Eliminación de contaminantes persistentes y móviles de las aguas residuales mediante tratamientos alternativos

Henry Beral, Jing Ma, Joaquim Comas, Jelena Radjenovic, Sara Rodríguez-Mozaz

Instituto Catalán de Investigación del Agua (ICRA), Girona

Santiago de Compostela,
8 de Noviembre 2024

Challenges posed by PMs

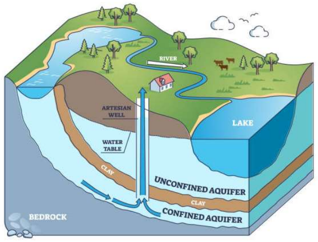
Persistent and Mobile substances (PMs)

not prone to be biodegraded or adsorbed by soils, riverbanks, aquifers or sediments

PMs **Wastewater**

Treated water

PMs



- **Conventional wastewater treatment** plant (EDAR)
  - Incomplete removal of **PMs**

- **Advance/alternative water treatment** methodologies are needed

Introduction : Alternative Wastewater Treatement

Biological treatments	Physico-chemical treatments	Physical treatments	Chemical treatments
Membrane bioreactors	Ozonation	(Micro/ultra/nano) Filtration	Chlorination
Fungi	UV/H_2O_2	Reverse Osmosis	
Microalgae	Fenton	Adsorption to activated Carbon	
Nature Based solutions	Electrochemical treatment		

Eliminación de contaminantes persistentes y móviles de las aguas residuales mediante tratamientos alternativos

Soluciones Basadas en la Naturaleza
Nature Based Solutions **(NBS)**

Introduction : NBS

Las Soluciones basadas en la Naturaleza (NBS) *integran características y procesos naturales en entornos urbanos, paisajes terrestres y marinos a través de intervenciones sistémicas, localmente adaptadas y eficientes en el uso de los recursos. Las NBS también favorecen la biodiversidad y el bienestar humano (Comisión Europea, 2016).*

European Commission

IUCN International Union for Conservation of Nature

Circular City
circular-city.eu

NBS son **sistemes inspirados en la naturaleza** y ofrecen beneficiós ambientales, sociales y económicos.

NBS dan respuesta a los **RETOS** de la sociedad.

RETOS

Cambio climático

Salud humana

Seguridad hídrica

biodiversidad

desastres naturales

Desarrollo economico

seguretat alimentària

Desarrollo social

Introduction : NBS

Treatment wetland

Bioretention

Green Wall

Green Roof

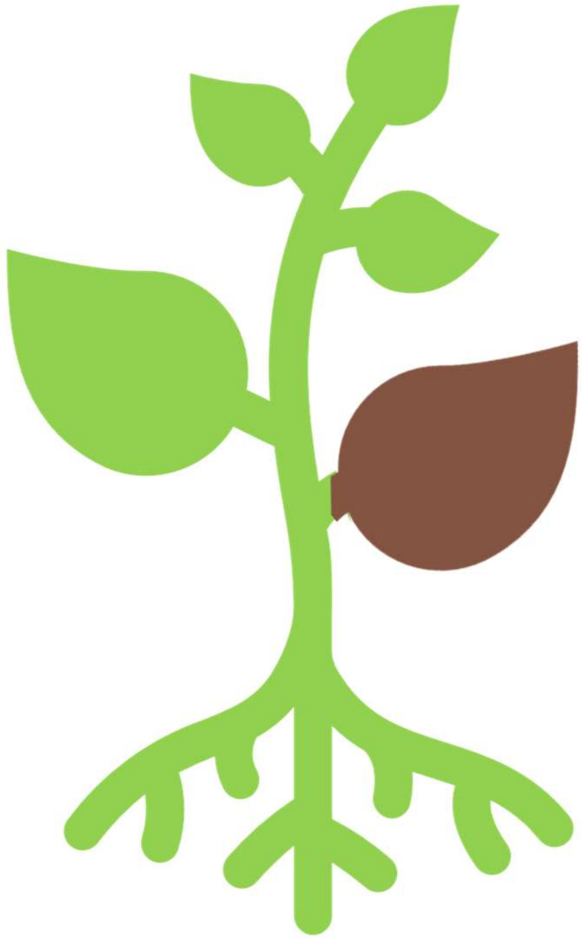
Tree pit

BGIs

Introduction : Phytoremediation

BGIs

PMTs



Biological process

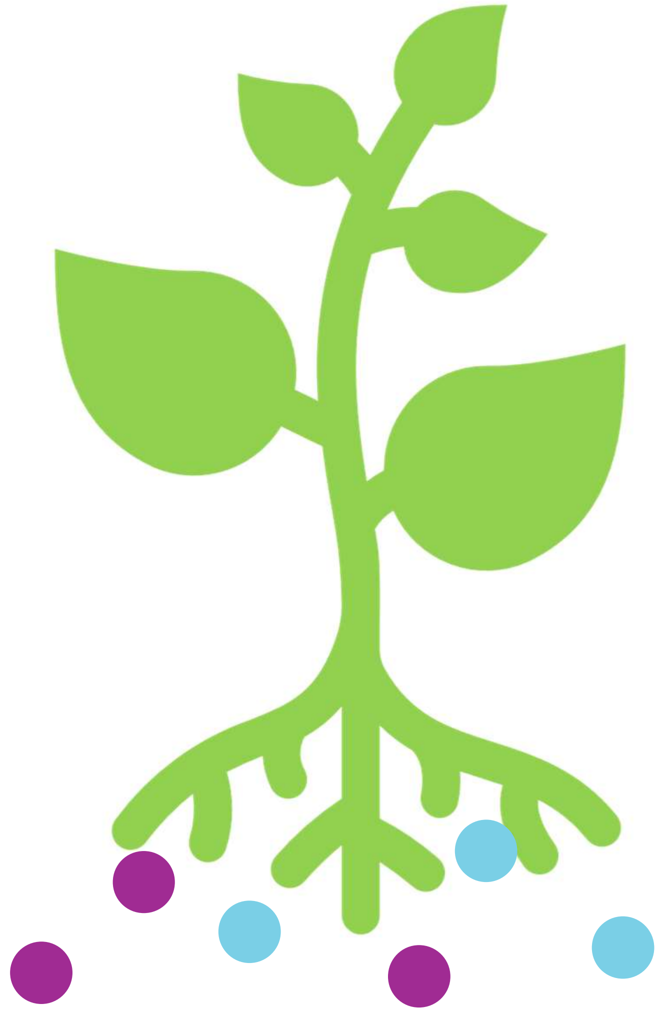
- Plant uptake
- Translocation
- Transformation
- (Phytotoxicity)

