



ADVANCED TREATMENT TECHNOLOGIES DEVELOPED IN NOR-WATER PROJECT

TECNOLOGIAS AVANÇADAS DE TRATAMENTO DESENVOLVIDAS NO PROJETO NOR-WATER

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FEUP FACULDADE DE ENGENHARIA
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LABORATORY OF SEPARATION AND REACTION ENGINEERING
LABORATORY OF CATALYSIS AND MATERIALS

ALiCE
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LABORATORY
IN CHEMICAL
ENGINEERING

VÍTOR J.P. VILAR
Final Conference

15th March 2022

CETMAR
CENTRO TECNOLÓGICO DEL MAR

TEAM

ADVANCED TREATMENT TECHNOLOGIES

- **PHOTOCATALYTIC MEMBRANE REACTOR (FILTRATION + OXIDATION)**
- **TUBE-IN-TUBE MEMBRANE REACTOR (OXIDATION - SMART DOSING OF LIQUID OXIDANTS OR CATALYST)**
- **TUBE-IN-TUBE MEMBRANE REACTOR (OXIDATION - SMART DOSING OF OZONE)**
- **FluHelik PHOTOREACTOR (OXIDATION - PHOTOCHEMICAL PROCESSES)**

FINAL REMARKS

TEAM

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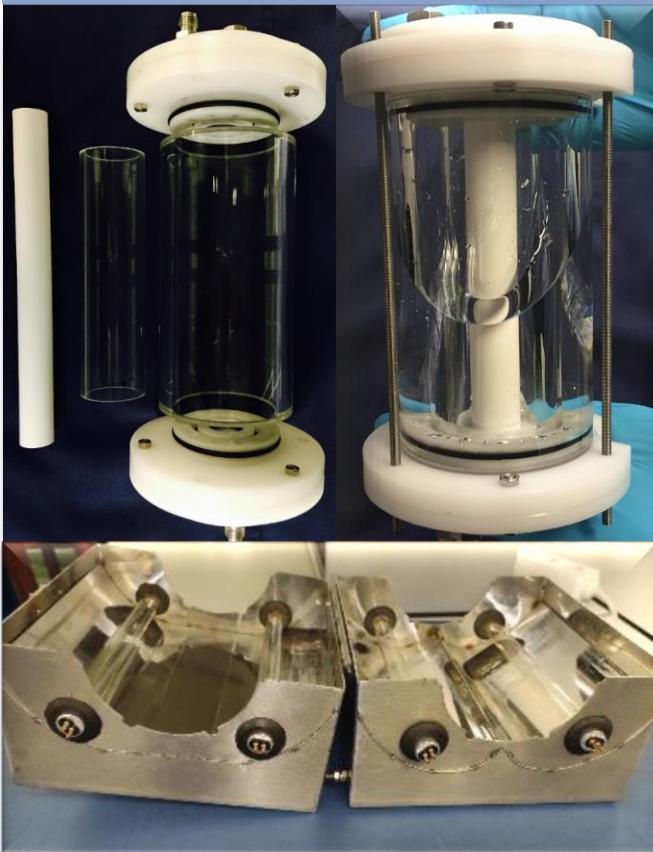
**efacec**

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Grupo Águas de Portugal

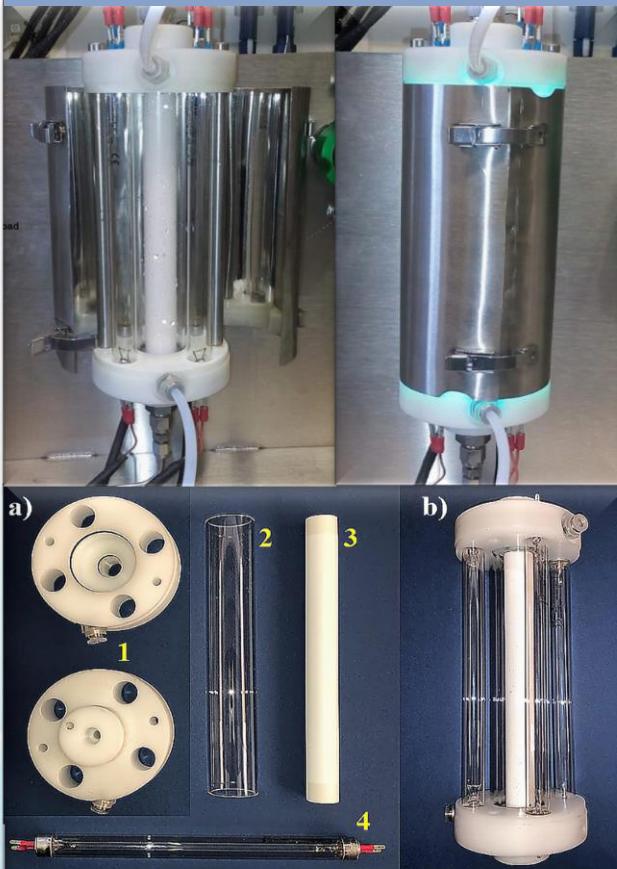
- ✓ Supply of urban wastewater samples for tests
- ✓ Installation of a pre-industrial plant at Ave WWTP

AOP, OZONATION AND MEMBRANE FILTRATION

PHOTOCATALYTIC MEMBRANE REACTOR

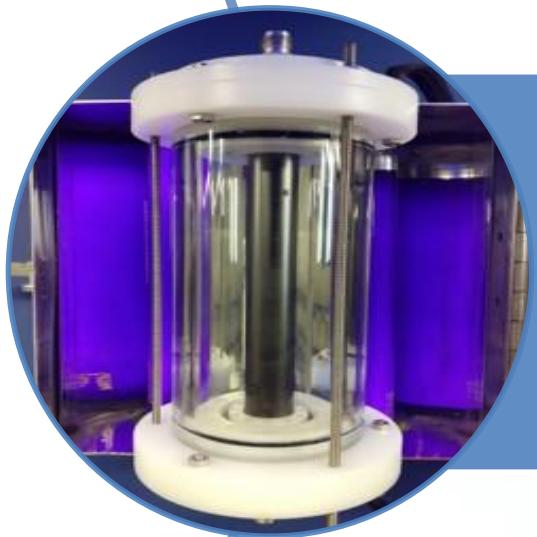


TUBE-IN-TUBE MEMBRANE PHOTOREACTOR



FluHelik PHOTOREACTOR





PHOTOCATALYTIC MEMBRANE REACTOR (FILTRATION + OXIDATION)



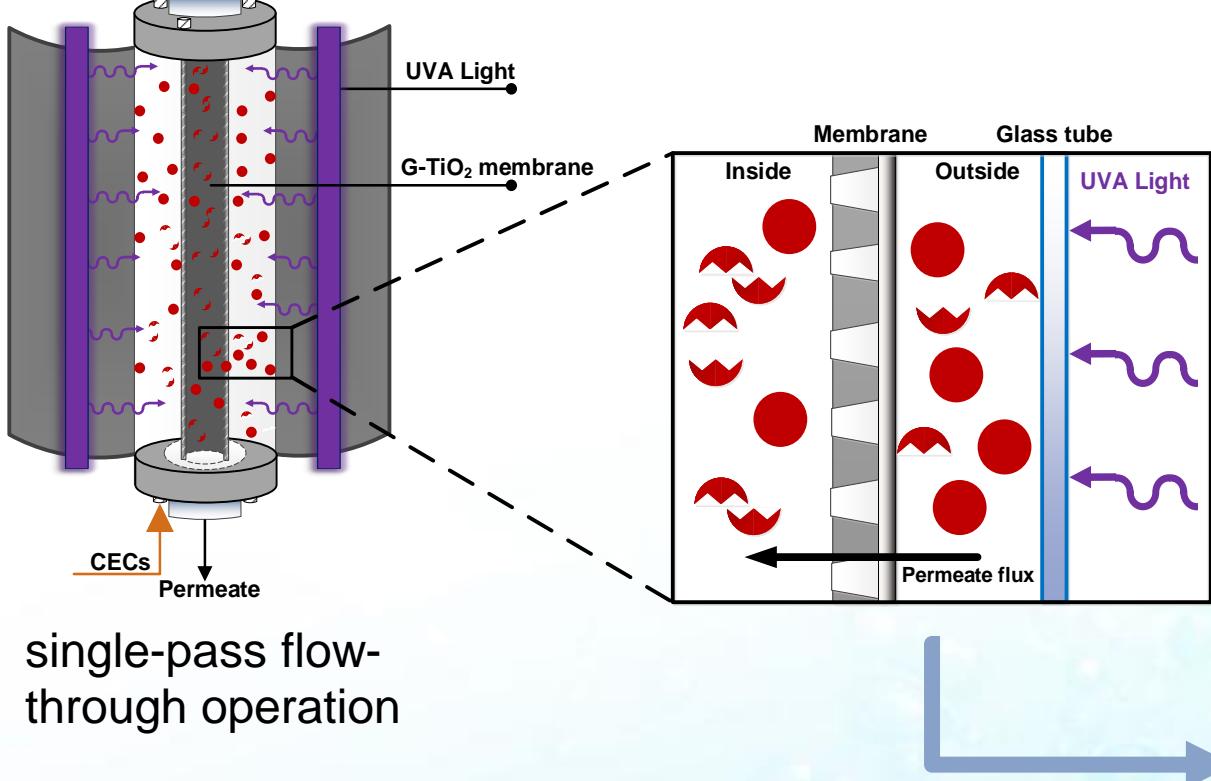
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norwater

