QUATERNARY TREATMENT OF MUNICIPAL WASTEWATERS TARGETING CECs REMOVAL: NANOFILTRATION *vs* OZONATION

Vítor J.P. Vilar

vilar@fe.up.pt

08th November 2024

ALiCE ASSOCIATE LABORATORY IN CHEMICAL ENGINEERING

SRE CM LABORATORY OF SEPARATION AND REACTION ENGINEERING
LABORATORY OF CATALYSIS AND MATERIALS

U.PORTO FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

Interreg España – Portugal

Cofinanciado por la Unión Europea
Cofinanciado pela União Europeia

blue water

INTRODUCTION

New EU Directive on Urban Wastewater Treatment
Revised Regulation, Renewed Challenges

Wastewater treatment

- Obligation to **all UWWTPs** treating a load ≥ 150 000 p.e. to **apply quaternary treatment by 2045,** in order to **eliminate the broadest possible spectrum of micro-pollutants**.
- Promote the **reuse of treated wastewater** from all urban wastewater treatment plants **where appropriate**.

Energy neutrality and renewables

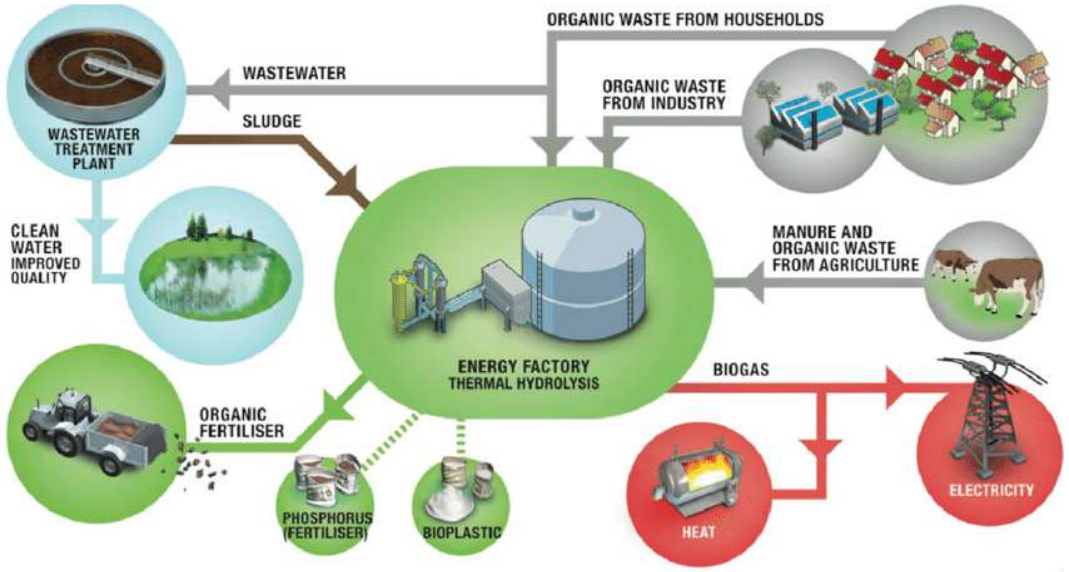
- Introduce an **energy neutrality target**, meaning that **by 2045** urban wastewater treatment plants will have to produce the energy they consume, with progressive intermediate targets.

Wastewater surveillance and risk assessment

- Obligation **to monitor health parameters in urban wastewaters** to track the presence of **pathogens responsible for human diseases and pandemics**, and **PFAS, Microplastics, Antimicrobial Resistance, and Greenhouse Gases.**

INTRODUCTION

- Although the original goal of wastewater treatment was to protect water quality, today scarcity of resources and sustainability are driving major global changes
- The **N-E-W Paradigm** focuses on **Recovering Resources** such as **Nutrients**, **Energy** and **Water**, towards a **Circular and Self-Sufficient Bio-Based Economy**



NEW GENERATION OF SUSTAINABLE WWTPs

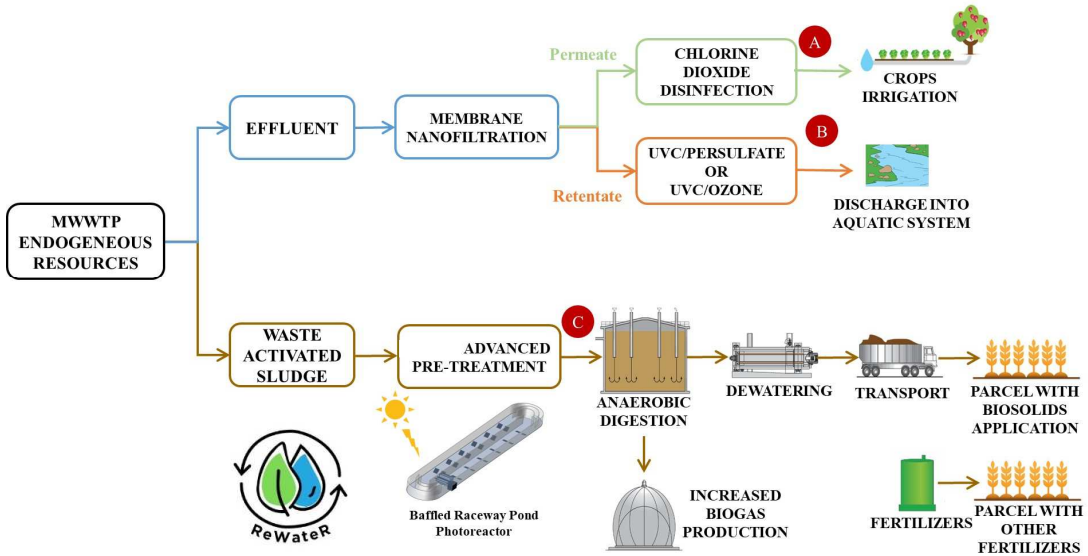
WWTPs 2.0

SERPIC AND HEALTHYWATERS PROJECTS

Integration of Nanofiltration and Advanced Oxidation Technology for Urban Wastewater Resources Recovery

SERPIC HealthyWaters

https://www.serpic-project.eu/



Objectives

Endogenous resources recovery from UWWTPs to:

- Support agricultural practices by **reusing the effluent for crops irrigation**;
- **Increase energy self-generation** by **enhancing biogas quality and production from anaerobic digestion**.

Research Team

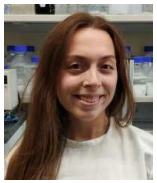

Vítor Vilar


F. Moreira


A. Gomes


C. Cruzeiro


J. Monteiro


C. Santos


A. Olivera

Partners

Fraunhofer IST; SolarSpring membrane solutions; Águas de Portugal; NIVA Norsk institutt for vannforskning Norwegian Institute for Water Research; Università degli Studi di Ferrara; UCLM; U.PORTO FEUP Faculdade de Engenharia Universidade do Porto; efacec

Selection of indicator contaminants of emerging concern when reusing reclaimed water for irrigation — A proposed methodology
Science of the Total Environment, 873 (2023) 162359
https://doi.org/10.1016/j.scitotenv.2023.162359

ALiCE SRE CM

SERPIC PLANT

Electricity and control

Membrane Photoreactor

Nanofiltration unit

Ozone Electrolyser

Persulfate Electrolyser

SERPIC PLANT - NANOFILTRATION UNIT

METHODOLOGY

Producer and brand name	MWCO [Da]	Membrane ID	Membrane type	Membrane material
SUEZ/GE, PW	10 000	NF#9	FS	Polyethersulfone
Alfa Laval, UFX-10pHt	10 000	NF#8	FS	Polysulphone
SUEZ/GE, GE	1 000	NF#7	FS	Polyamide
Pentair, HFW	1 000	NF#6	HF	Polyethersulfone
NX Filtration, dNF80	800	NF#5	HF	Polyethersulfone
DuPont NF270	200-400	NF#1	FS	Polyamide
SUEZ/GE, DL	250	NF#2	FS	Polyamide
SUEZ/GE, DK	150-300	NF#4	FS	Polyamide
Toray, TM600	150	NF#3	FS	Polyamide
Toray, TMH	100-150	NF#10	FS	Polyamide

MWCO – molecular weight cut off [Da] **FS** - Flat sheet **HF** – Hollow fibre

Effectiveness for rejection of genetic marker, representing a microbial CEC

Effectiveness in separating nutrients (TP, TN, K, Ca, Mg, NH_4^+, NO_3^-) from WWTP effluent

Effectiveness in separating selected chemical CECs (DCF, SMX e VLX)

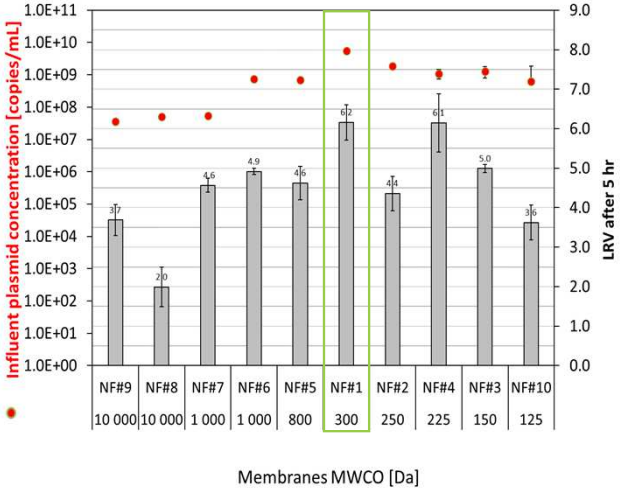
Effectiveness in separating antibiotic resistant bacteria (ARB) (*E. coli*) and sul1 ARG marker.