Objectives : Phytoremediation

PHN
Phenazone

DTG
1,3-dio-tolyl guanidine

PMTs



Biological process

- Plant uptake
- Translocation
- Transformation
- (Phytotoxicity)

M&M: The hydroponic system

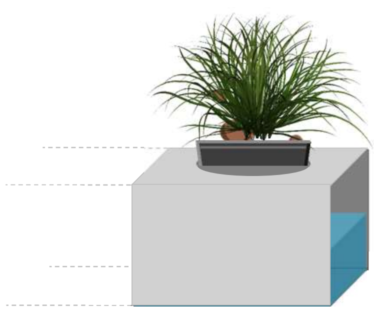
RBW LED lamp

Carex flacca

LECA (lightweight expanded clay aggregate)

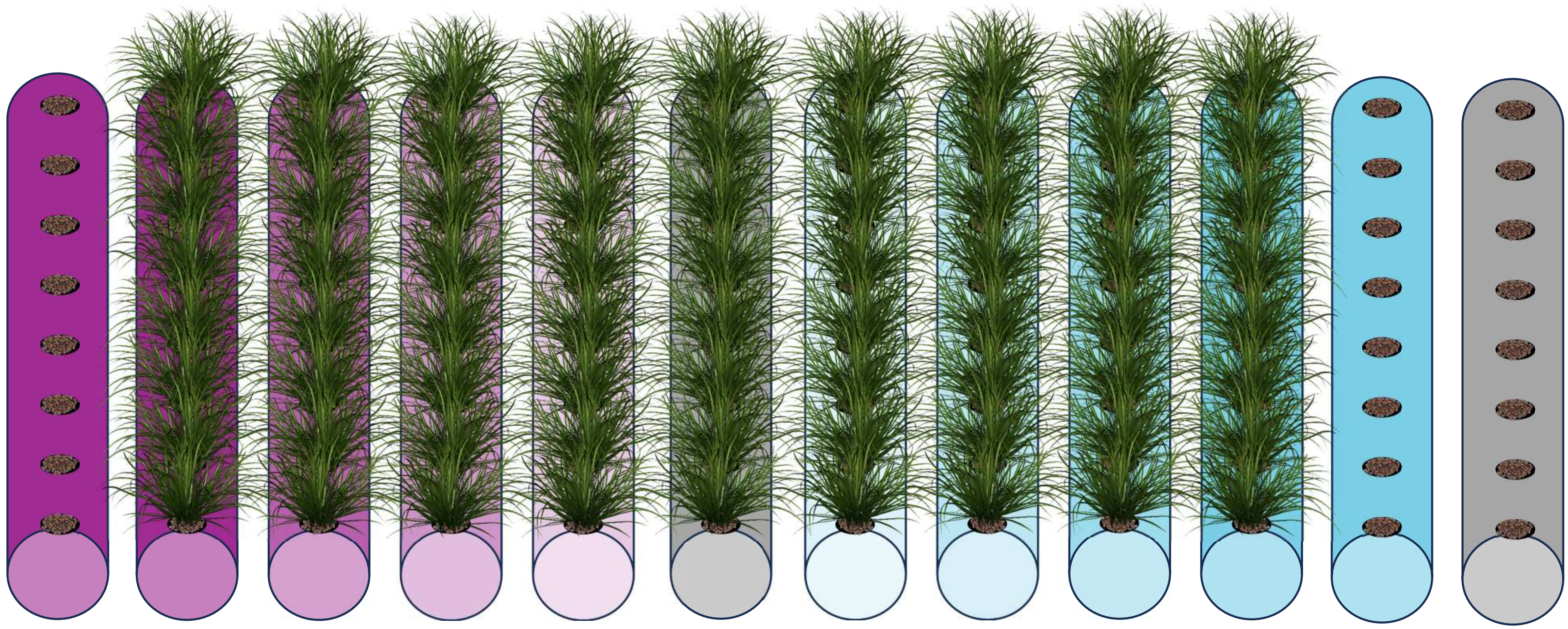
Pot

Kratky hydrop. system



M&M: Experimental design

Spiked PMT
- DTG
- PHN



Concentration µg/L:	1000	1000	100	10	1	0	1	10	100	1000	1000	0
Replication:	X1	X1	X1	X1	X1	X4	X1	X1	X1	X1	X1	X1

PHN Control +	Phytotoxic threshold Biomass for tissue analysis	WT	Phytotoxic threshold Biomass for tissue analysis	DTG Control +	Control -