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PMRs are a very promising technology

- ✓ Photocatalysis with membrane filtration in a single unit (retention and oxidation);
- ✓ Enhanced membrane permeability;
- ✓ Enhanced antifouling membrane properties through oxidation of organic molecules;



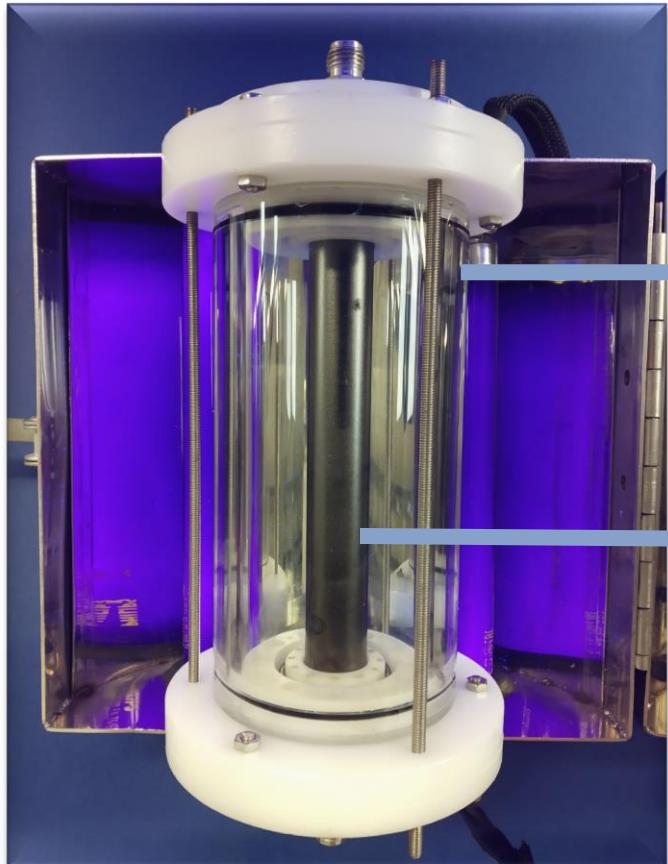
High CECs Rejection and High Permeate Quality



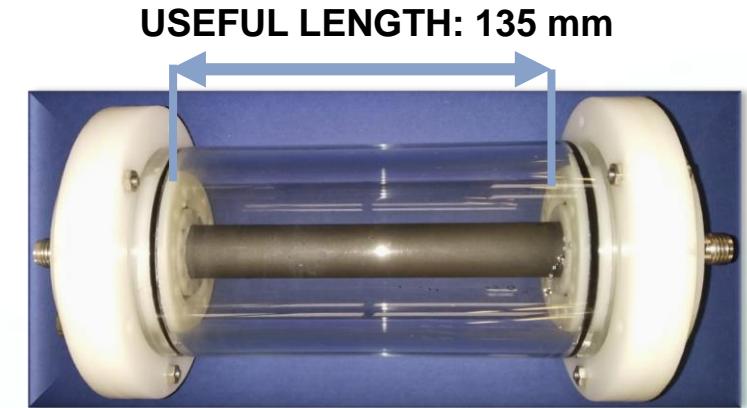
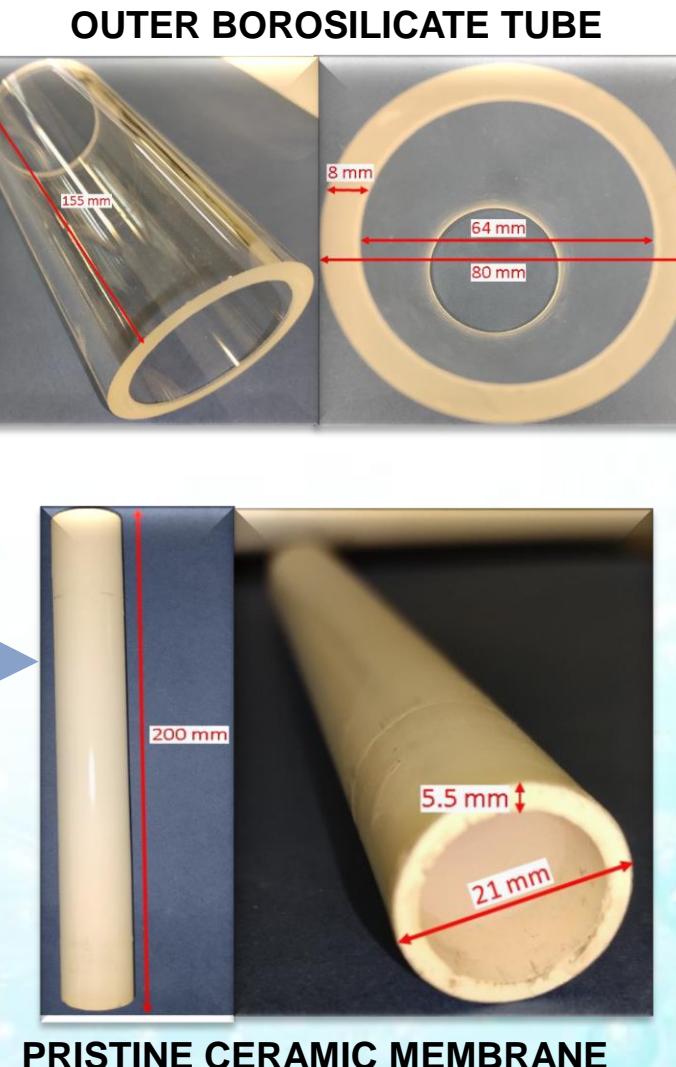
Concentrate with a Lower Organic Load

CECs are forced towards the membrane surface

PMR: MEMBRANE MODULE



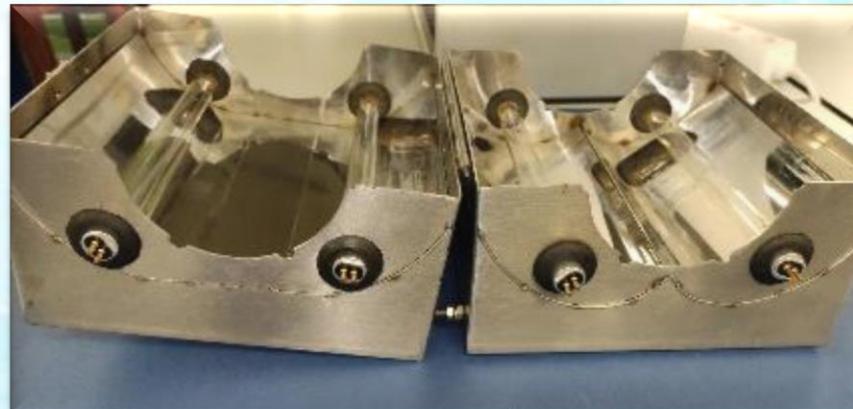
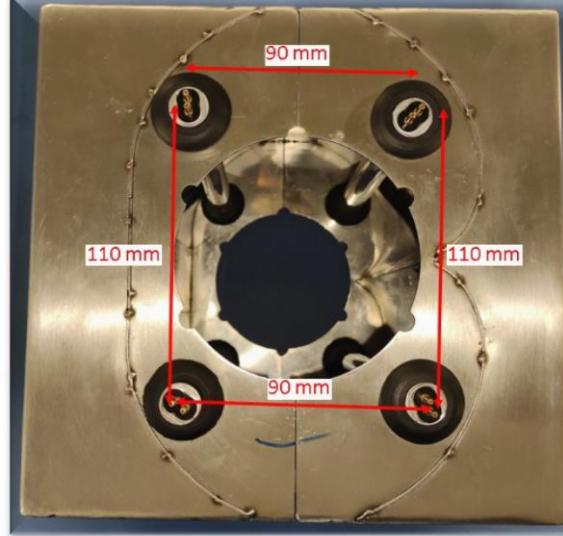
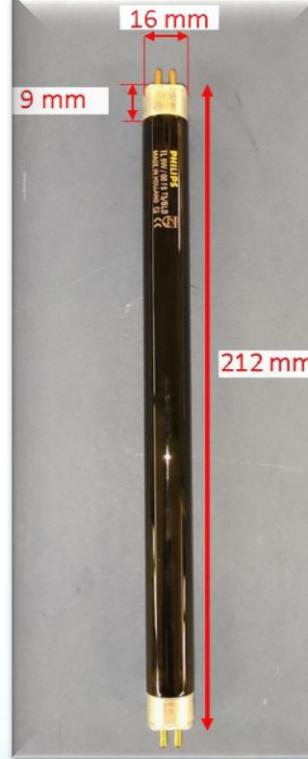
MAXIMUM PRESSURE: 12.5 bar