RESULTS – MEMBRANE SELECTION

Membrane supplier and product type	Membrane ID	ARB	ARG	Nutrients	Organic CECs
		E. coli	sul1	TN, TP, K, Ca, Mg	DCF, SMX, VLX
		% of rejection	LRV	% of rejection	% of rejection
DuPont, NF270	NF#1	100	6.2	17, 91, NM•, NM, NM	NM, NM, NM, 79*
Toray, TM600	NF#3	100	2.0	12, 96, 32, 68, 76	88, 85, 89
SUEZ/GE, DK	NF#4	100	2.2	11, 76, 25, 34, 29	44, 43, 41
NX Filtration, dNF80	NF#5	100	3.0	10, 90, 19, 37, 32	61, 65, 72
Pentair, HFW	NF#6	100	2.1	9, 74, 9, 37, 32	28, 33, 37

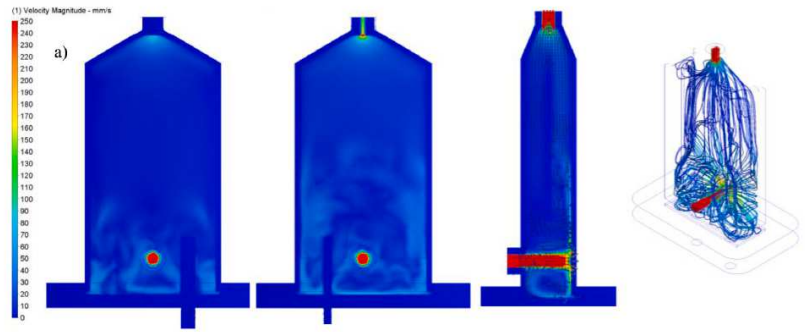
• NM - Not measured

* average removal of the 11 CECs (DEET, BP3, OC, EHMC, UV-329, HHCB, AHTN, TCPP, TCEP, DBPP, TBP).



The NF#1 (DuPont NF270, NANO7-XL-1812, Oltremare) membrane provided > 6 LRV for ARG, >70 % retention of TN, and app. 80 % rejection of chemical CECs, and it was compatible with the pilot unit and readily available.

SERPIC PLANT - OZONE ELECTROLYZER

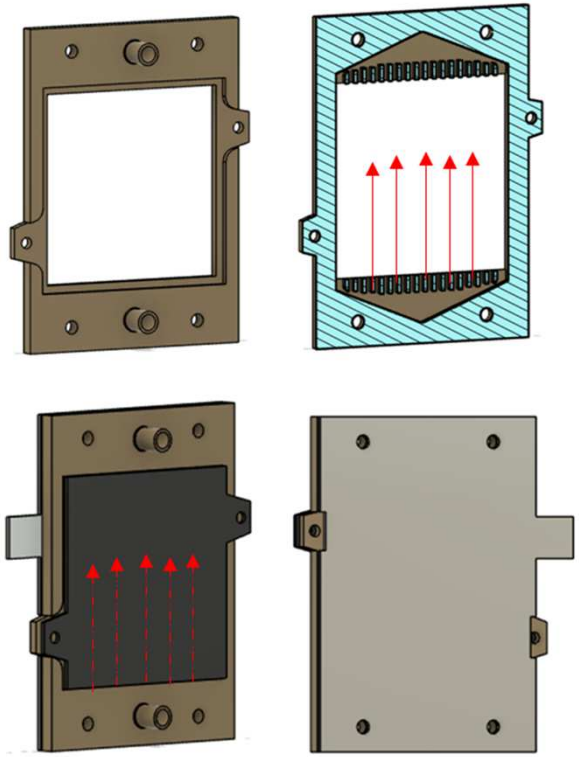


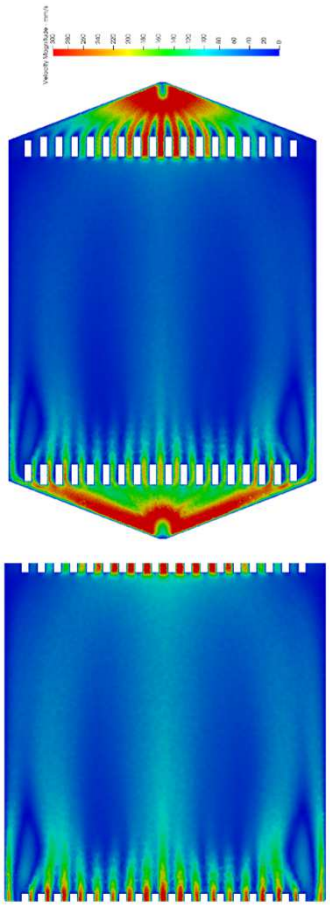
Production: 500 mg O_3/h
Current Efficiency = 6%
330 mA/cm^2

MEA – Membrane Electrode Assembly
2 DIACHEM® lattice BDD electrodes
NAFION® proton exchange membrane
Electrolyte 1mM $HClO_4$; 25 °C

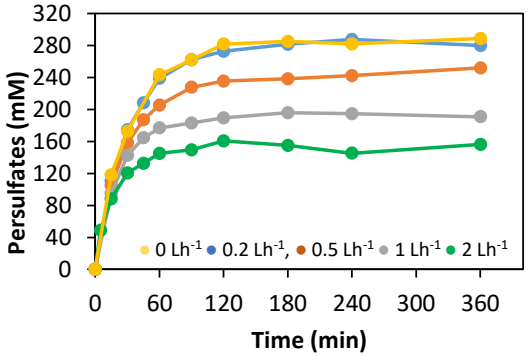
Improving performance of proton-exchange membrane (PEM) electro-ozonizers using 3D printing
Chemical Engineering Journal, 464 (2023) 142688
https://doi.org/10.1016/j.cej.2023.142688

