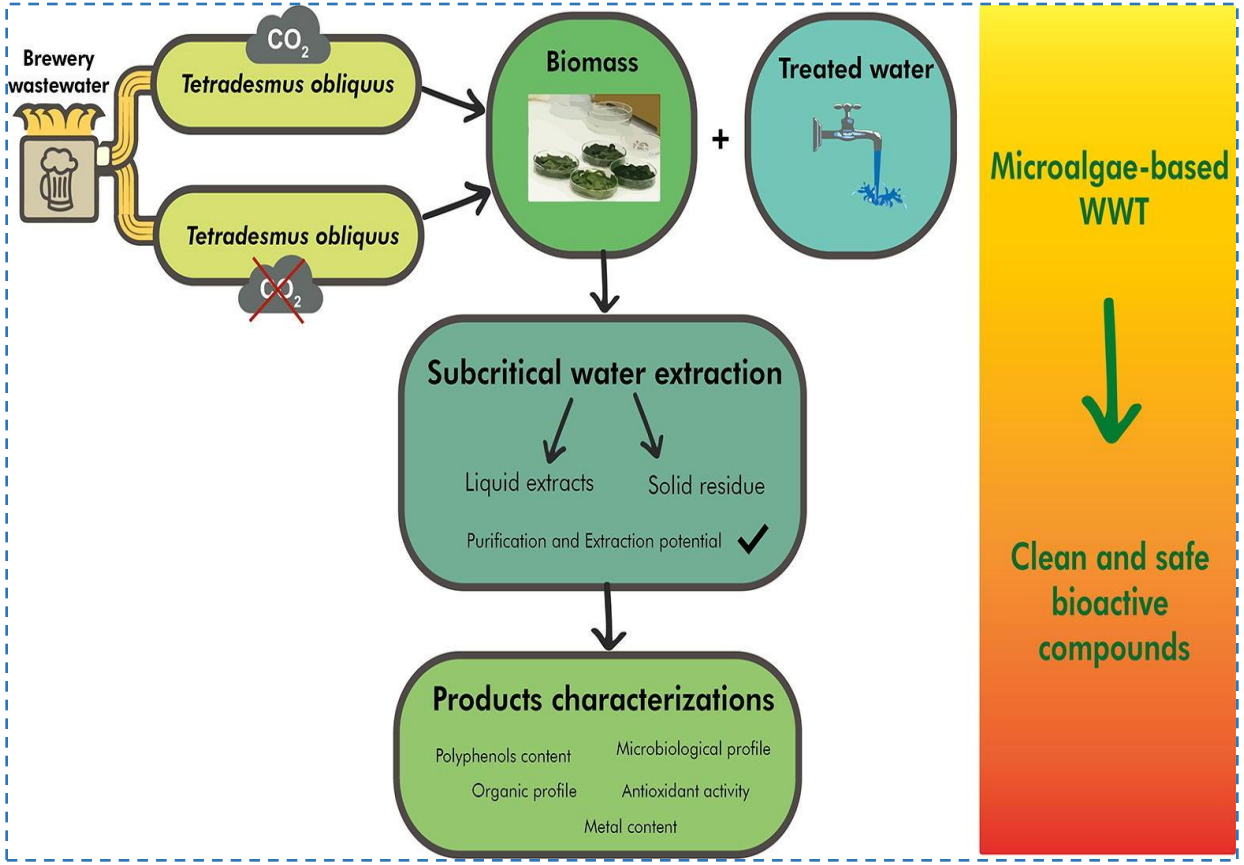
E-izomer *Z*-izomer

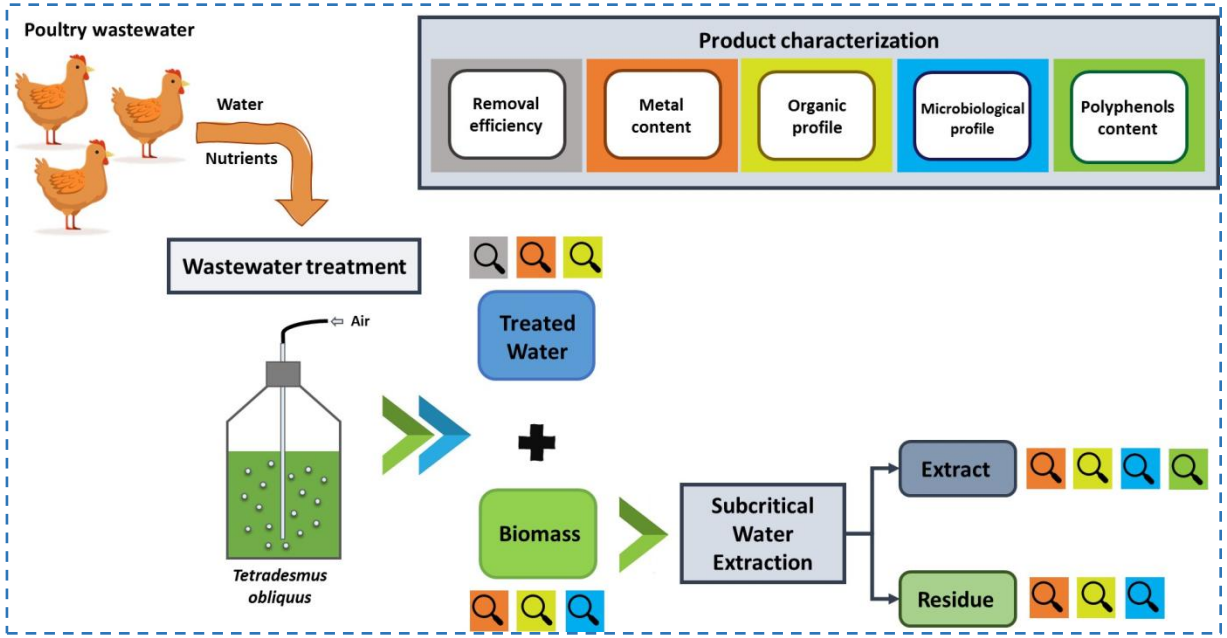






AOPs kao predtretman otpadne vode mikroalgama i valorizacija biomase





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Chemical Engineering Journal

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

Valorisation of microalga *Tetradesmus obliquus* grown in brewery wastewater using subcritical water extraction towards zero waste

Alice Ferreira [a], Jelena Molnar Jazić [b], Luisa Gouveia [a,c], Snežana Maletić [b], Milan Tomić [d], Jasmina Agbaba [b], Jelena Vladić [e,*]

molecules

MDPI

Article

Application of Green Technology to Extract Clean and Safe Bioactive Compounds from *Tetradesmus obliquus* Biomass Grown in Poultry Wastewater

Jelena Vladić [1], Jelena Molnar Jazić [2], Alice Ferreira [3], Snežana Maletić [2], Dragoljub Cvetković [1], Jasmina Agbaba [2], Senka Vidović [1] and Luisa Gouveia [3,4,*]

Валоризација биомасе микроалги добијене у третману пречишћавања отпадних вода (142-451-2576/2019-01) 2019-2020. Покрајински секретаријат за високо образовање и научноистраживачку делатност.