M&M: Experimental design

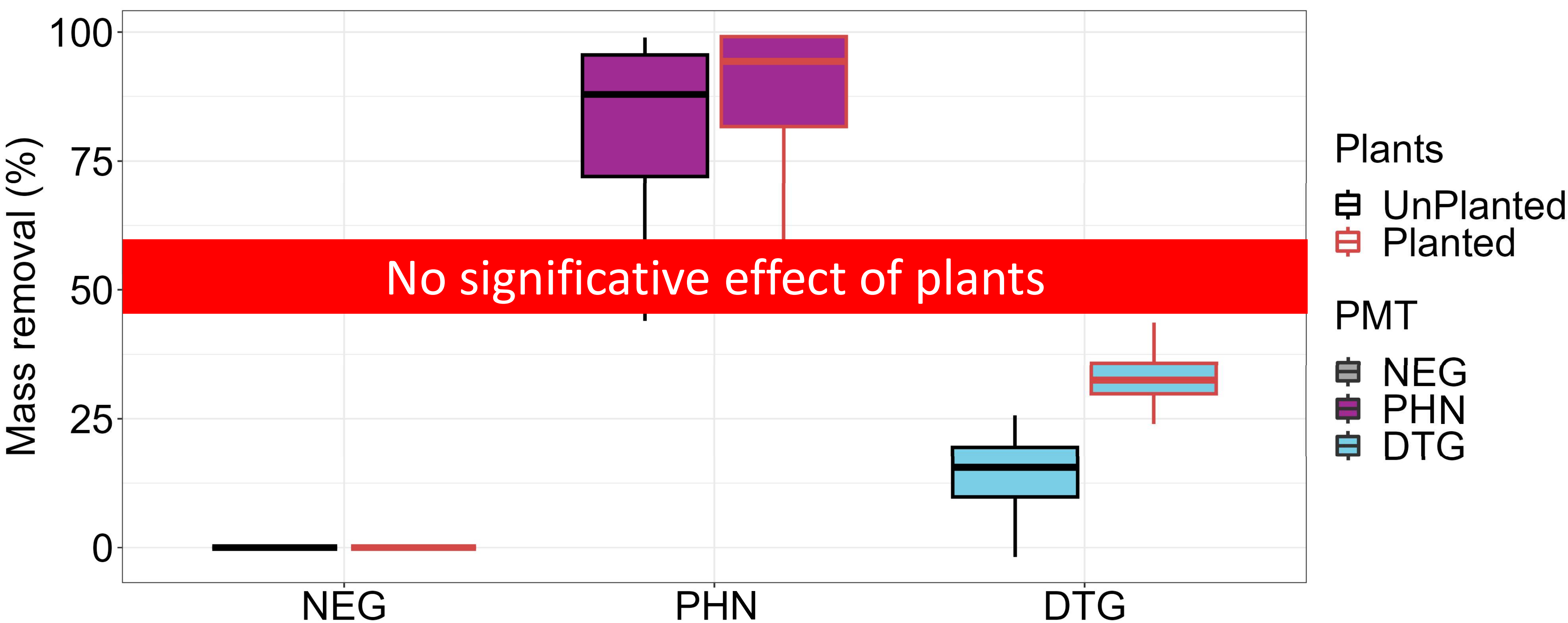
M&M: The watering

1.5L

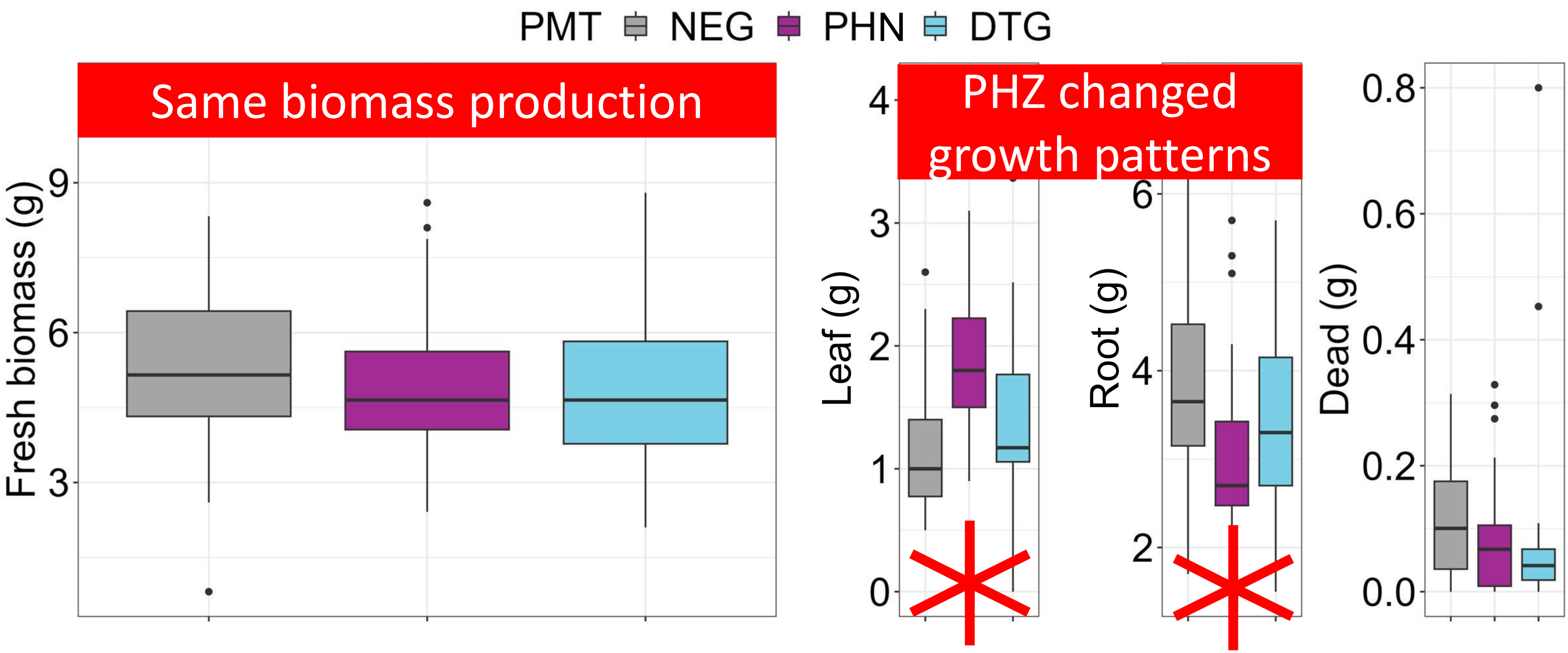
2 watering/week
4 weeks

Hoagland II nutrition solution	mg/L
Ammonium Phosphate	115.0
Boric Acid	2.9
Calcium Nitrate	656.4
Cupric Sulfate• 5H	0.1
Na 2 -EDTA	33.5
Ferrous Sulfate• 7H	25.0
Magnesium Sulfate	240.8
Manganese Chloride· 4H	1.8
Molybdenum Trioxide	0.02
Potassium Nitrate	606.6
Zinc Sulfate• 7H	0.2

Results : Removal from water



Results : Phytotoxicity and growth patterns

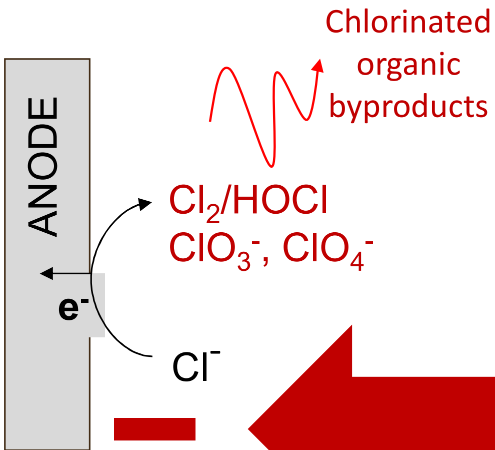


Eliminación de contaminantes persistentes y móviles de las aguas residuales mediante tratamientos alternativos

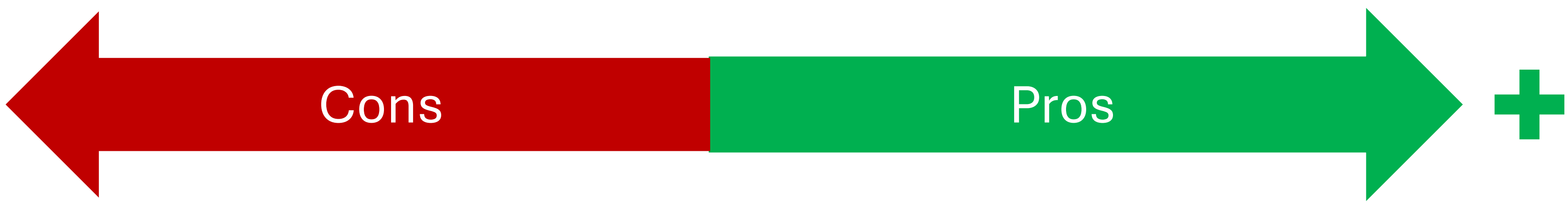
Sistemas electroquímicos de tratamiento

Electrochemical Systems **(EC)**

Electrochemical system for PMs removal



Why Electrochemical water treatment systems?



- Generation of **toxic and persistent organic chlorinated byproducts**, as well as chlorate and perchlorate at high anodic currents required for the degradation of organic pollutants.

- **High anode price** (e.g., boron-doped diamond (BDD): €6,000/m^2) limits the employed anode surface area, which translates into **high energy consumption**.

- Modular design and small footprint makes them very well-suited for **decentralized and distributed (waste)water treatment.**

- **Robust** operation; variations in influent composition and flowrate are easily managed.

- Operation **ambient temperature and pressure**.

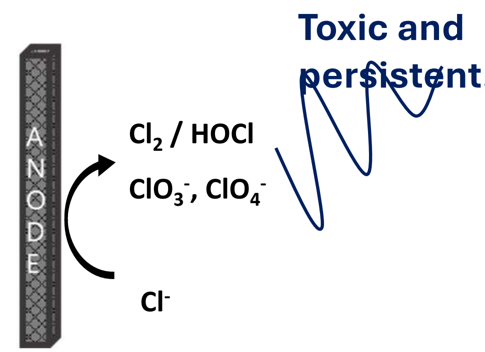
- **Chemical-free process**; strong oxidant species ($OH^{\bullet}$, O_3, H_2O_2) are formed *in situ.*