Characteristics of Non-Photoactive Membrane

Substrate	Material: $\alpha\text{-Al}_2\text{O}_3$ Pore size: $d_{50} = 3 \mu\text{m}$
Membrane	Material: $\alpha\text{-Al}_2\text{O}_3$ Pore size: $d_{50} = 100 \text{ nm}$ Porosity: 40-55% Useful length: 135 mm Effective area: 84 cm^2

PMR: ILLUMINATION SOURCE



UVA Lamps Characteristics

4 UVA Lamps - Philips TL 6 W

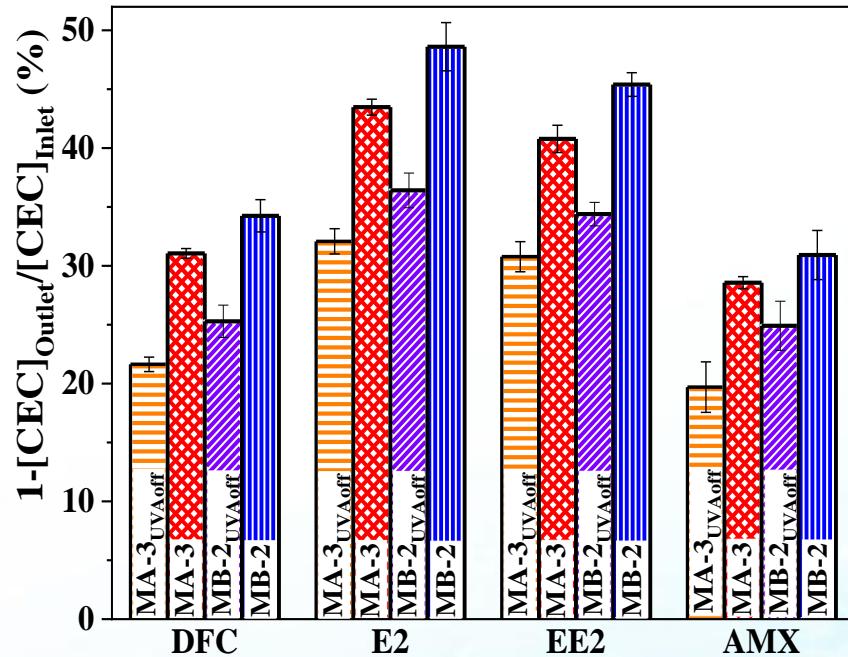
Power (Rated) (Nom) = 6 W

$\lambda_{\text{max}} = 365 \text{ nm}$

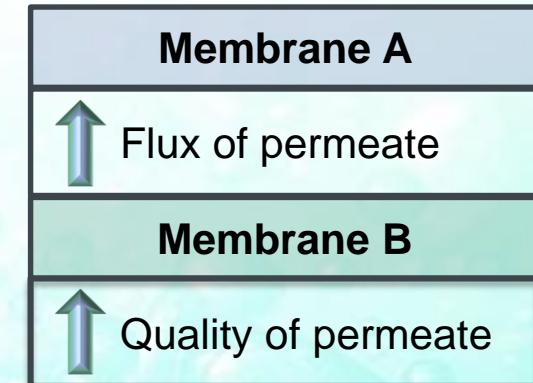
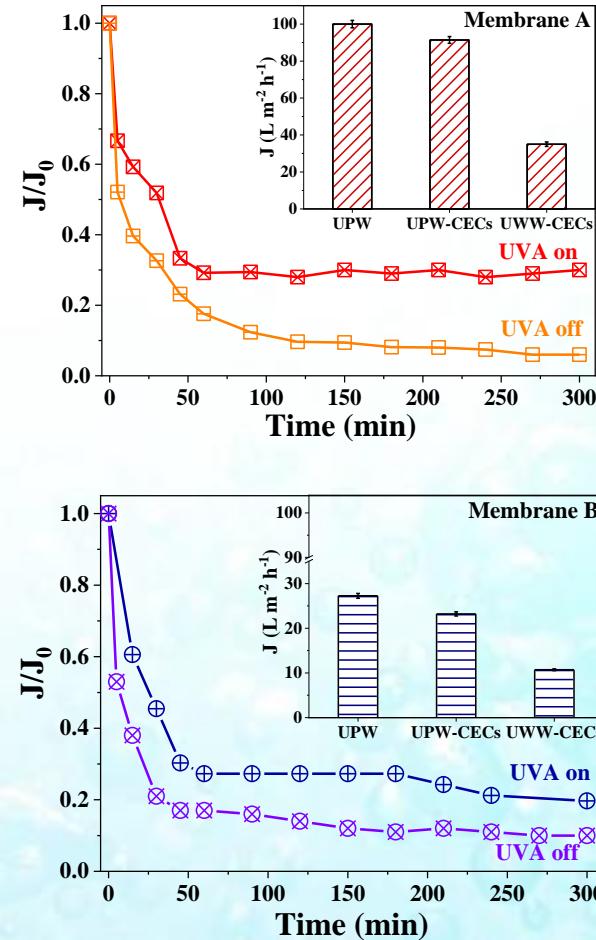
Photonic flux = $1.19 \pm 0.02 \text{ J s}^{-1}$

PMR: TESTS SINGLE-PASS FLOW-THROUGH OPERATION

EFFECT OF GRAPHENE/TiO₂ DEPOSITION METHODS - UWW



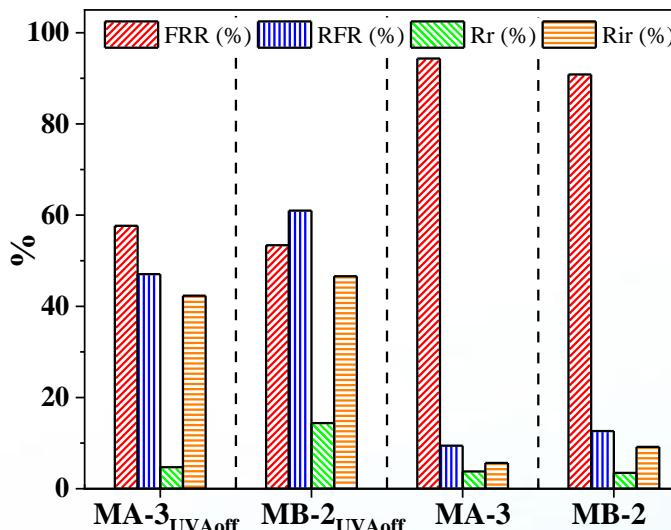
Chemical Engineering Journal 430 (2022) 132639



PMR: TESTS SINGLE-PASS FLOW-THROUGH OPERATION

EFFECT OF GRAPHENE/TiO₂ DEPOSITION METHODS - UWW

Antifouling Performance



Flux Recovery Ratio (FRR)
Relative Flux Reduction Ratio (RFR)
Reversible Fouling Ratio (Rr)
Irreversible Fouling Ratio (Rir)

Absence of UVA light

Higher RFR due to membrane fouling

Ecotoxicity

Effective reduction of toxicity in zebrafish embryos after treatment for both functionalized membranes