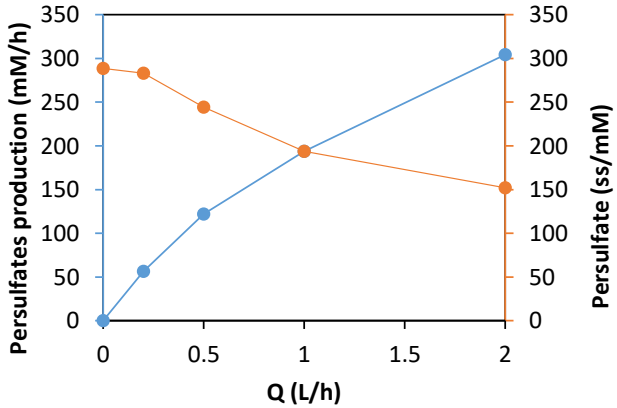
SERPIC PLANT – PERSULFATE ELECTROLYZER





BDD anode
SS cathode

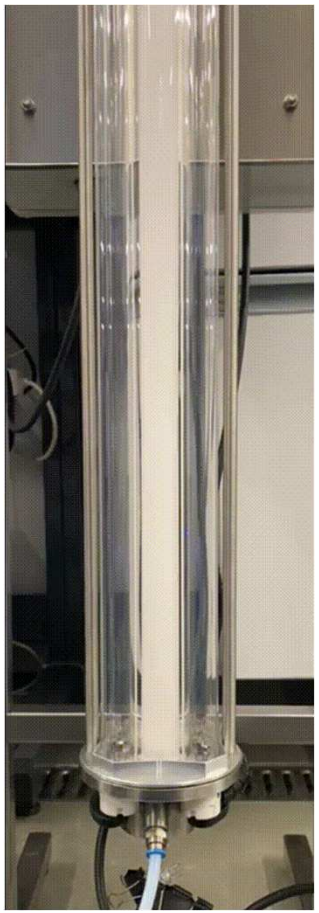




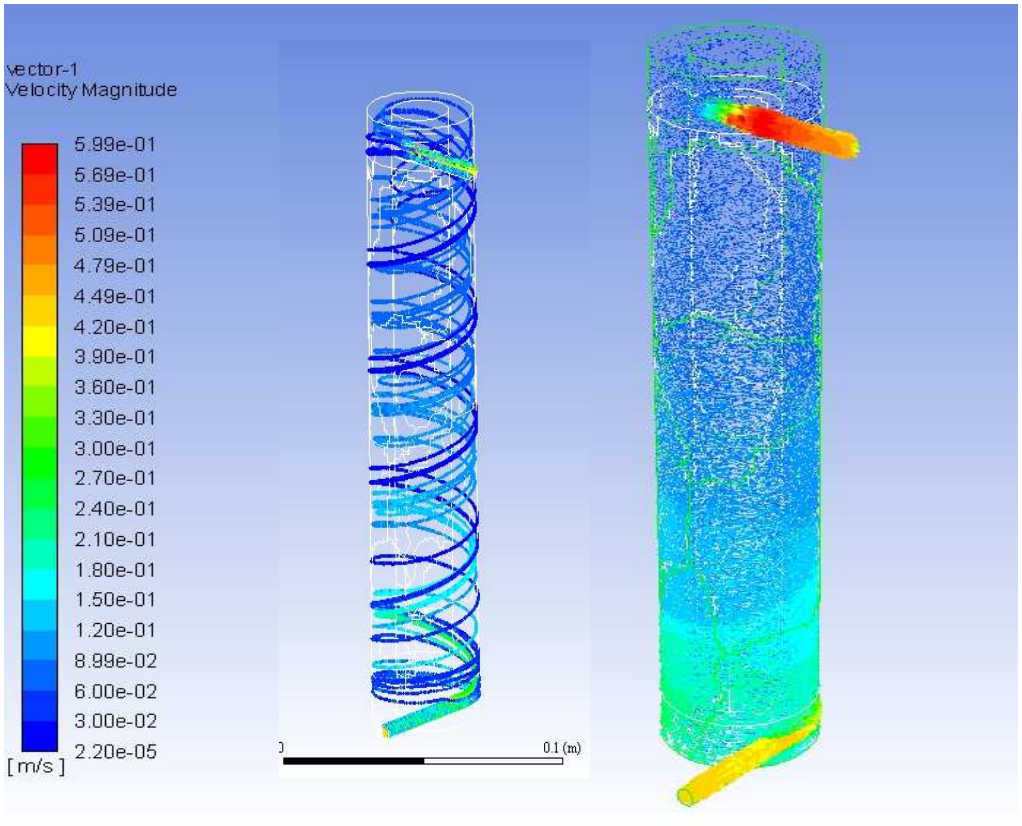
Electrolyte 1M H_2SO_4, 300 $mAcm^{-2}$, 25ºC
Current efficiency = 57%

Outstanding productions of peroxymonosulfuric acid combining tailored electrode coating and 3D printing
Journal of Water Process Engineering, 53 (2023) 103902
https://doi.org/10.1016/j.jwpe.2023.103902

SERPIC PLANT – MEMBRANE PHOTOREACTOR



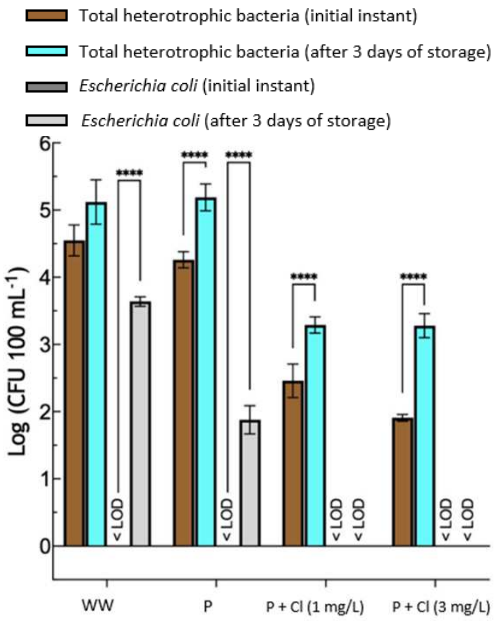
VELOCITY FIELD – FLOW PATTERN



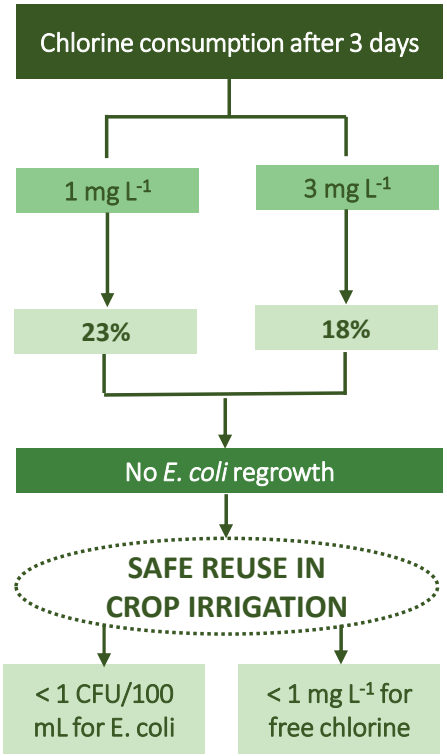
DISINFECTION OF NF PERMEATE

POTENTIAL REUSE OF NANOFILTRATION PERMEATE

Regrowth of *E. coli*

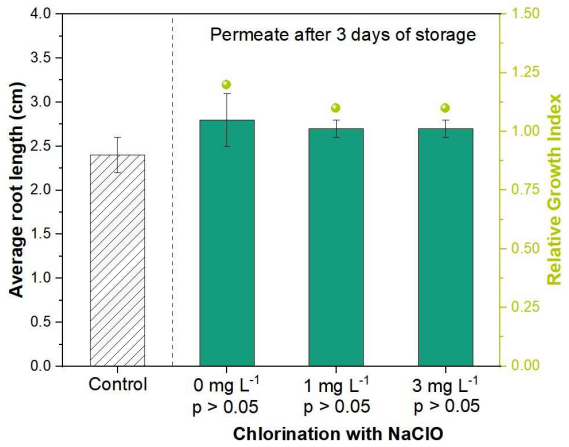


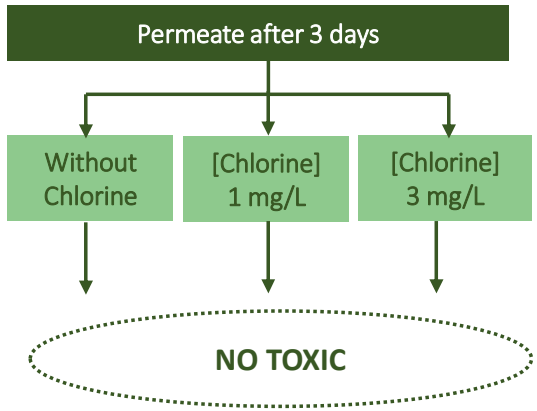
WW – Wastewater
P – Permeate
P + Cl (1 mg/L) – Permeate + disinfection by chlorine at 1 mg/L
P + Cl (3 mg/L) – Permeate + disinfection by chlorine at 3 mg/L
*** - Statistically different samples (p < 0.05)



Phytotoxicity Tests

Lactuca sativa seeds
after 3-day storage

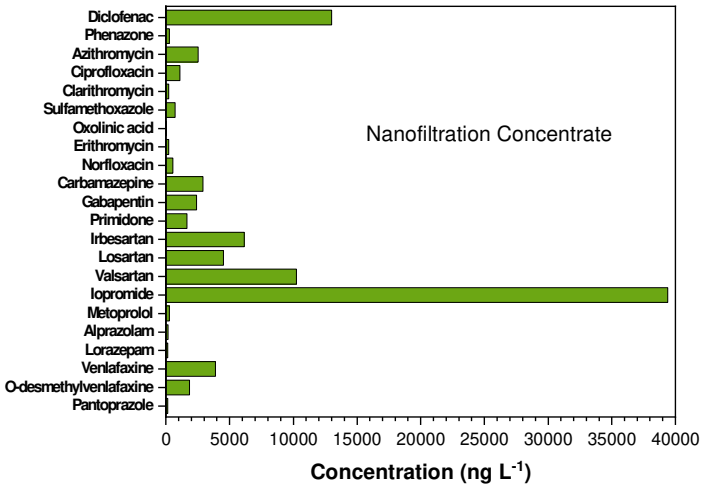




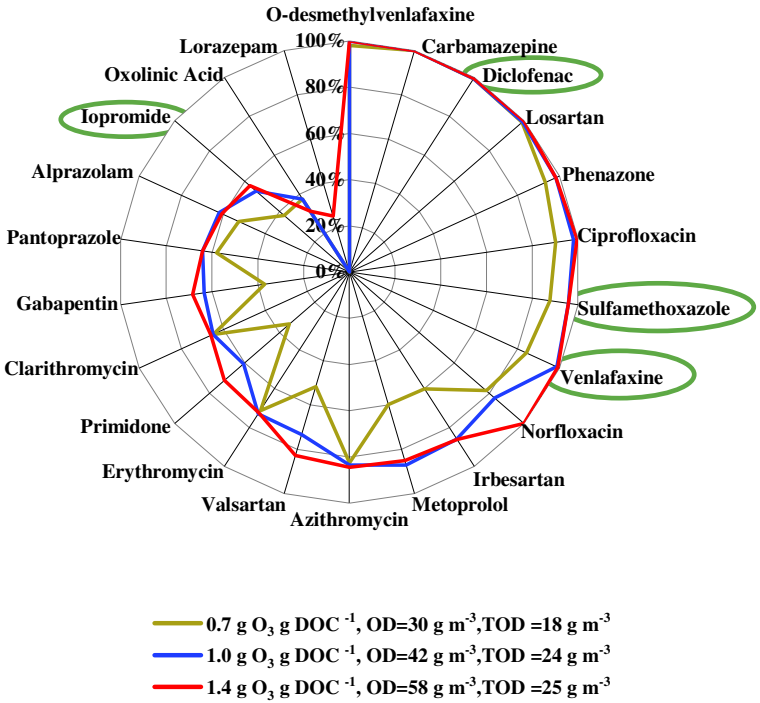
CECs REMOVAL FROM NF CONCENTRATE – O_3

NF CONCENTRATE

Conductivity (mS cm $^{-1}$)	2634
pH	8.0
Turbidity (NTU)	26
TSS (mg L^{-1})	152
VSS (mg L^{-1})	40
COD (mg O2 L^{-1})	154
DIC (mg C L^{-1})	165
DOC (mg C L^{-1})	43
SUVA (L mg^{-1} m^{-1})	2.5
UV254nm (cm^{-1})	1.21
Ammonium (NH_4^+) (mg L^{-1})	151
Clorides (Cl^-) (mg L^{-1})	211
Nitrite (NO_2^-) (mg L^{-1})	17.6
Sulfate (SO_4^{2-}) (mg L^{-1})	149
Nitrate (NO_3^-) (mg L^{-1})	3.8
Phosphates (PO_4^{3-}) (mg L^{-1})	41.5