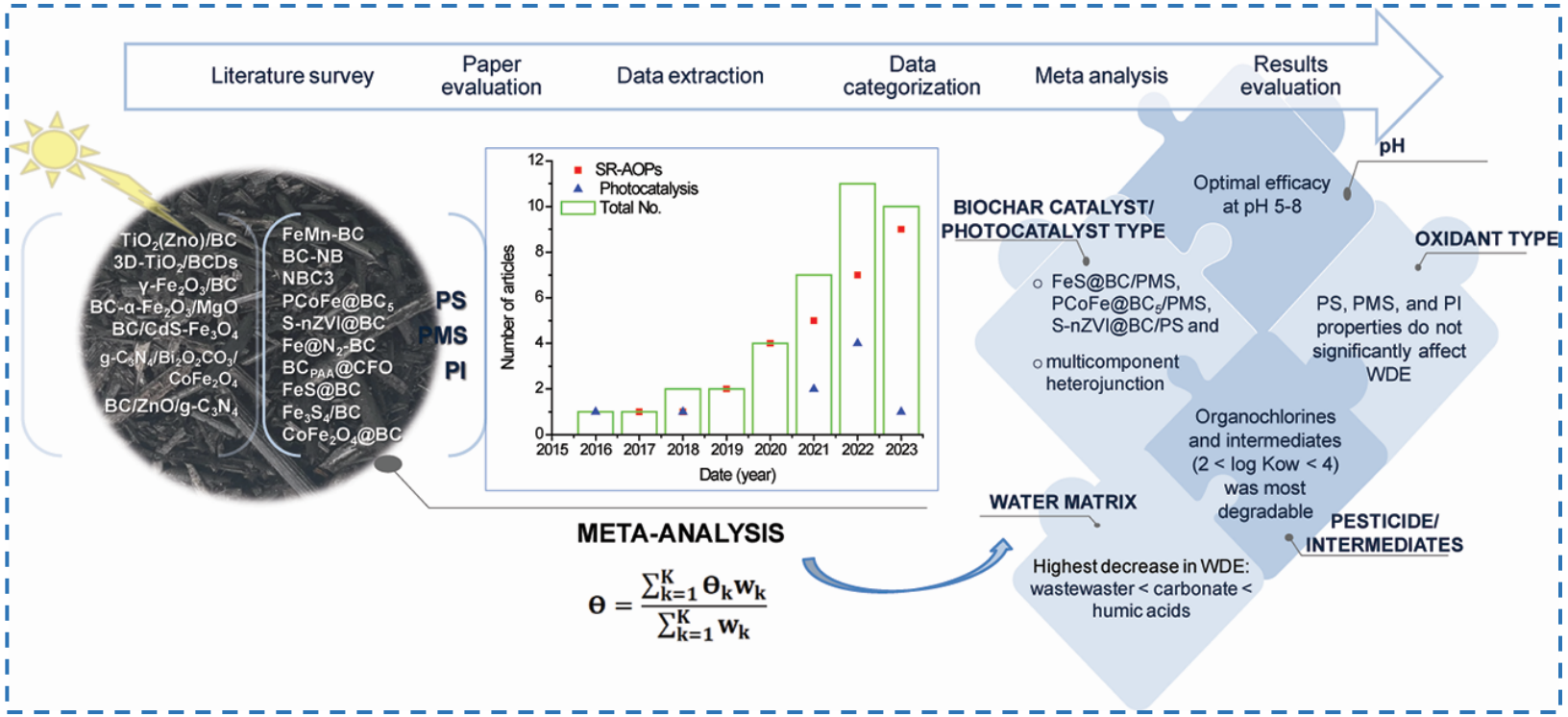
Biougalj kao katalizator za SR-AOPs i fotokatalizu u tretmanu voda

Journal of Environmental Chemical Engineering

Boosting advanced oxidation processes by biochar-based catalysts to mitigate pesticides and their metabolites in water treatment: a meta-analysis

--Manuscript Draft--

Jelena Molnar Jazić, Arthur Gross, Bruno Glaser, Jasmina Agbaba, Tajana Simetić, Jasmina Nikića, Snežana Maletić