Electrochemical system for PMs removal

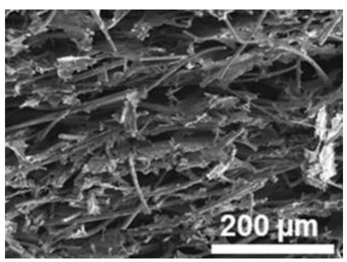
- ## Commercial Electrode Materials

E.g. MMO, BDD, Ti_4O_7, …

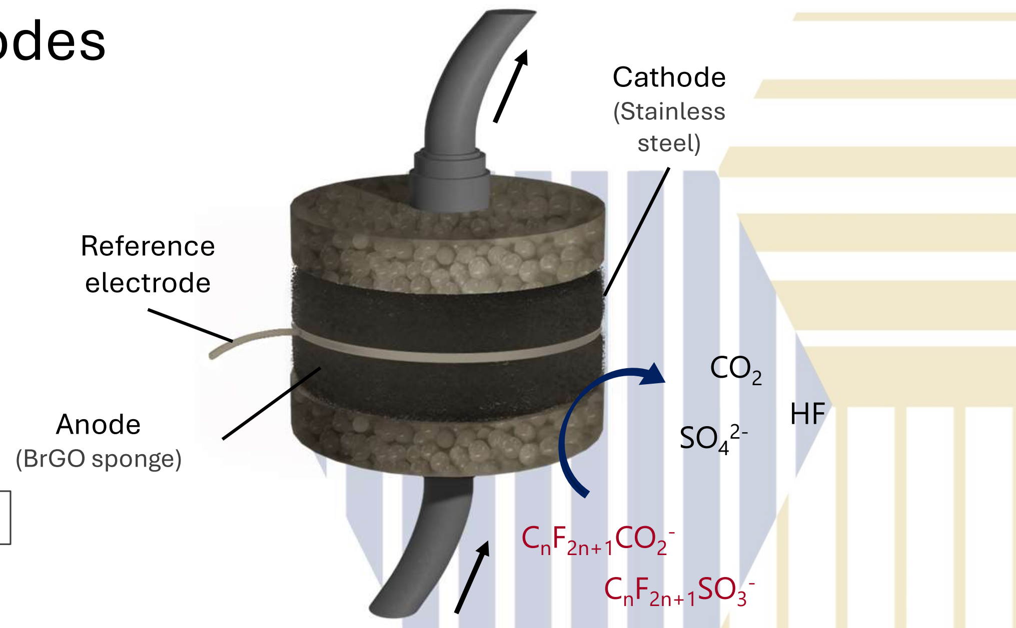
Oxidation of Cl^- through → direct electrolysis / → reaction with $OH^{\bullet}$



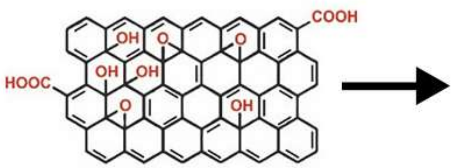
- ## Graphene-based sponge electrodes
  - Current efficiency for Cl_2 & HOCl formation 0,04%
  - No formation of ClO_3^- & ClO_4^-



L. Baptista-Pires, G. Norra, J. Radjenović, *Graphene-based sponges for electrochemical degradation of persistent organic contaminants*, ***Water Research***, Volume 203, 2021, 117492, https://doi.org/10.1016/j.watres.2021.117492.

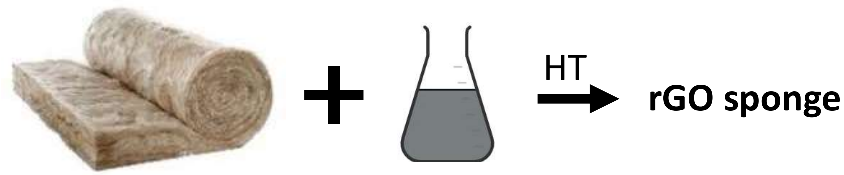


Reduced graphene oxide sponge



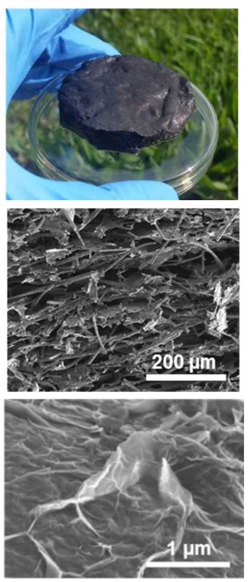
Graphene oxide
(0.02 S/m)

Reduced graphene oxide
(225 S/m)



Mineral wool

Graphene oxide



WO2022069621A1

☑ Synthesized by easily scalable, low-cost (< 50 €/m²) method

☑ Electrode that is mechanically and electrochemically stable

☑ Synthesized method and its 3D geometries allow easy introduction of dopants to tailor its electrocatalytic activity

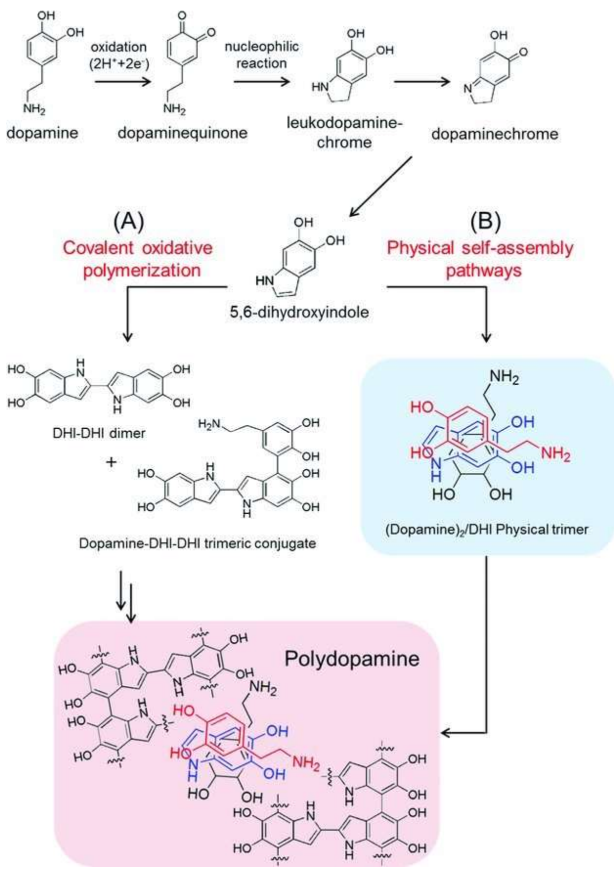
☐ Increase hydrophilicity

☐ Introduction of functional groups

} Polydopamine

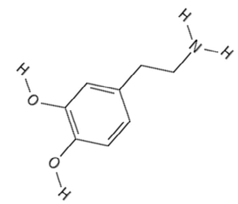
HT – Hydrothermal process, rGO – Reduced graphene oxide