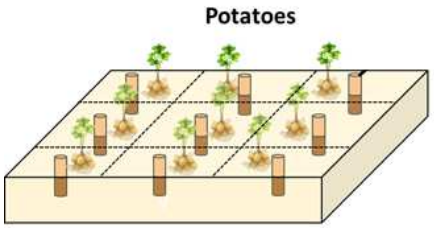


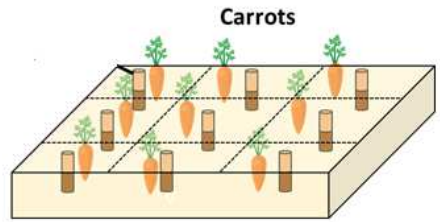
CECs REMOVAL

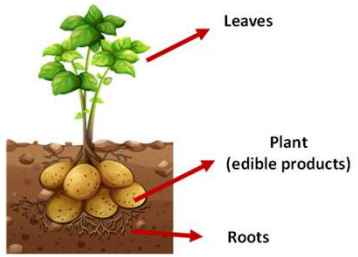


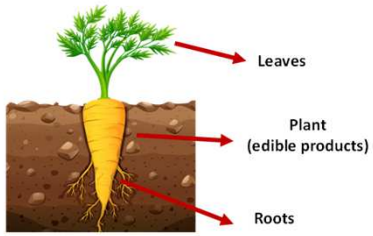
CROPS PRODUCTION

Gravel layer → Sand layer → Silty loam





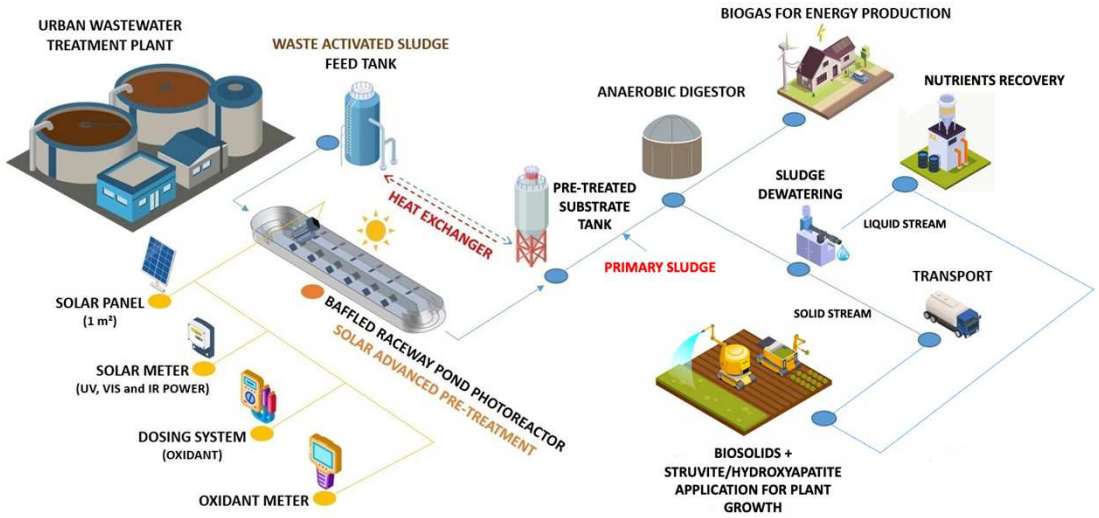




ReWateR project

Recovery of Wastewater Resources in Agriculture

"la Caixa" Foundation



Objectives

ReWateR aims **SUSTAINABLE WWTPs** by:

- INCREASING **ENERGY SELF-PRODUCTION** by enhancing **biogas quality and production** from anaerobic digestion;
- **PRODUCTION OF FERTILIZERS** obtained from the liquid and solid streams of AD after sludge dewatering (biosolids, as sources of N, P, K, micronutrients & organic matter, and N&P recovery through crystallization-based systems).

Research Team

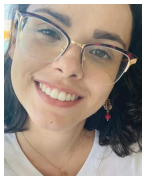

C. Cruzeiro


Vítor Vilar


R. Santos


L. Cullen


J. Monteiro


L. Sena


A. Narcizo

Partners

U.PORTO FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

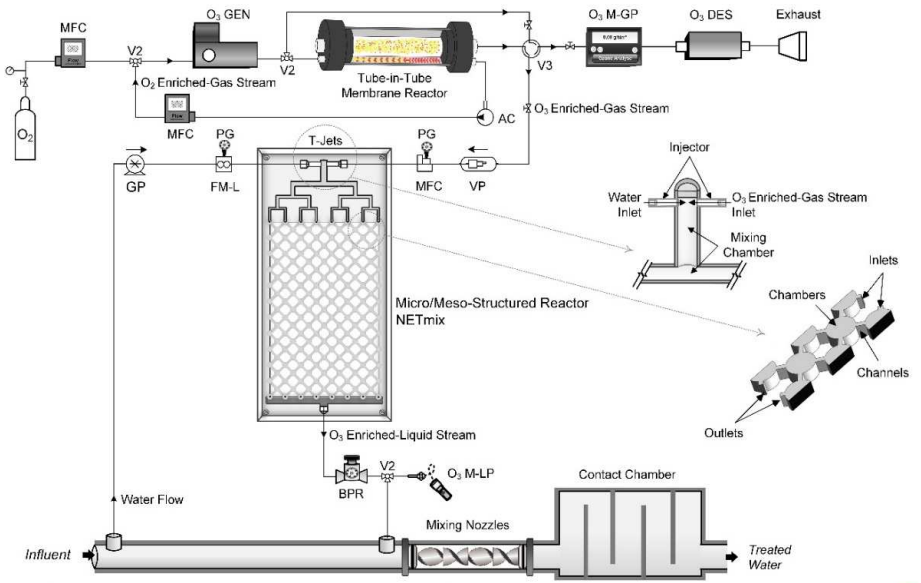
ALiCE ASSOCIATE LABORATORY IN CHEMICAL ENGINEERING

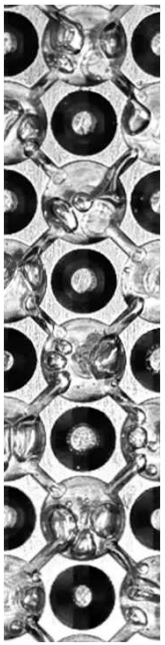
SRE CM ASSOCIATE LABORATORY LABORATORY OF SEPARATION AND REACTION ENGINEERING LABORATORY OF CATALYSIS AND MATERIALS

OZONE4WATER PROJECT

Cutting-Edge Ozone-Technology for Water Treatment

OZONE4WATER www.ozone4water.com





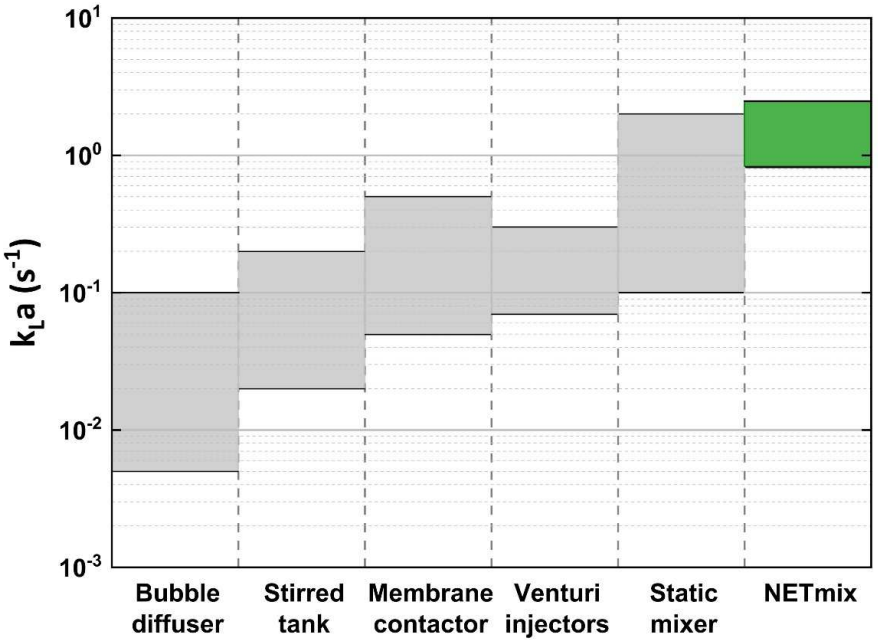
Objectives

- **Functionalized membranes for O_3/O_2 separation** to obtain an O_3-enriched gas stream, and simultaneously the O_2 from the mixture of O_2/O_3 can be recovered and recycled back to the ozone generator thereby reducing oxygen consumption;
- **Pressurized static micro/meso-structured mixer (NETmix)** able to enhance the ozone mass transfer from the gas phase to the liquid phase to 100% or very close to it;
- **Low footprint ozone side stream contacting train**;
- **Powerful cost-effective ozonation system.**