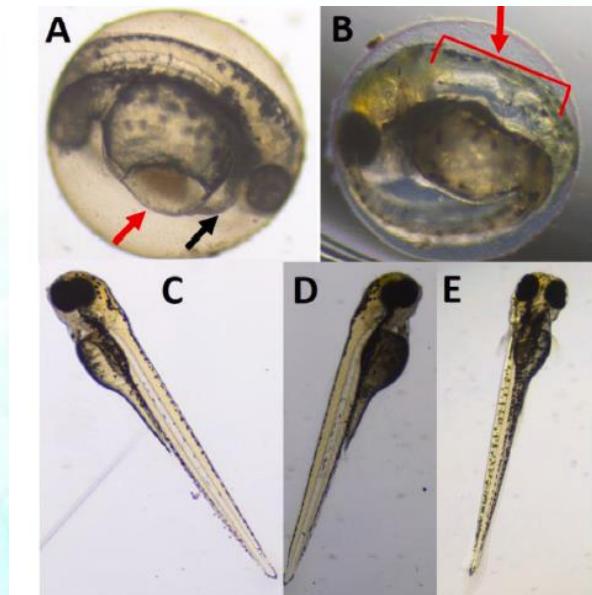
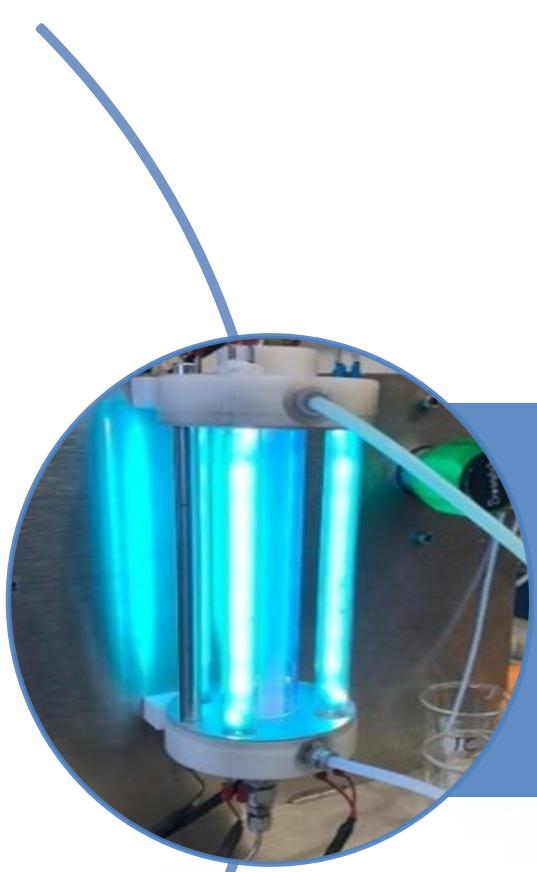


Fig. 7. Abnormalities observed in the zebrafish embryo bioassay: Pericardial oedema – black arrow; yolk sac oedema – red arrow at 48 hpf exposition to CECs + real matrix (A); Abnormal notochord formation at 96 hpf exposition to CECs + synthetic matrix (B); normal development at 96 hpf recorded in CECs + real matrix + MA-3 (C), CECs + real matrix + MB-2 (D) and control – synthetic water (E).



TUBE-IN-TUBE MEMBRANE REACTOR

(OXIDATION - SMART DOSING OF LIQUID OXIDANTS OR CATALYST)



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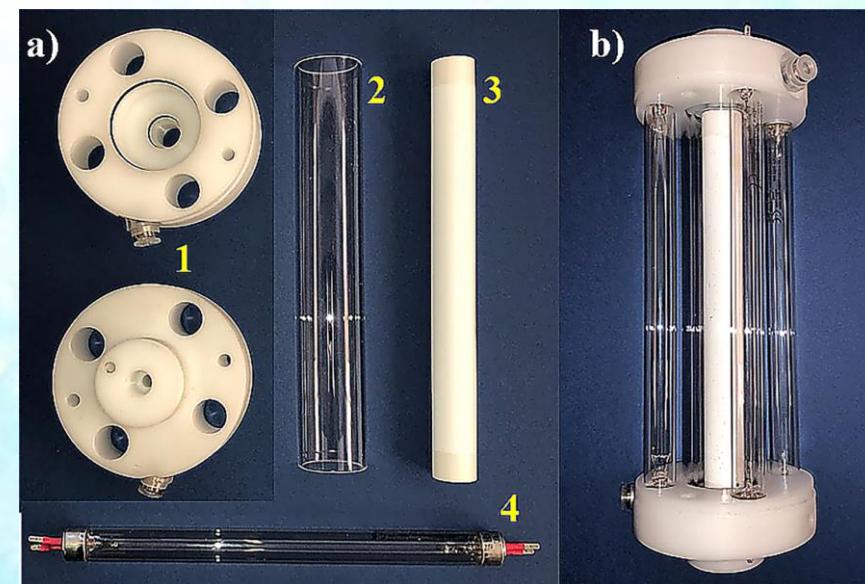


TUBE-IN-TUBE MEMBRANE REACTOR

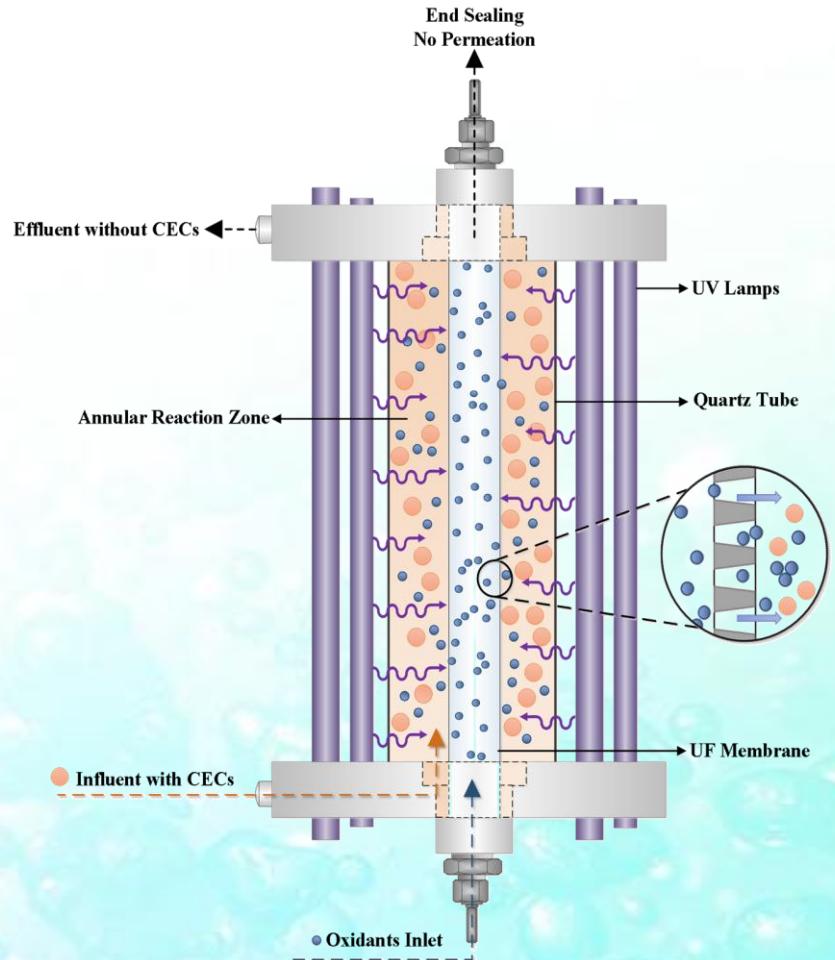
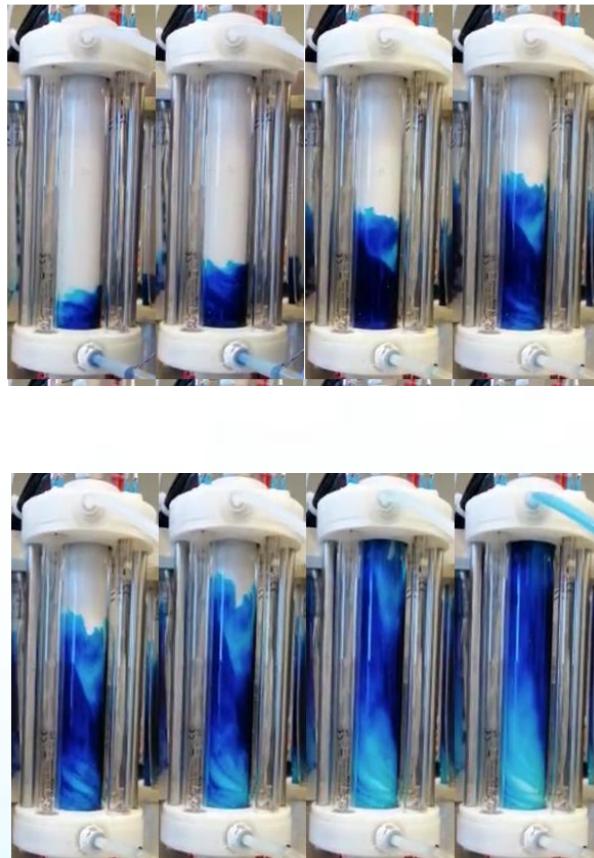


Apparatus

- The system comprises an inner tubular membrane and an outer quartz tube.
- 4 UVC lamps are located externally to the quartz tube.
- Liquid or gas stream is introduced by the lumen side of the membrane.
- The water is fed tangentially to the inner wall of the quartz tube.