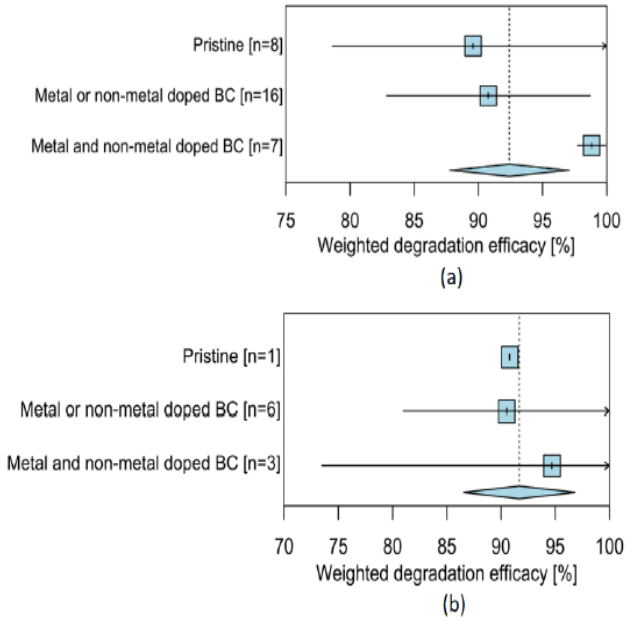
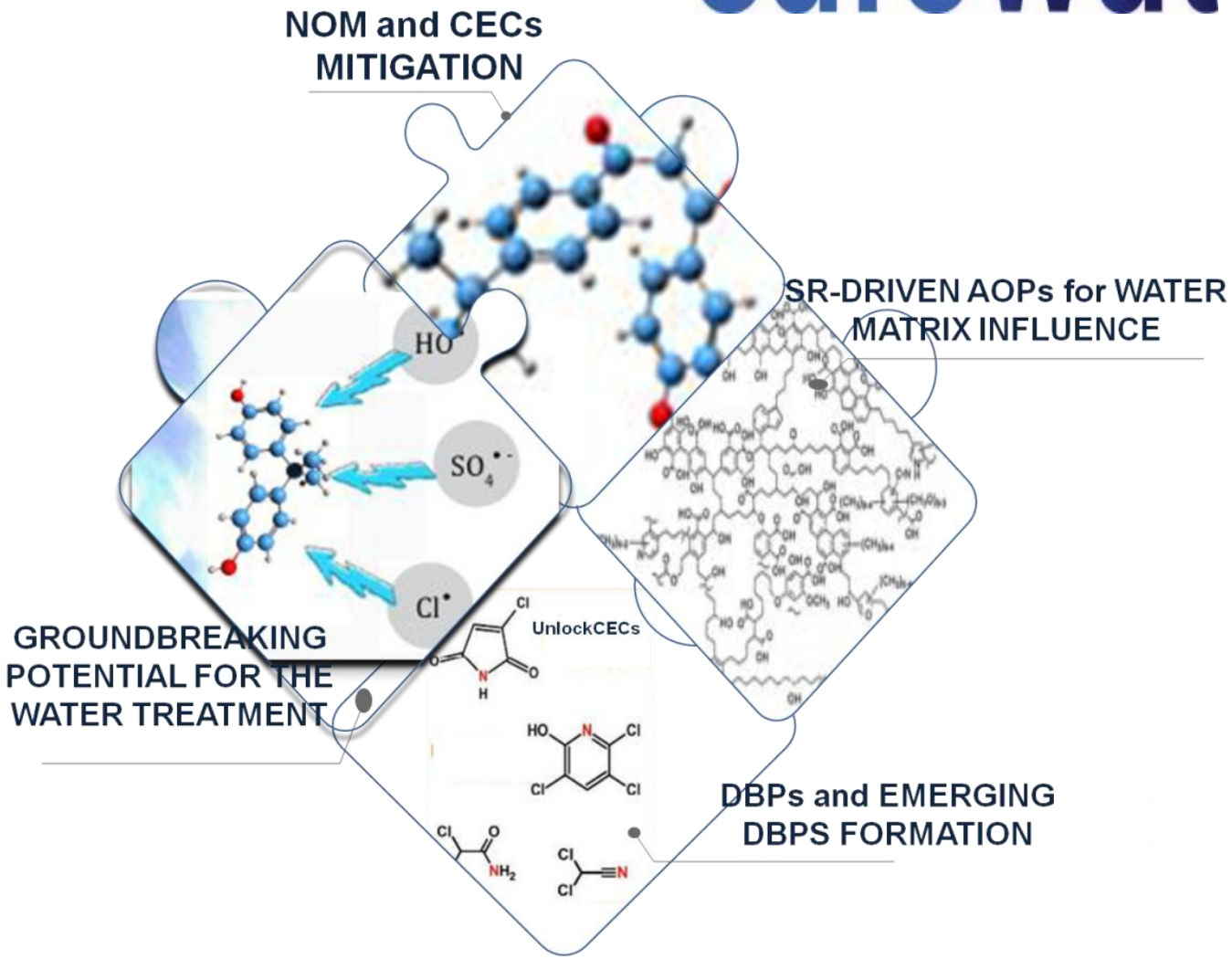


Figure 3. Forest plot of the effects of the catalyst type on weighted efficacy of pesticide/intermediate compounds degradation during the (a) SR-AOPs and PI-AOPs and (b) photocatalysis, based on the random effects model (CI = 95%) of the average effect size. The vertical black dotted line represents the mean overall degradation efficacy (%) per category. Blue squares indicate the mean degradation efficacy per subgroup. Each effect size is presented as the range between the upper and lower 95% confidence interval. The extend of the blue rectangle represents the confidence interval of the overall degradation efficacy. Group category names are presented on the y-axis black letters. The number of included treatments is given in brackets.

Zaključak

- AOPs se efikasno primenjuju u tretmanu voda za oksidaciju POM i oksidativnu razgradnju/uklanjanje organskih mikropolutanata.
- SR-AOPs kao alternativa konvencionalnijim HR-AOPs, omogućavaju prevazilaženje izazova usled efekata matriksa.
- Pažnja treba da bude usmerena na praćenje sporednih nusprodukata oksidativne razgradnje i DBPs tokom dezinfekcije i merama za ublažavanje ovih rizika.



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