Graphene cOmposites FOR advanced drinking WATER treatment

GO-FOR-WATER

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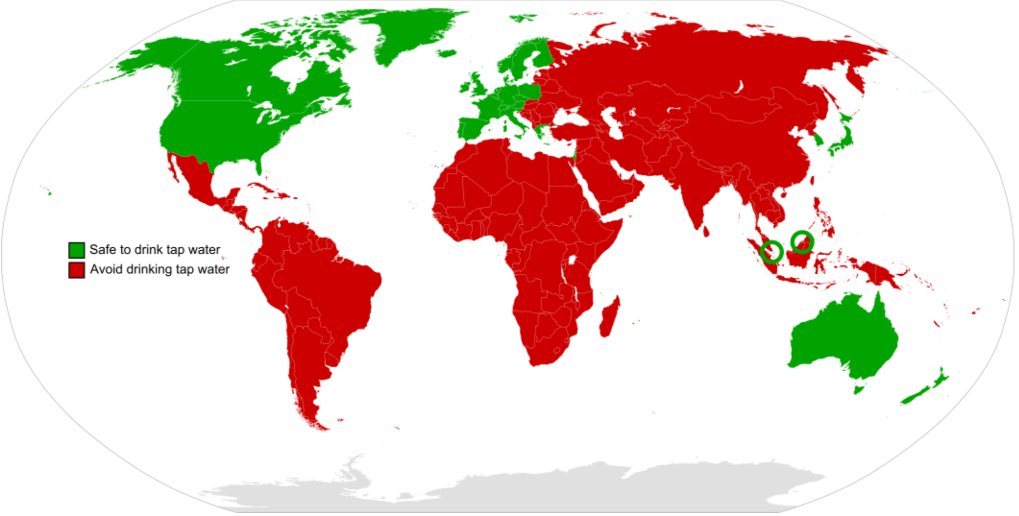
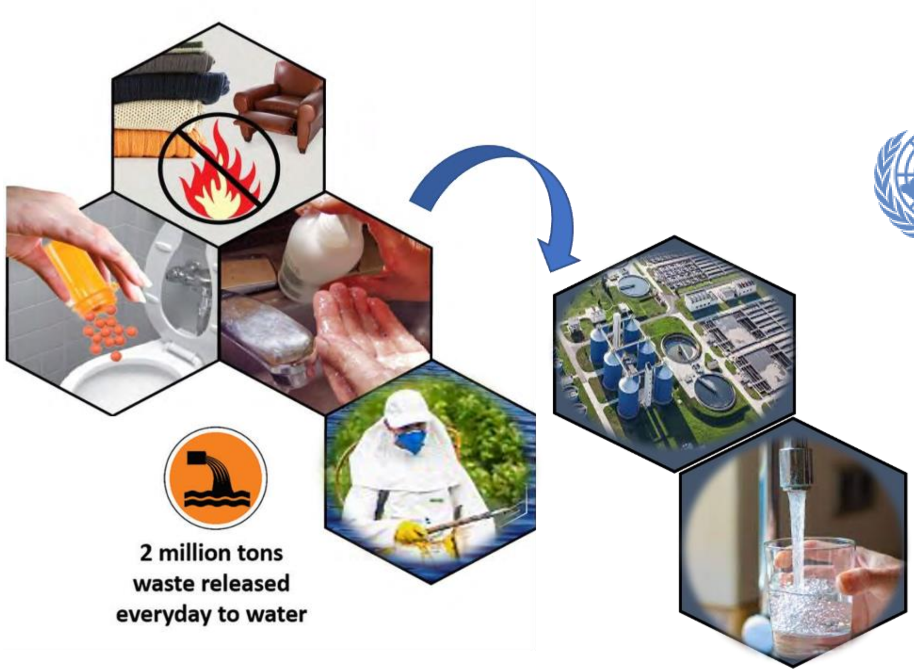
WATER CHALLENGES

Emerging Contaminants (ECs)