TUBE-IN-TUBE MEMBRANE REACTOR



Water Research 191 (2021) 116815
Science of the Total Environment
743 (2020) 140629

TUBE-IN-TUBE MEMBRANE REACTOR

SELECTED CONTAMINANTS OF EMERGING CONCERN

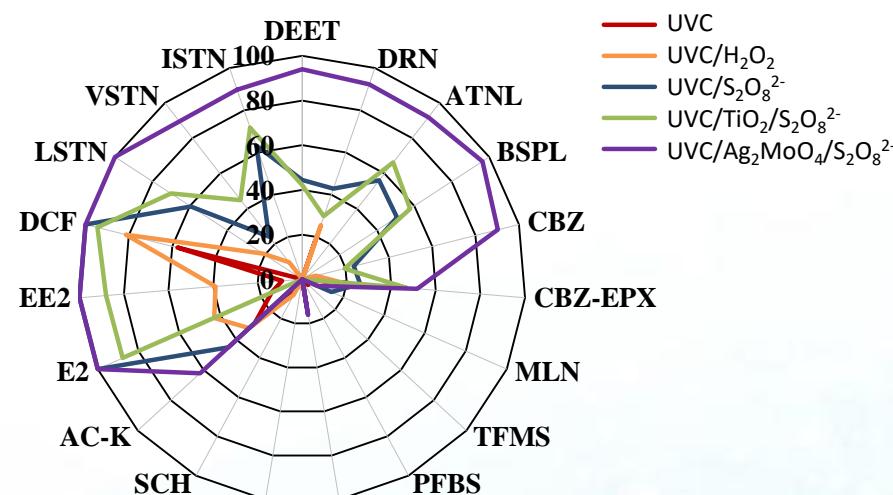
Contaminants Groups	Emerging Contaminants	Abbreviation	Chemical Composition	Chemical Structure	Contaminants Groups	Emerging Contaminants	Abbreviation	Chemical Composition	Chemical Structure
Perfluorinated Compounds	Heptafluorobutyric acid	HFBA	C ₄ HF ₇ O ₂		Artifical Sweeteners	Acesulfame	ACK	C ₄ H ₄ KNO ₄ S	
	Potassium nanofluoro-1-butanesulfonate	PFBS	C ₄ F ₉ KO ₃ S			Saccharin	SCH	C ₇ H ₅ NO ₃ S	
	Perfluorooctanoic acid	PFOA	C ₈ HF ₁₅ O ₂		Carbamazepine and Metabolites	Carbamazepine	CBZ	C ₁₅ H ₁₂ N ₂ O	
	Trifluormethanesulfonic acid	TFMS	CHF ₃ O ₃ S			10,11 Carbamazepine-epoxide	CBZ-EPX	C ₁₅ H ₁₂ N ₂ O ₂	
Angiotensin II Receptor Blockers	Valsartan	VSTN	C ₂₄ H ₂₉ N ₅ O ₃		Beta blockers	Atenolol	ATNL	C ₁₄ H ₂₂ N ₂ O ₃	
	Irbesartan	ISTN	C ₂₅ H ₂₈ N ₆ O			Bisoprolol	BSPL	C ₁₈ H ₃₁ NO ₄	
	Losartan	LSTN	C ₂₂ H ₂₂ ClKN ₆ O		Hormones	17-beta-estradiol	E2	C ₁₈ H ₂₄ O ₂	
Flame Retardant	Melamine	MLN	C ₃ H ₆ N ₆			17-alpha-ethynylestradiol	EE2	C ₂₀ H ₂₄ O ₂	
Herbicide	Diuron	DRN	C ₉ H ₁₀ C ₂ N ₂ O		Non Steroidal Anti-Inflammatory Drugs	Diclofenac	DCF	C ₁₄ H ₁₀ Cl ₂ NNaO ₂	
Insect Repellent	DEET	DEET	C ₁₂ H ₁₇ NO		DW - Demineralized Water UWW – Urban Wastewater				[CECs] _{each} = 10 µg L ⁻¹

TUBE-IN-TUBE MEMBRANE REACTOR

PHOTOCATALYTIC MEMBRANE (TiO_2 OR Ag_2MoO_4) + PERMEATION OF OXIDANTS (H_2O_2 OR $\text{S}_2\text{O}_8^{2-}$)

UF membrane coated with TiO_2 or Ag_2MoO_4
Permeation H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (1.2 mM)
UVC = 1.7 W; HRT = 6.1 s

DW



Higher efficiency with UV/ $\text{Ag}_2\text{MoO}_4/\text{S}_2\text{O}_8^{2-}$

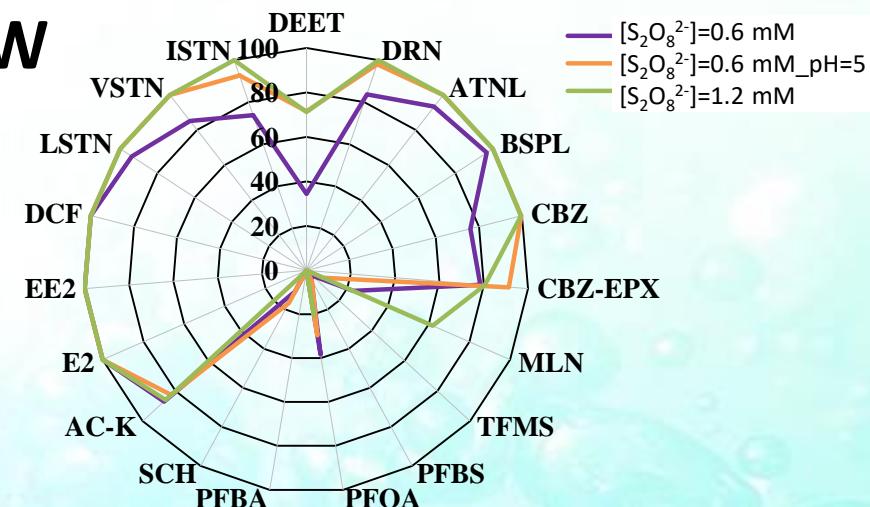
50%-60% removal for CBZ and AC-K
> 80% removal for 11/19 CECs

Not oxidized

MLN, SCH and 4 perfluorinated compounds

UF membrane coated with Ag_2MoO_4
Permeation $\text{S}_2\text{O}_8^{2-}$
UVC = 1.7 W; HRT = 73.2 s

UWW



- ✓ Partial recirculation: ↑ residence time (×12)
- ✓ Acidification pH 5: elimination of inorganic carbon species (CO_3^{2-} , HCO_3^-)

~ 20% PFOA and 60% - 70% removal DEET and MLN
> 80% removal for 12/19 CECs
Not oxidized SCH, TFMS, PFBS, PFBA

TUBE-IN-TUBE MEMBRANE REACTOR

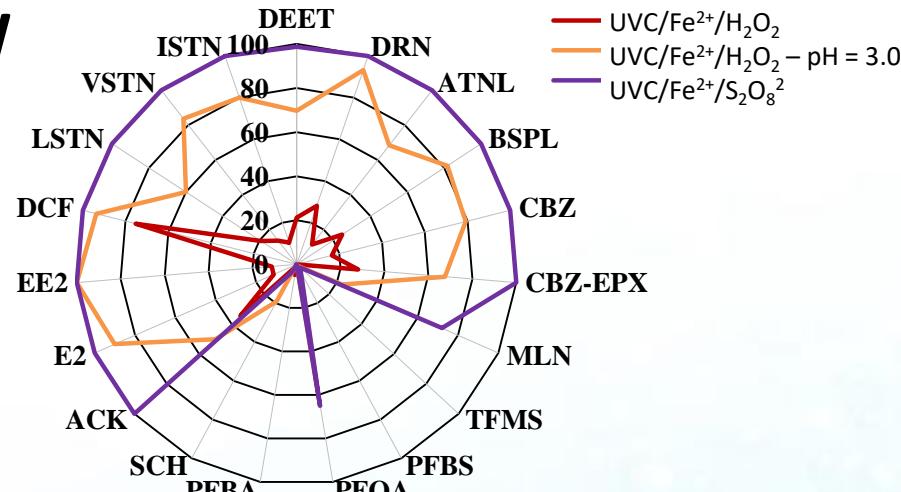
PERMEATION OF FERROUS SOLUTION

UF membrane - Permeation Fe^{2+} (2 mg L⁻¹)