Polydopamine doped rGO sponge



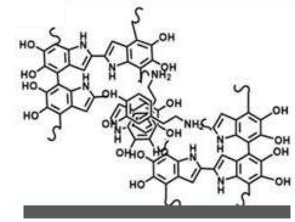
rGO sponge

\+

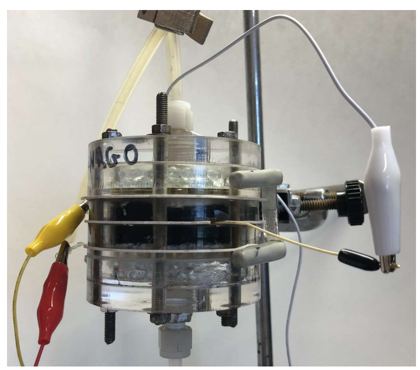


Dopamine

pH 8.5



Polydopamine/rGO

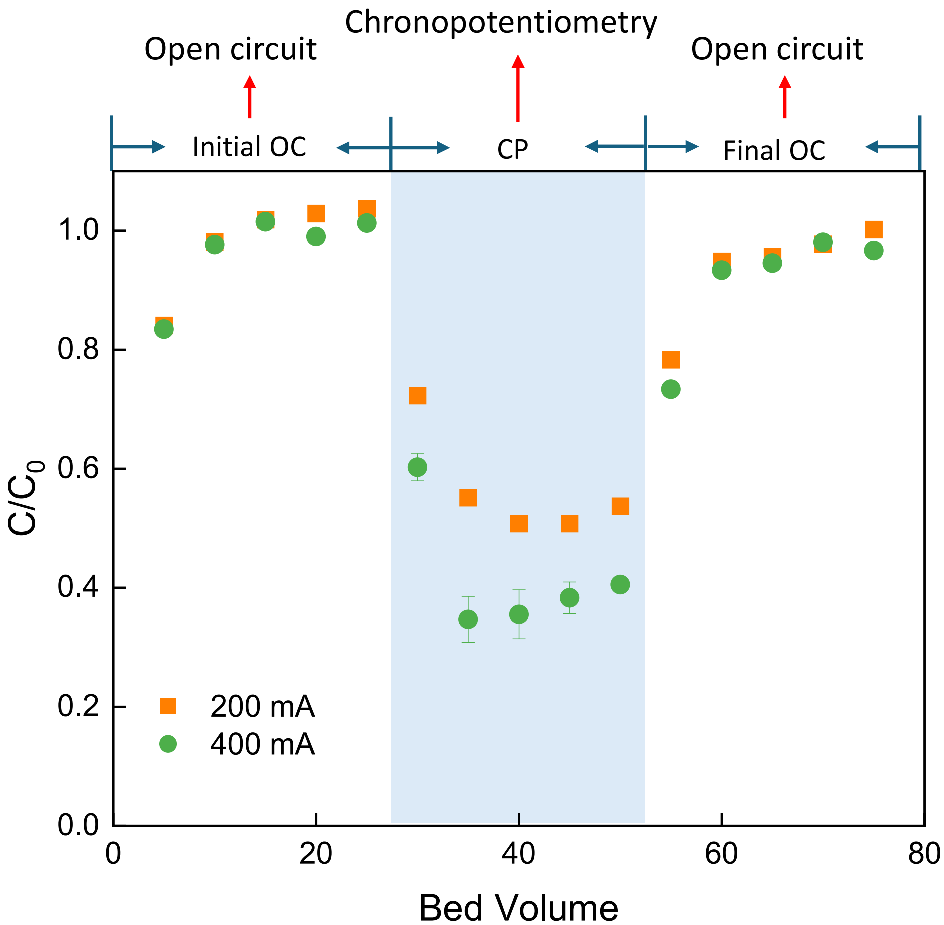


Removal of PMs

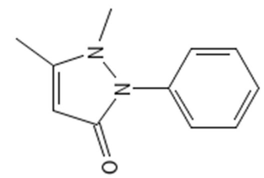
- Phenazone (PHZ)
- 1,3-dio-tolylguanidine (DTG)
- Tris-chloroethyl phosphate (TCEP)
- Perfluorobutanoic acid (PFBA)
- Trifluoroacetic acid (TFA)