- Pharmaceuticals and Personal Care Products (PPCP), Hormones, Stain repellants/non- stick surfaces (PFAS), Metals, Fertilizers, Pesticides, Plasticizers
- More than 30000 new products every year
- Not fully removed by conventional technologies





https://sdgs.un.org/goals

European Parliament

New Drinking Water Directive
EU 2020/2184

SAFETY	MONITORING	ACCESSIBILITY

12/01/2021

https://eur-lex.europa.eu/eli/dir/2020/2184

https://www.theguardian.com/environment/2022/jan/18/chemical-pollution-has-passed-safe-limit-for-humanity-say-scientists

CONSORTIUM

NATIONAL RESEARCH COUNCIL (CNR-ISOF, BOLOGNA CNR- IRSA, ROME, ITALY)	UNIVERSITY OF PATRAS (UP)	SABANCI UNIVERSITY (SU) INSTANBUL (TK)	CHALMERS UNIVERSITY (CUT), GOTHEBORG, (SE)
PI: M. Melucci B. Casentini (IRSA) S. Amalfitano (IRSA) V. Palermo (ISOF) M. L. Navacchia (ISOF) A. Kovtun (ISOF), B. F. Tunioli (ISOF)	**PI: C. Galiotis** G. Gorgolis G. Paterakis C. Androulidakis I. Sfougaris	**PI: B. Saner Okan** Prof. Y. Menceloglu M. Hezarkhani M.S. Sorayani Bafqi	**PI: Z. Xia**

Technical contributions

- **GRAPHENE FUNCTIONALIZATION**
- **WATER TREATMENT**
- **WATER QUALITY**

- **AEREOGELS**
- **GRAPHENE COMPOSITES**

- **GRAPHENE FROM WASTES**
- **GRAPHENE COMPOSITE MEMBRANES**

- **MULTIPHASE CHARACTERIZATION**

GO-FOR-WATER Pert chart

m1

TRL 4 — Phase 1

TRL 4/5 — Phase 2

TRL 7 — Phase 3

m36

WP1:
Project management and dissemination
Lead: CNR, Partners: all (m1-m36)

WP2:
GRM synthesis and structure-property relationships
Lead: CUT, Partners: CNR, SU
(m1-m18)

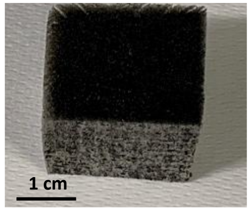
WP3:
GRM deposition/processing in 3D structures and characterization
Leaders: SU-UP, Partners: CUT, CNR
(m6-m24)

WP4:
Performances in small scale filters
Lead: CNR, Partners: UP, CUT
(m9-m30)

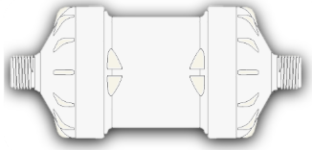
WP5:
Filters scale up and integration in POU pilot line
Lead: CNR, Partners: UP, CUT, SU
(m18-36)