H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (0.3 mM)

UVC = 1.7 W; HRT = 6.1 s

DW



Higher efficiency with $\text{UV}/\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$

60%-70% removal for MLN and PFOA
> 80% removal for 13/19 CECs

Not oxidized

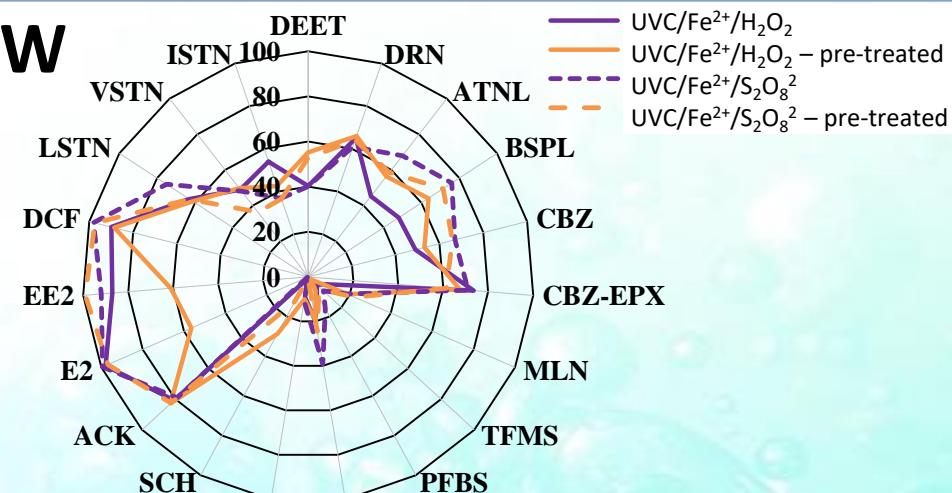
SCH and 3 perfluorinated compounds

UF membrane - Permeation Fe^{2+} (5 mg L⁻¹)

H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ (1.2 mM)

UVC = 1.7 W; HRT = 73.2 s

UWW



- ✓ No significant difference using H_2O_2 or $\text{S}_2\text{O}_8^{2-}$
- ✓ PO_4^{3-} precipitation occurs during the photo-treatment
- ✓ Pre-treatment (PO_4^{3-} precip./filtration) not required

~ 20% MLN; 40%-80% removal for 11/19 CECs (including PFOA)
> 80% removal for 3/19 CECs

Not oxidized SCH, TFMS, PFBS, PFBA



TUBE-IN-TUBE MEMBRANE REACTOR (OXIDATION - SMART DOSING OF OZONE)



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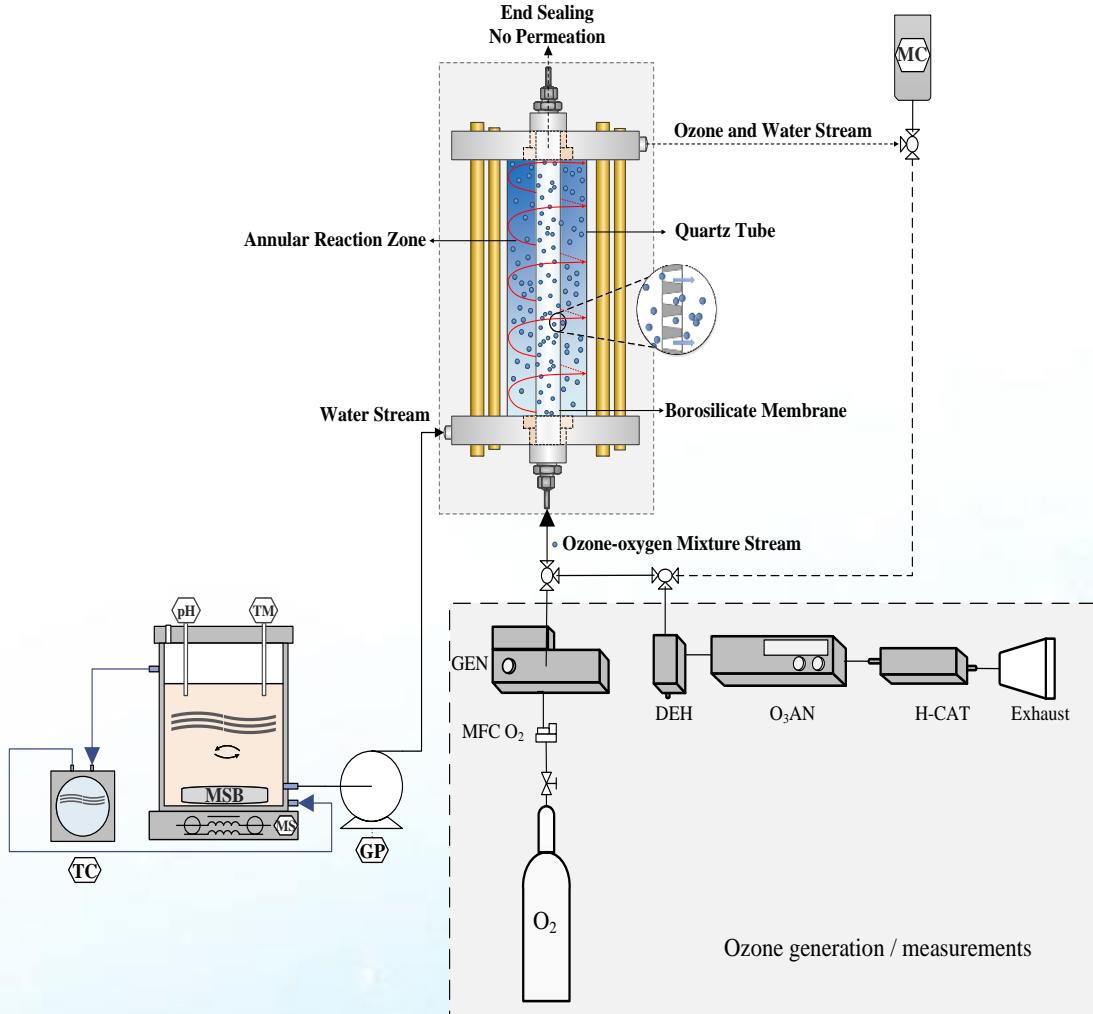
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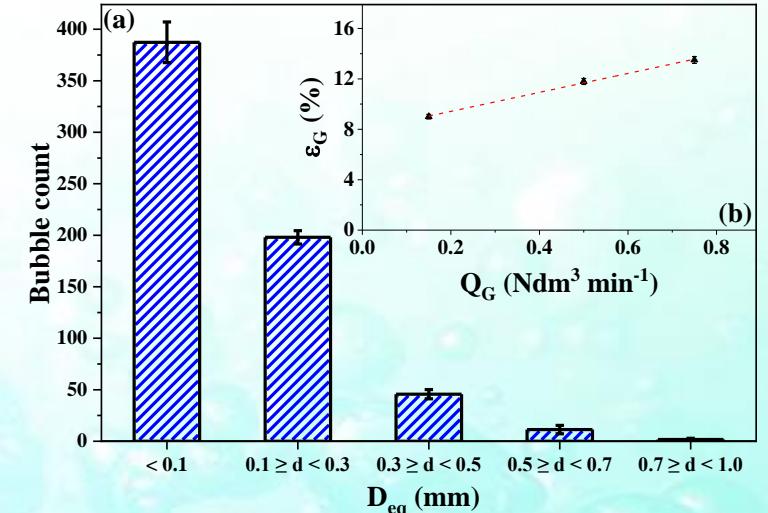
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TUBE-IN-TUBE MEMBRANE REACTOR