Adv Funct Materials, 2012, 22, 4711-4717

PMs removal by PDA/rGO



Phenazone



pK_a= 1.4

log D (pH 7.3)=1.22

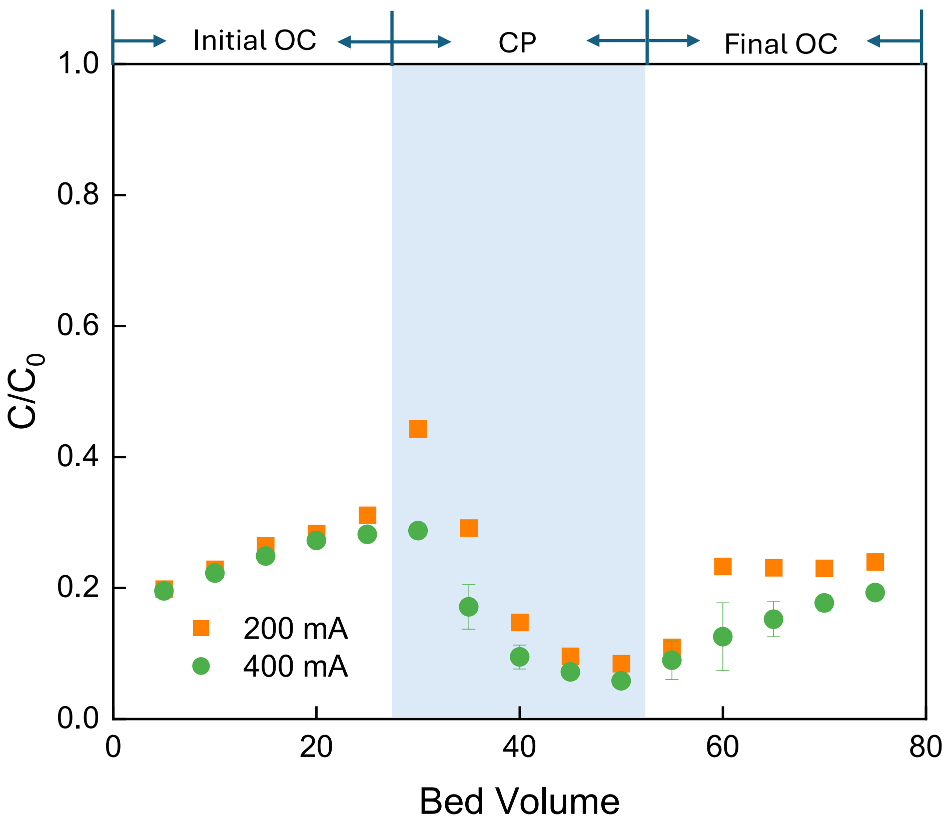
Neutral

- Phenazone doesn't tend to be adsorbed or electrosorbed on PDA-doped rGO
- Increasing applied current density promotes higher phenazone removal efficiency due to higher production of oxidants

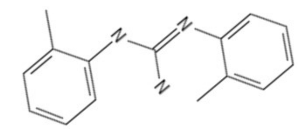
Cathode: stainless steel, C_0 = 0.2 µM, electrolyte: 10 mM PB (~ 1 mS cm^{-1}, pH 7), flow rate: 5 ml min^{-1}

PDA - Polydopamine

PMs removal by PDA/rGO



1,3-dio-tolylguanidine



pK_a=9.43

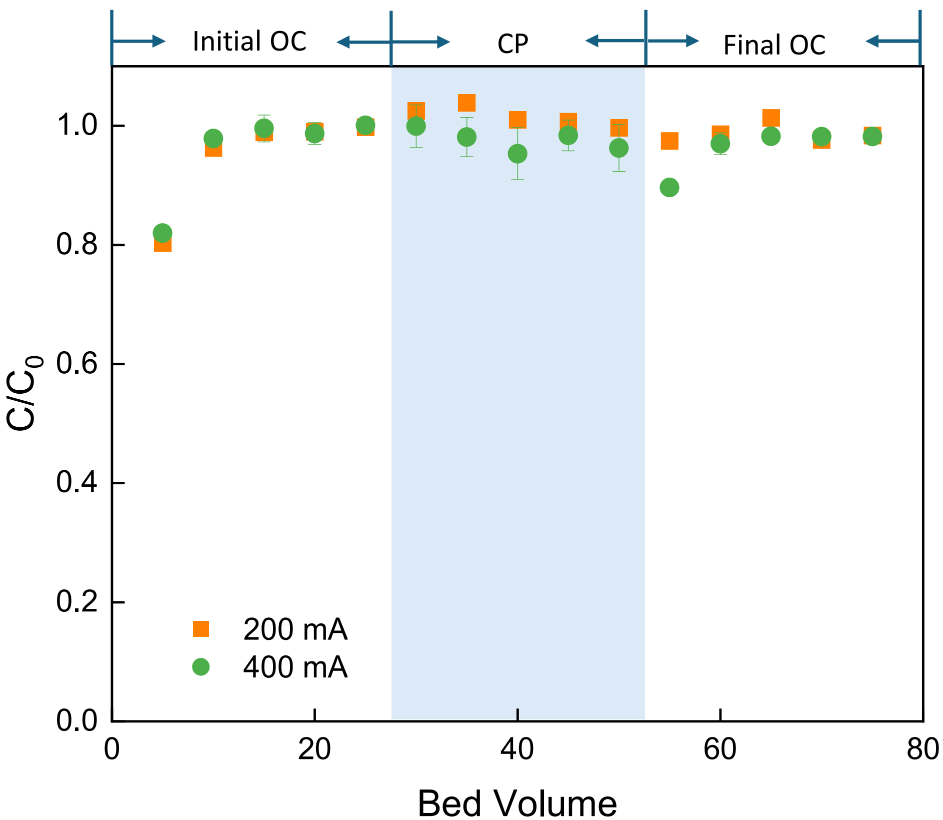
log D (pH 7.0)=2.25

Positive

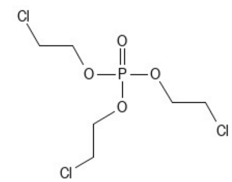
- Negatively charged PDA/rGO can adsorb positively charged DTG through electrostatic attraction
- π-π interactions might also contribute to DTG adsorption
- PDA/rGO can degrade DTG efficiently through direct electron transfer and oxidant-mediated oxidation