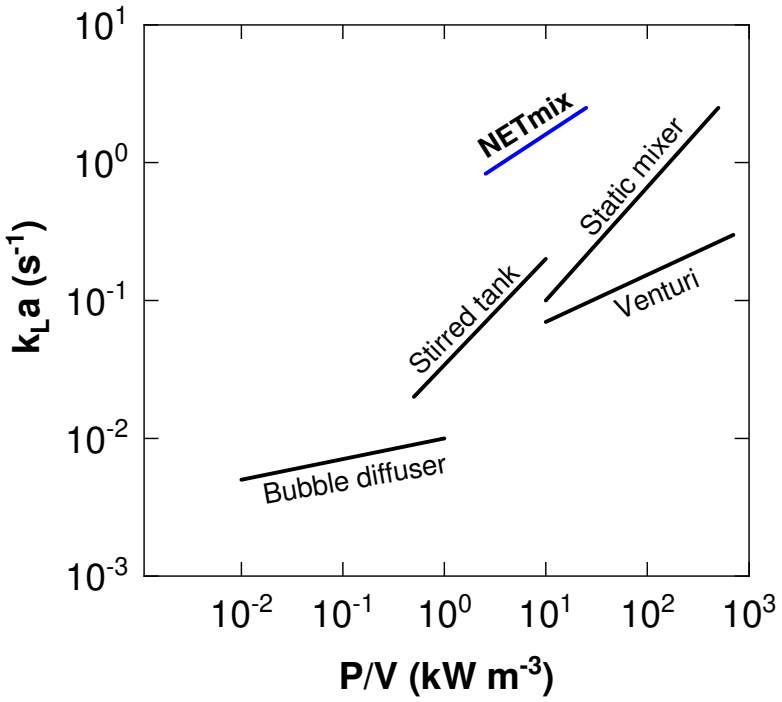
Research Team

GAS/LIQUID INJECTOR

k_La comparison with conventional equipment

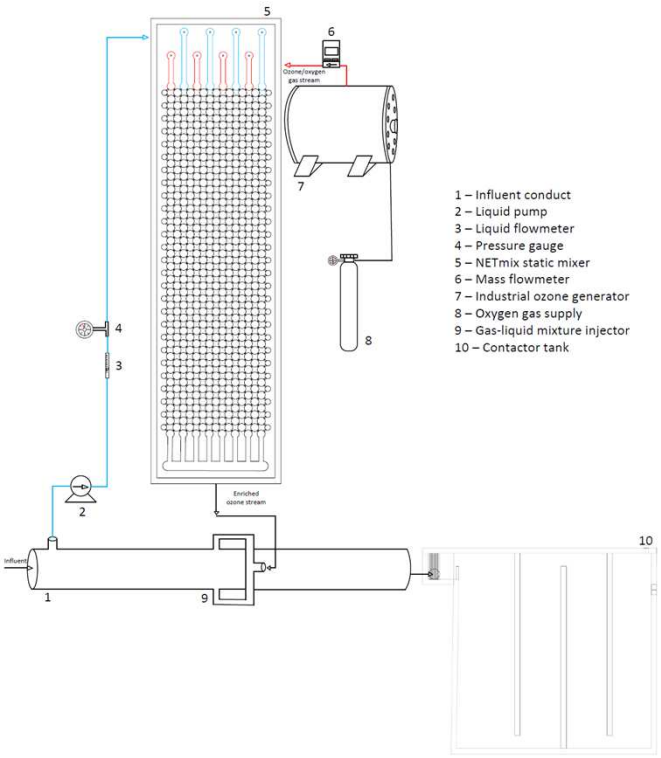


k_La *vs* P/M
(Power consumption per mass of water injected)

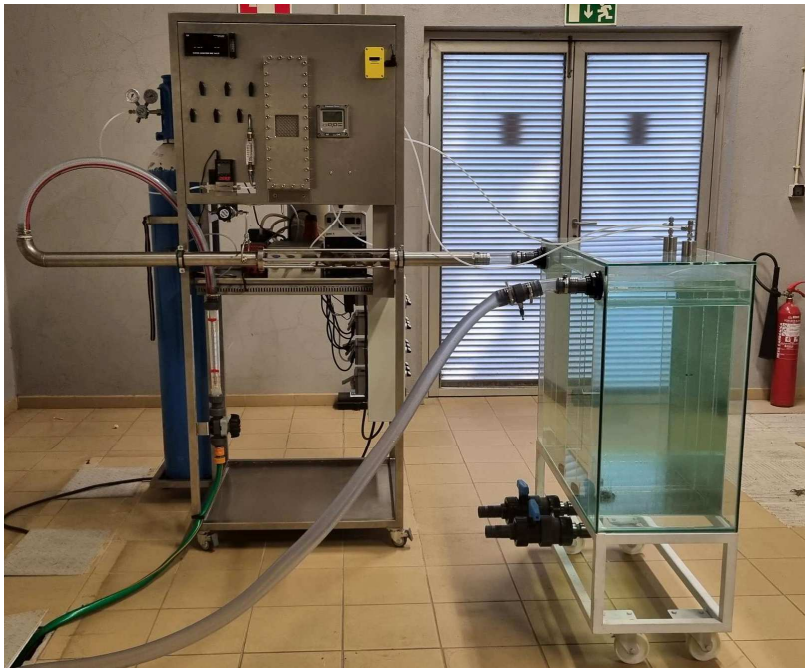


NETmix technology as ozone gas injection system: Assessment of the gas-liquid mass transfer
Chemical Engineering and Processing - Process Intensification 14 (2023) 109566
https://doi.org/10.1016/j.cep.2023.109566

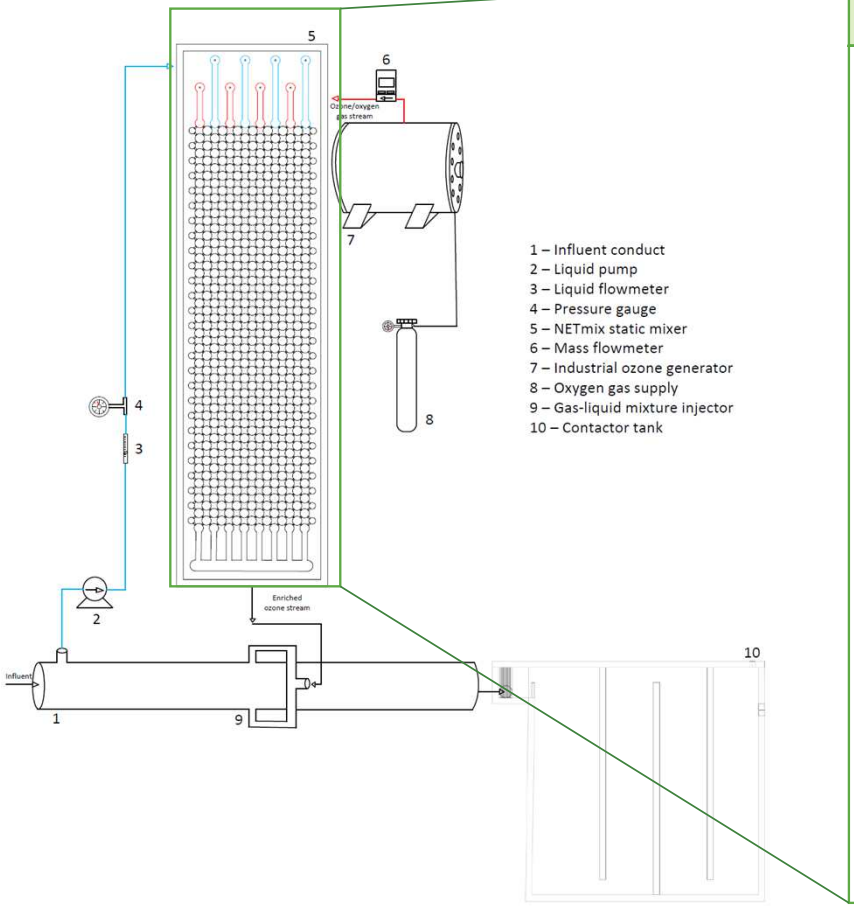
SIDESTREAM OZONE INJECTION PROTOTYPE



1 – Influent conduct
2 – Liquid pump
3 – Liquid flowmeter
4 – Pressure gauge
5 – NETmix static mixer
6 – Mass flowmeter
7 – Industrial ozone generator
8 – Oxygen gas supply
9 – Gas-liquid mixture injector
10 – Contactor tank