OZONE MEMBRANE CONTACTOR



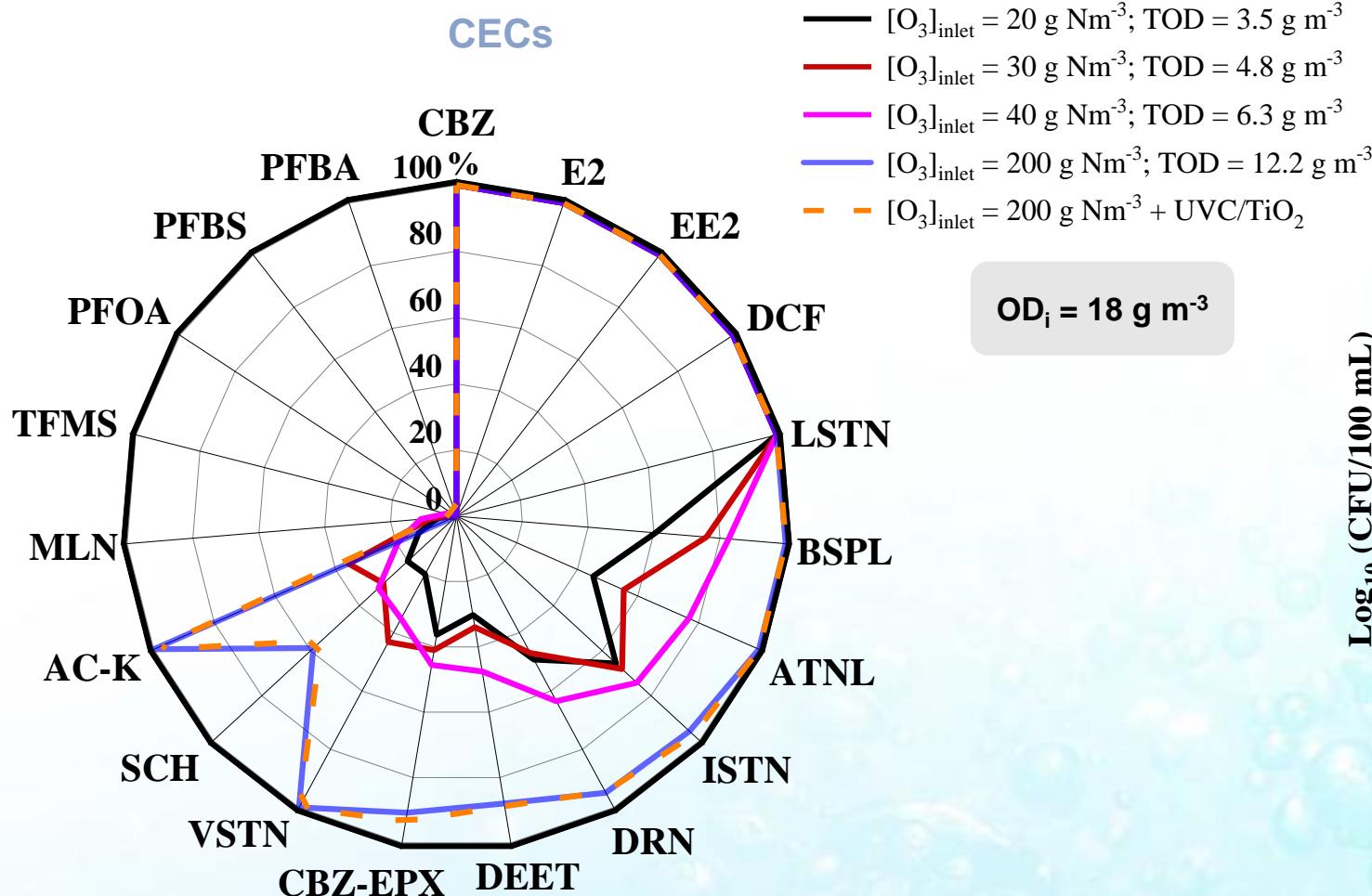
Bubble size distribution



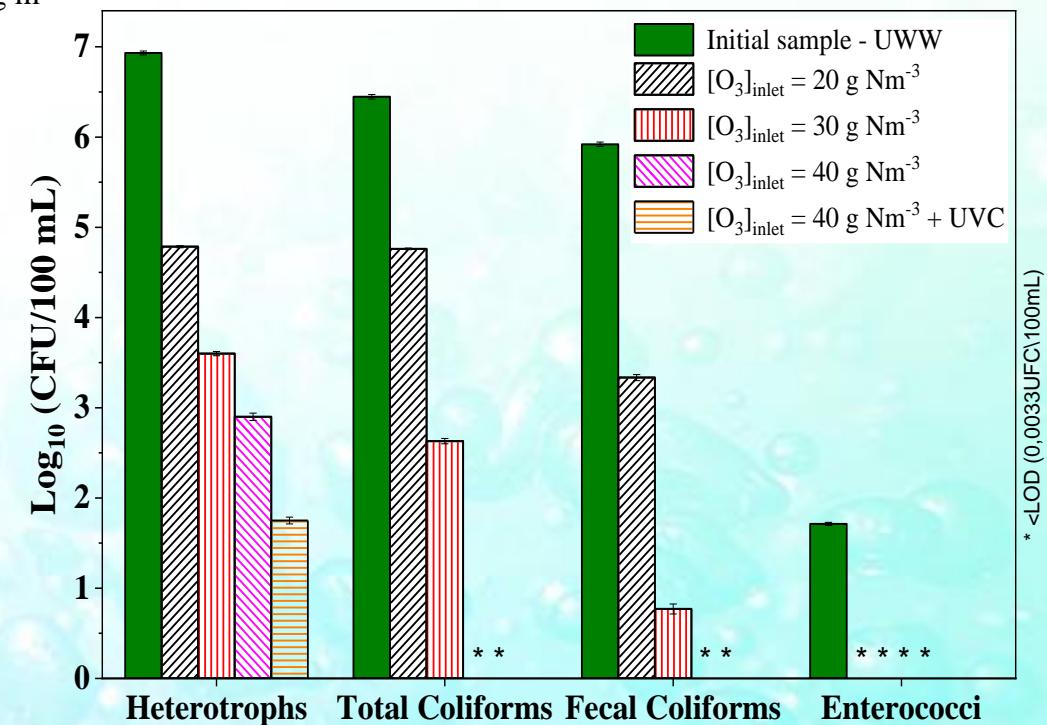
The O₃ is rapidly driven into the water through “virtually” unlimited number of O₃ addition points along the membrane length.

TUBE-IN-TUBE MEMBRANE REACTOR

OZONE MEMBRANE CONTACTOR: CECs removal and disinfection from UWW



Microbiology





PHOTOREACTOR FluHelik (ONGOING WORK)



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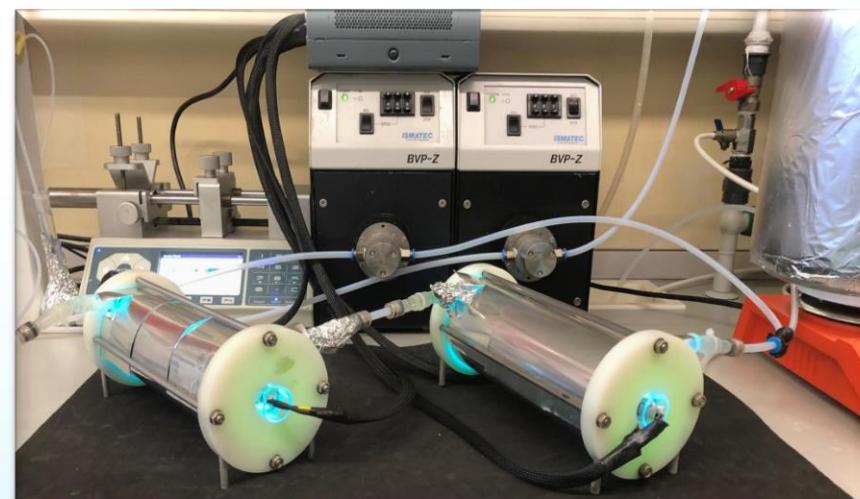
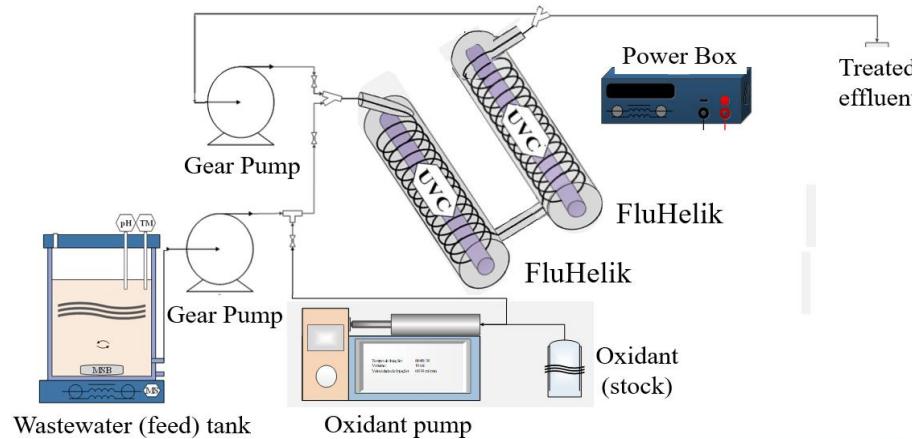
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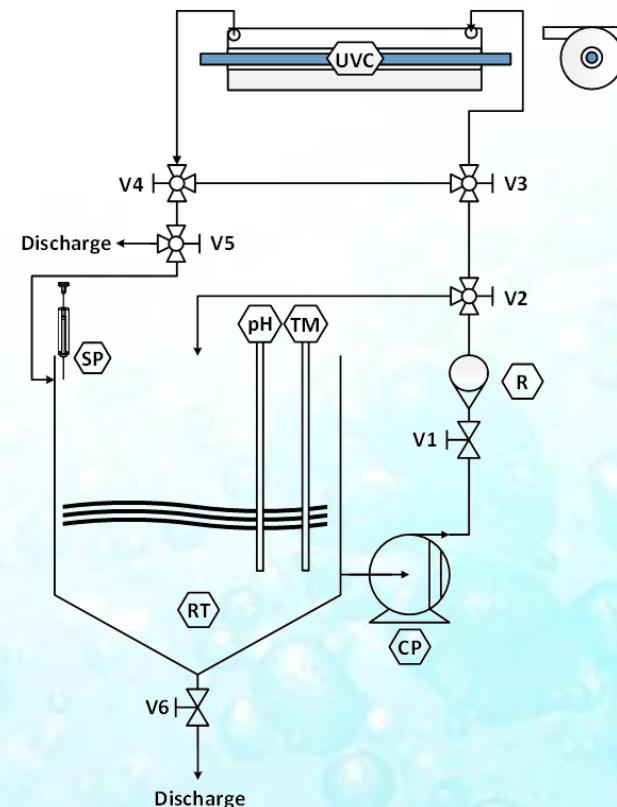
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PHOTOREACTOR: FluHelik