Cathode: stainless steel, C_0 = 0.2 µM, electrolyte: 10 mM PB (~ 1 mS cm^{-1}, pH 7), flow rate: 5 ml min^{-1}

PMs removal by PDA/rGO



Tris-chloroethyl phosphate



pK_a=7.7

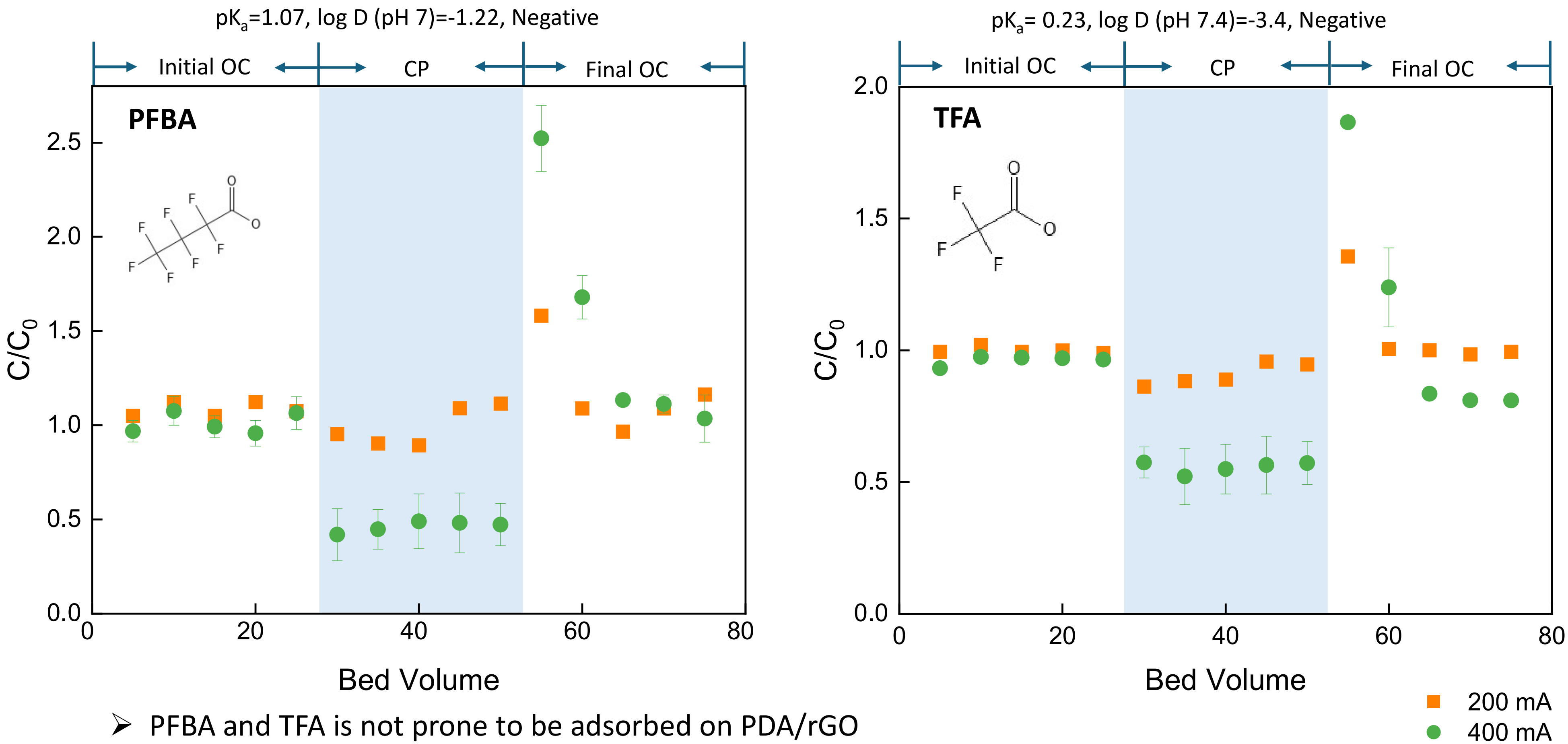
log D (pH 7.4)=0.48

Neutral

- TCEP can hardly be removed due to its neutral charge, lack of π-π electron donor-acceptor interactions and hydrogen bond interactions

Cathode: stainless steel, C_0 = 0.2 µM, electrolyte: 10 mM PB (~ 1 mS cm^{-1}, pH 7), flow rate: 5 ml min^{-1}

PMs removal by PDA/rGO



- PFBA and TFA is not prone to be adsorbed on PDA/rGO
- Application of electric field promotes PFBA and TFA removal via electrosorption

Cathode: stainless steel, C_0 = 0.2 µM, electrolyte: 10 mM PB (~ 1 mS cm^{-1}, pH 7), flow rate: 5 ml min^{-1}

Conclusions and future work

Nature Based Solutions

- Effective mass removal of DTG 25% and PHN (80%) , but no clear influence of the plant CAREX FLACCA
- Next Steps: Looking for plant accumulation and PM transformation products and investigate other PMs and plants

Electrochemical Systems

- PMs can be removed by PDA/rGO through different adsorption/degradation mechanisms due to its abundant functional groups
- Next Step: Introduction of secondary dopant or catalyst might boost degradation efficiency of PMs

Future Work

- Coupling of NBS with EC systems

NePMTune

Grazes
Gracias
Obrigada

HR EXCELLENCE IN RESEARCH
Universitat de Girona
Agència Catalana de l'Aigua
CERCA Centres de Recerca de Catalunya
CERCAGINYS
Generalitat de Catalunya
MINISTERIO DE CIENCIA E INNOVACIÓN
ICRA Institut Català de Recerca de l'Aigua
www.icra.cat