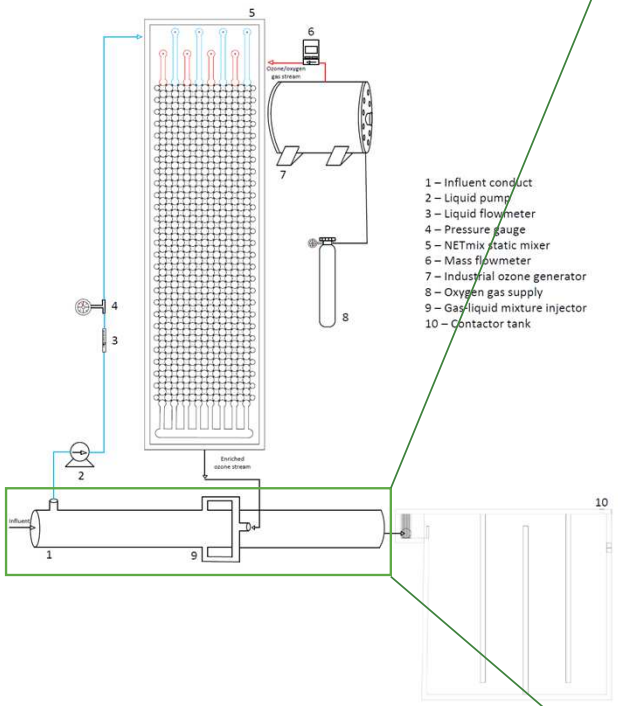
SIDESTREAM OZONE INJECTION PROTOTYPE



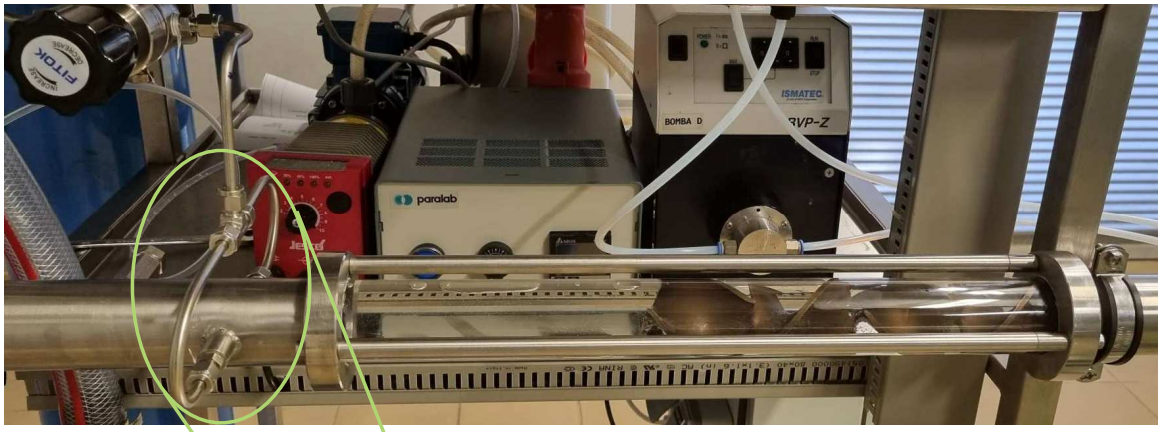
1 – Influent conduct
2 – Liquid pump
3 – Liquid flowmeter
4 – Pressure gauge
5 – NETmix static mixer
6 – Mass flowmeter
7 – Industrial ozone generator
8 – Oxygen gas supply
9 – Gas-liquid mixture injector
10 – Contactor tank