LAB-SCALE

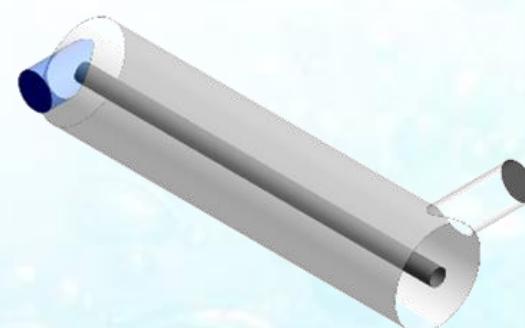
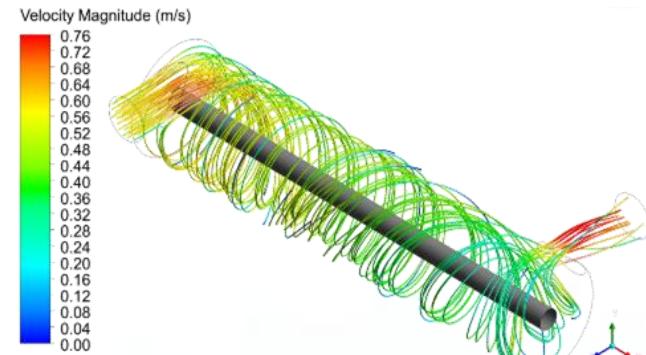
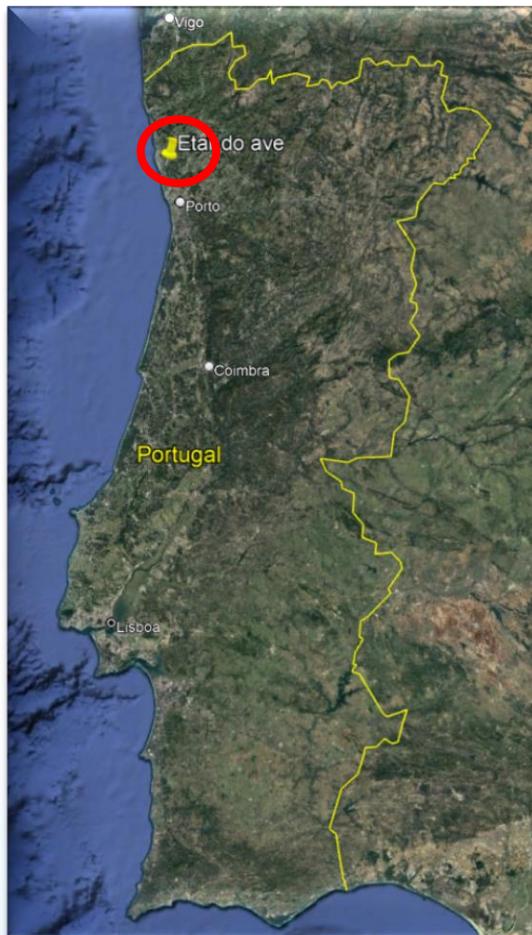


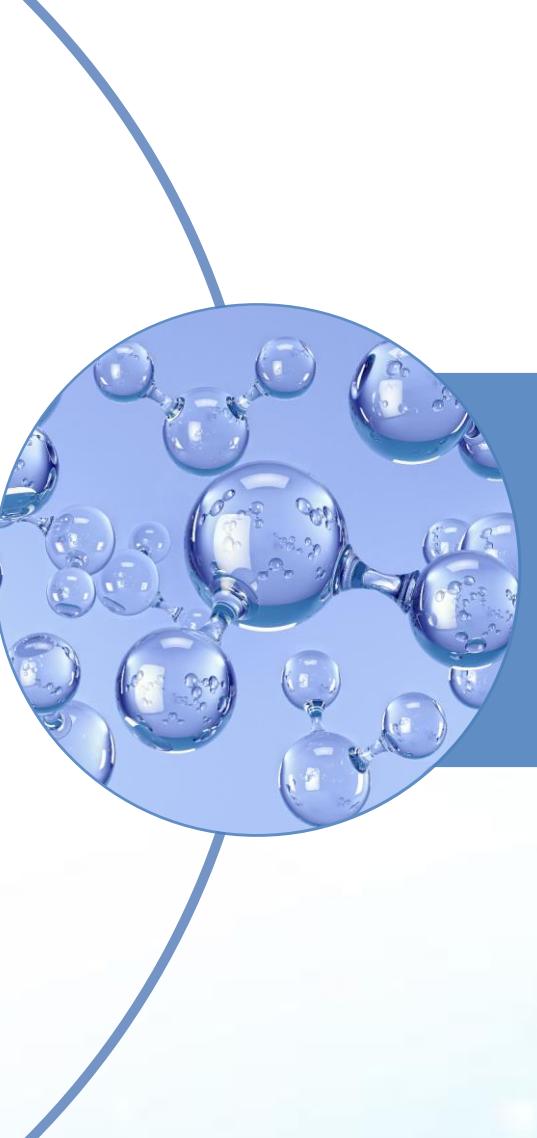
PILOT-SCALE



PHOTOREACTOR: FluHelik

PRE-INDUSTRIAL





FINAL REMARKS



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FINAL REMARKS

PHOTOCATALYTIC MEMBRANE REACTOR FOR CONCURRENT FILTRATION AND OXIDATION

PHOTOCATALYTIC MEMBRANE REACTOR FOR SMART DOSING OF OXIDANTS AND CATALYST

- **Oxidant-catalyst/water contactor**, was successfully applied for the **synergetic activation** of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ by energy (UVC photolysis), chemical electron transfer (TiO_2 -P25 or Ag_2MoO_4 photocatalysis) and chemical interaction with TiO_2 -P25 or Ag_2MoO_4 nanoparticles
- **O_3 -catalyst/water contactor**, was successfully applied for **CECs removal and disinfection of secondary UWW**

FLUHELIK PHOTOREACTOR: SIMPLE AND COMPACT TECHNOLOGICAL SOLUTION FOR SCALING-UP

- Ongoing work: pre-industrial scale with 4 FluHelik photoreactors coupled in series installed at a WWTP

ACKNOWLEDGMENTS



CIIMAR (Centro Interdisciplinar de Investigação Marinha e Ambiental, Univ. do Porto (Coordinador)



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Universidade de Santiago de Compostela



Laboratório Associado LSRE - LCM
(Laboratório de Processos de Separação e Reação - Laboratório de Catálise e Materiais), Univ. do Porto

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(Agência Portuguesa do Ambiente, IP - Administração da Região Hidrográfica do Norte)



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Asociación Naturalista "Baixo Miño"



EFACEC



Águas do Norte



Augas de Galicia



Confederación Hidrográfica del Miño-Sil, CHMS



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