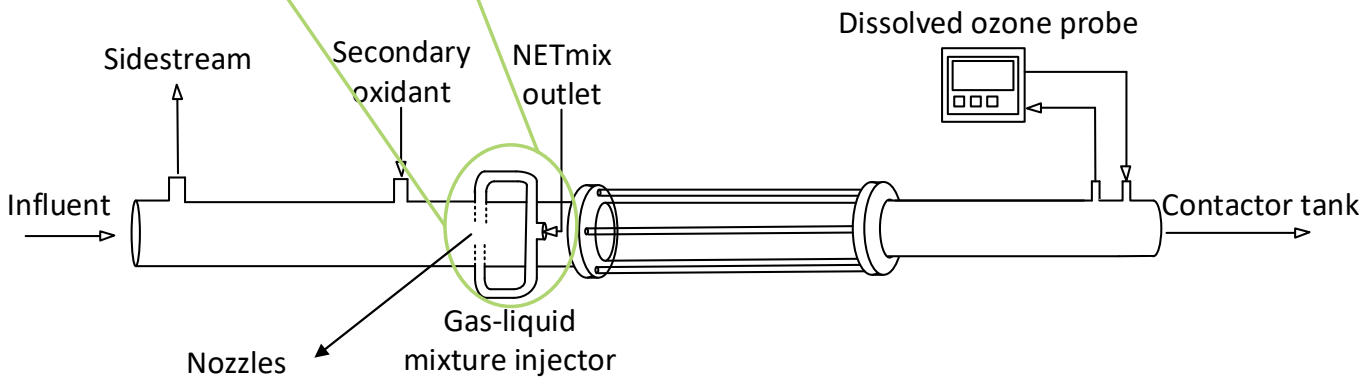
NETmix Static Mixer

SIDESTREAM OZONE INJECTION PROTOTYPE

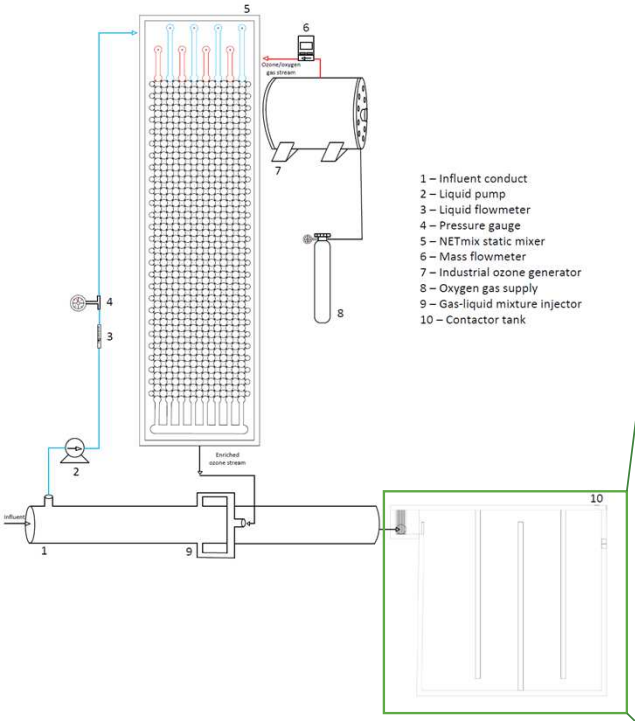


Conduct and injection system



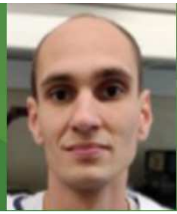


SIDESTREAM OZONE INJECTION PROTOTYPE



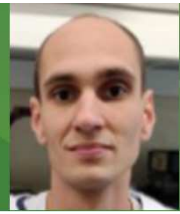
Contactor tank

QUATERNARY TREATMENT OF URBAN WASTEWATERS



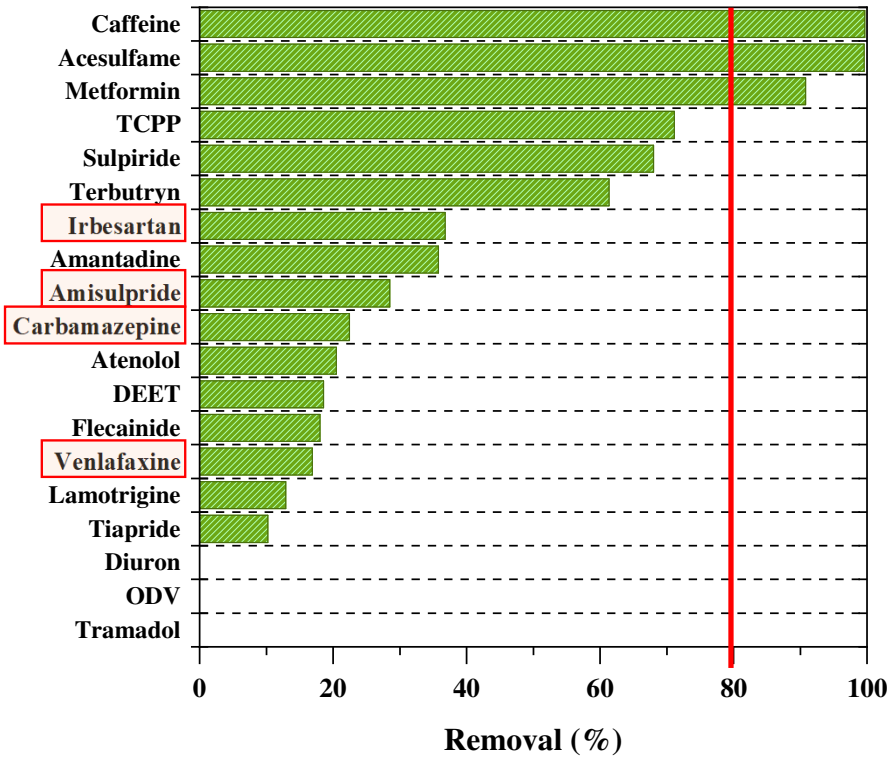
Freixo WWTP

QUATERNARY TREATMENT OF URBAN WASTEWATERS

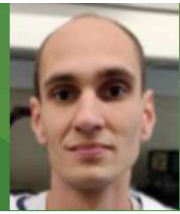


Occurrence and Removal of CECs - Freixo WWTP

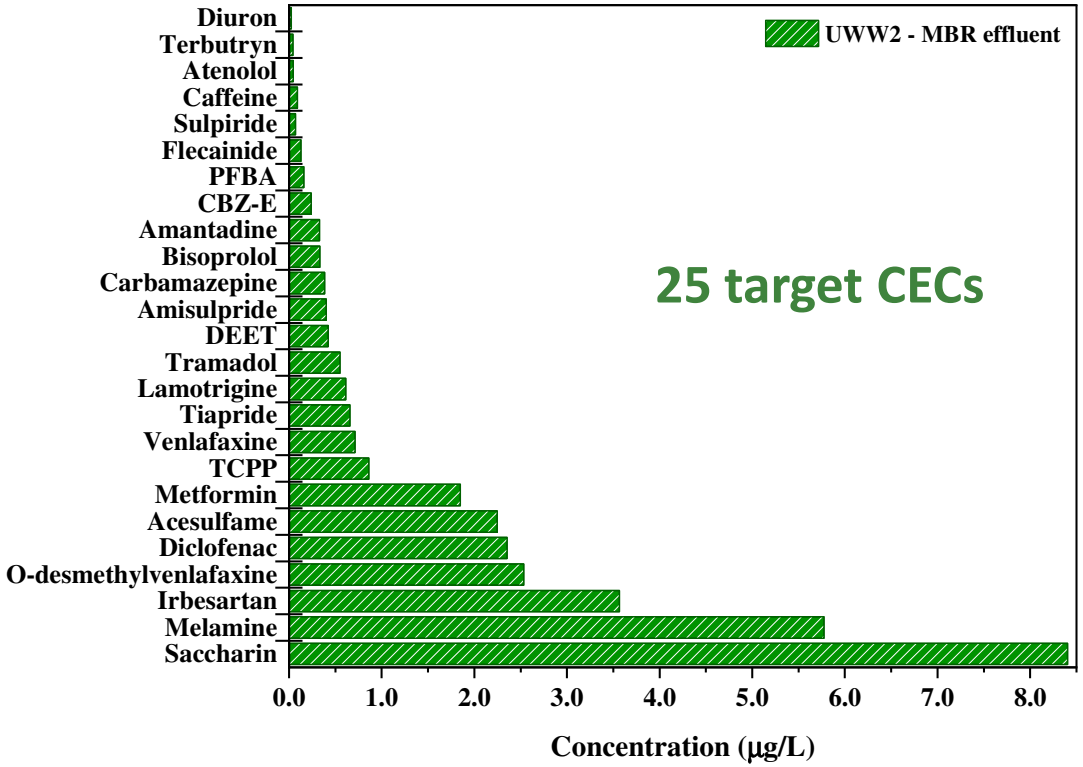
Compounds	Group	Influent (µg/L)	Effluent (µg/L)
Caffeine	Food additive	19.0	0.07
Acesulfame	Food additives	58.3	0.30
Metformin	Pharmaceutical	66.8	6.16
Tris (2-chloroisopropyl) phosphate (TCPP)	Chemicals Industrial	1.60	0.46
Sulpiride	Pharmaceutical	0.23	0.07
Terbutryn	Pesticide	0.12	0.05
Irbesartan	Pharmaceutical	6.61	4.18
Amantadine	Pharmaceutical	0.53	0.34
Amisulpride	Pharmaceutical	0.55	0.40
Carbamazepine	Pharmaceutical	0.27	0.21
Atenolol	Pharmaceutical	0.06	0.04
Diethyltoluamide (DEET)	Pesticide	0.52	0.42
Flecainide	Pharmaceutical	0.18	0.14
Venlafaxine	Pharmaceutical	1.13	0.94
Lamotrigine	Pharmaceutical	0.64	0.55
Tiapride	Pharmaceutical	0.83	0.74
Diuron	Pesticide	0.02	0.03
O-Desmethylvenlafaxine (ODV)	Pharmaceutical (metabolite)	3.25	3.28
Tramadol	Pharmaceutical	0.56	0.59



QUATERNARY TREATMENT OF URBAN WASTEWATERS

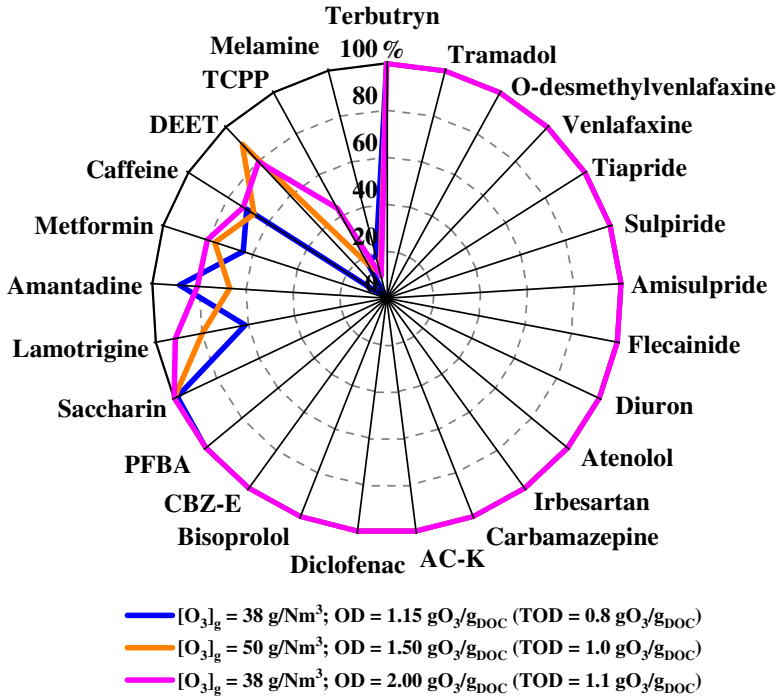


CECs occurrence after the MBR



25 target CECs

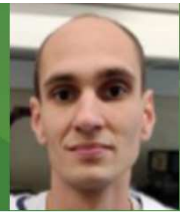
CECs removal by Ozonation



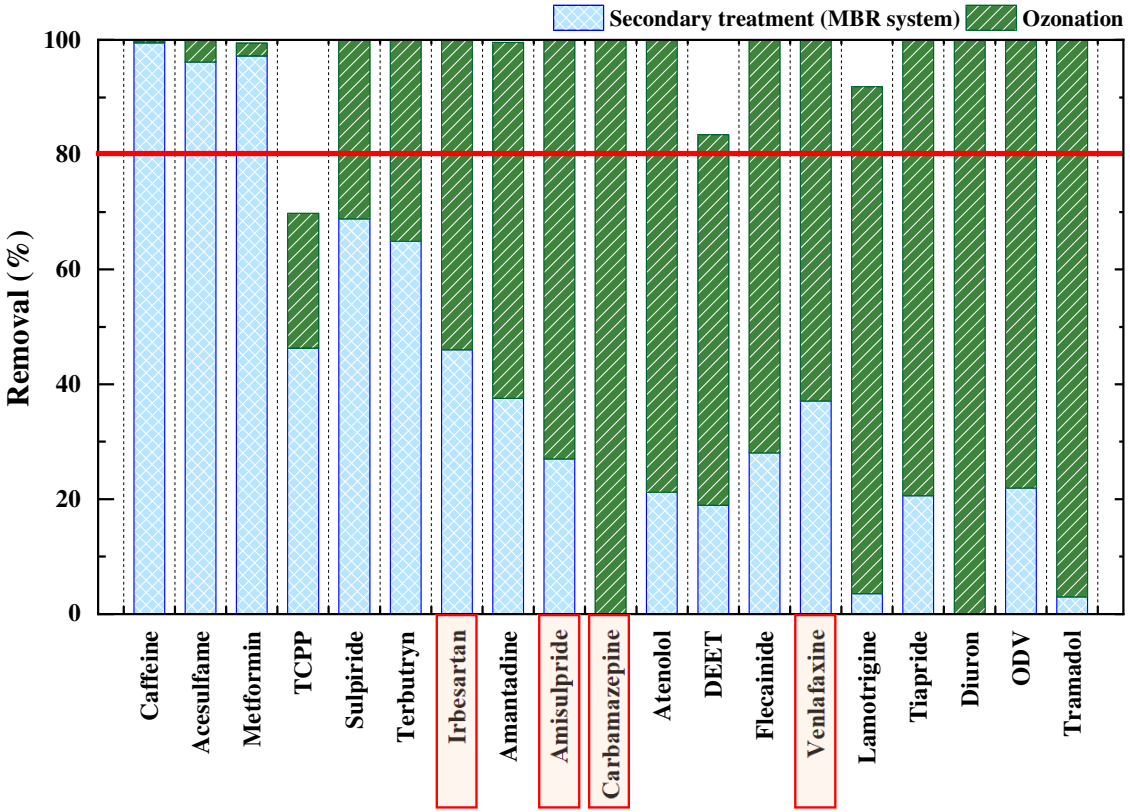
≥ 80% removal for **22** of the 25 CECs

(TOD = 1.1 g_{O3}/g_{DOC}; HRT = 54s)

QUATERNARY TREATMENT OF URBAN WASTEWATERS



Overall CECs Removal



Global removal **≥ 80%** for **18** of the 19 CECs

(TOD = 1.1 g_{O3}/g_{DOC} and HRT = 54s)

CHALLENGES AND POSSIBLE ACTIONS

Wastewater treatment

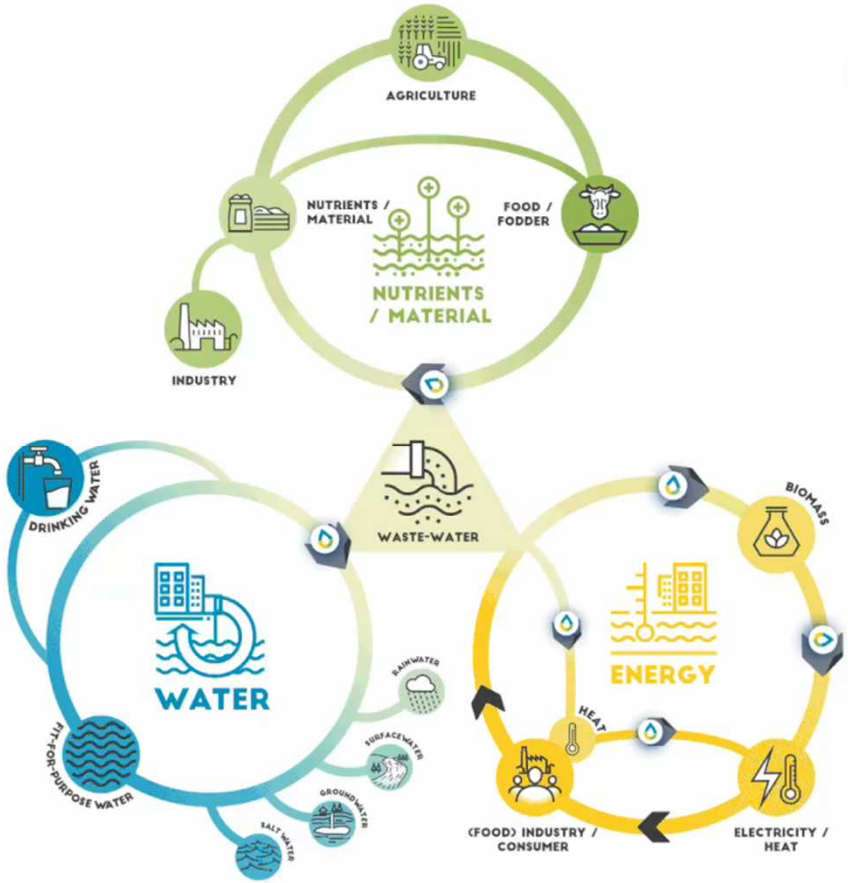
- Multi-barrier approach to eliminate the broadest possible spectrum of micro-pollutants, minimizing ecological and human health risks - One Water One Health;
- Safe reclaimed water distribution;
- Solutions to promote the recovery of nutrients.

Energy neutrality and renewables

- Introduce measures/solutions to reduce energy consumption and maximize biogas production (WAS pre-treatment, co-digestion).

Wastewater surveillance and risk assessment

- Analytical capacity for PFAS, Microplastics, Antimicrobial Resistance, Greenhouse Gases



ACKNOWLEDGEMENTS

U.PORTO FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

ALiCE ASSOCIATE LABORATORY IN CHEMICAL ENGINEERING

SREM LABORATORY OF SEPARATION AND REACTION ENGINEERING LABORATORY OF CATALYSIS AND MATERIALS

Lepabe Laboratory for Process Engineering, Environment, Biotechnology and Energy

FCT Fundação para a Ciência e a Tecnologia

PRR Plano de Recuperação e Resiliência

REPÚBLICA PORTUGUESA

Financiado pela União Europeia NextGenerationEU

Aquatic Pollutants

Water JPI

jpiamr Joint Programming Initiative on Antimicrobial Resistance

JPI OCEANS

Interreg España – Portugal

Cofinanciado por la Unión Europea Cofinanciado pela União Europeia

Water4All Water security for the planet

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

UJI UNIVERSITAT JAUME I

"la Caixa" Foundation

Faculdade de Engenharia da Universidade do Porto | Rua Dr. Roberto Frias s/n | 4200-465 Porto, Portugal | T. +351 220 414 567 | alice.info@fe.up.pt | www.alice.fe.up.pt

WINTER SCHOOL

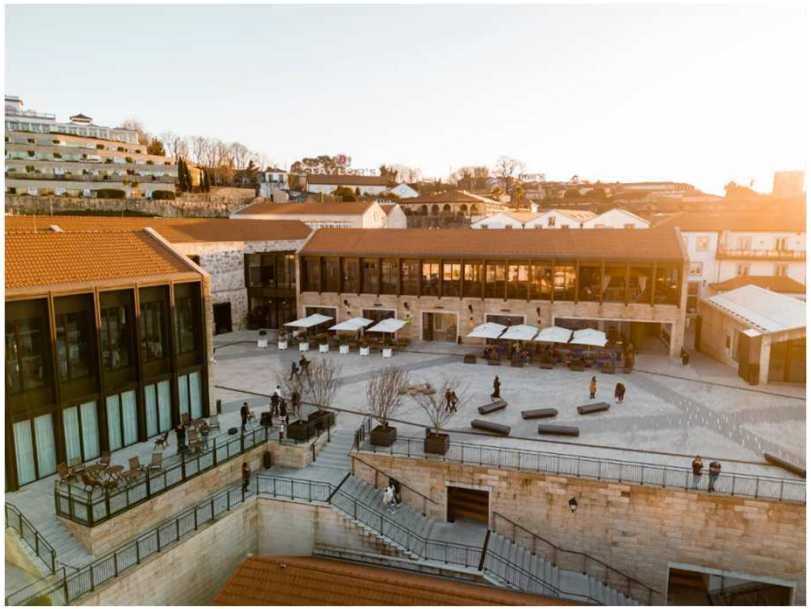
Winter School on Contaminants of Emerging Concern (CECs) and Disinfection By-Products (DBPs): Occurrence, Impact and Elimination

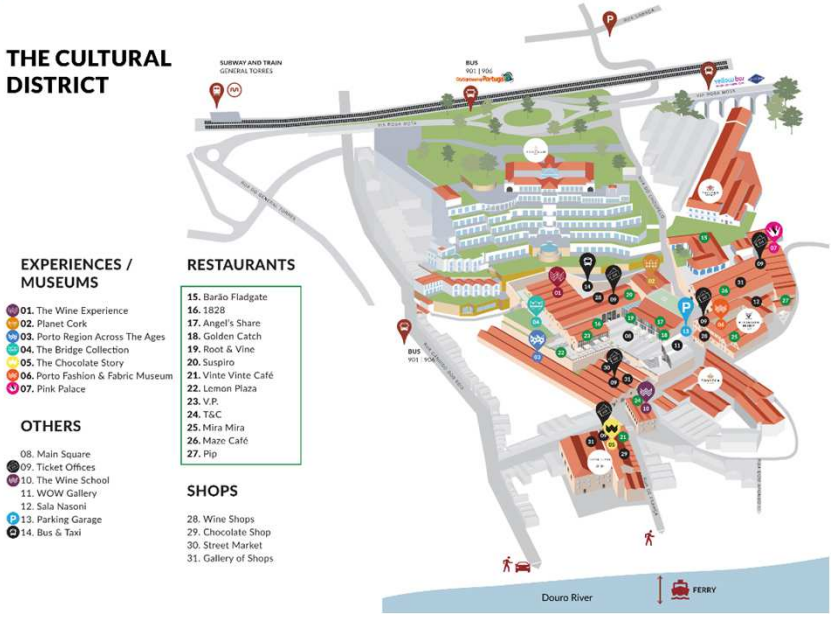
Venue: World of Wine (WOW), Vila Nova de Gaia, Porto, Portugal

Date: 25 and 26 November 2024

Website: https://mar2protect.eu/winter-school-2024/

Winter School





EA3G2024 – INTERNATIONAL CONFERENCE ON OZONE AND ADVANCED OXIDATION

International Conference on Ozone and Advanced Oxidation-EA3G2024

European-African-Asian-Australasian Group

Congress venue: **World of Wine (WOW)**, Vila Nova de Gaia, Porto, Portugal

Date: 27-29 November 2024

Website: https://www.ioa-ea3g.org

INTERNATIONAL OZONE ASSOCIATION
Europe Africa Asia Australasia Group

Vítor Vilar
vilar@fe.up.pt

Thank You For Your Kind Attention