WP2

WP3

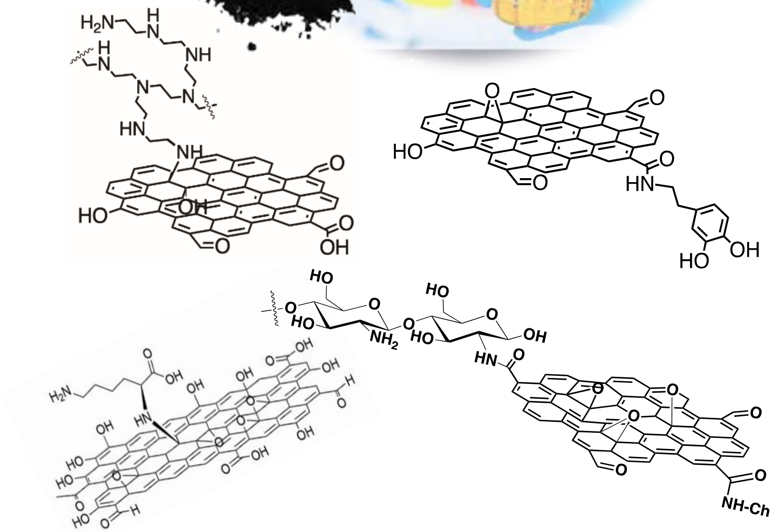


WP4



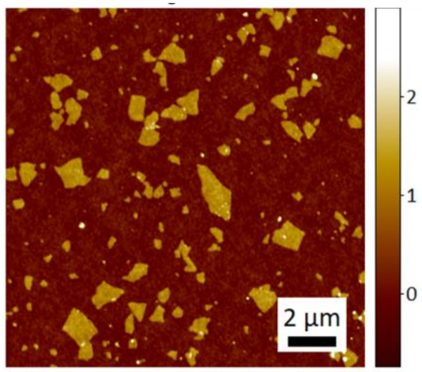
WP5

TAILORING GRAPHENE MATERIALS AND COMPOSITES FOR WATER PURIFICATION



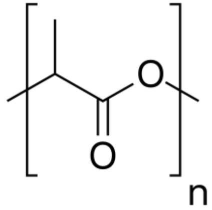
- Chemical tailoring for specific sorption
- Kinetic–efficiency
- Working mechanism
- Regeneration
- Safety

2D → 3D

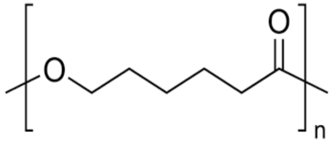


NATURAL POLYMERS for 3D assembling

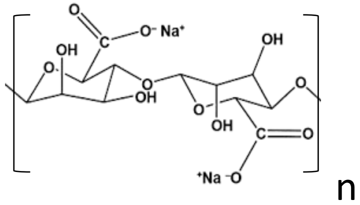
Polylactic acid (PLA)



Poly(ε)-caprolactone (PCL)



Sodium Alginate

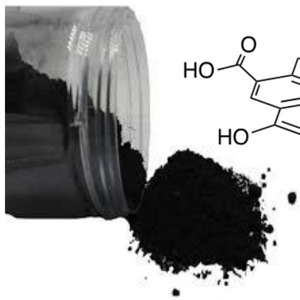


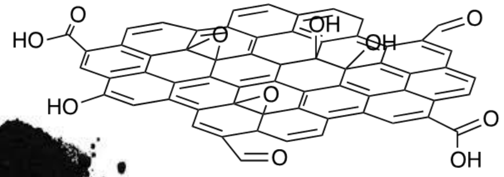
Membrane

Aerogel

Beads

CARBON NANOMATERIALS and TESTED CONTAMINANTS

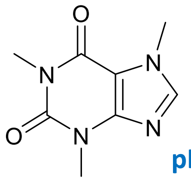




Graphene Oxide

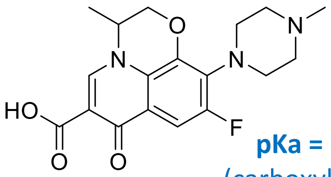
	GO	rGO	GNP	GAC
O/C	0.350 ± 0.001	0.010 ± 0.003	0.050 ± 0.005	-
Surface A (m^2/g)	1191	378	148	1000
ζ Potential (mV)	-43.1 ± 2.4	-35.3 ± 3.1	-39.2 ± 1.1	-
pH in H_2O TAP	6.60	7.29	7.19	7.21

Mix of 8 Emerging Organic Contaminants (MIX8)



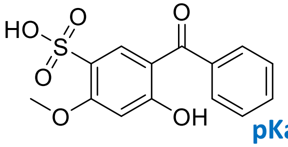
pKa= 14

Caffeine, CAF



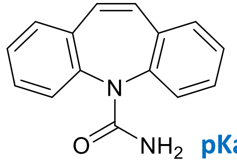
pKa = 5.97
(carboxylic acid)

Ofloxacin, OFLOX



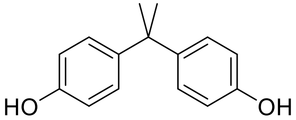
pKa = 7.6
(hydroxyl)

Benzophenone-4, BP4



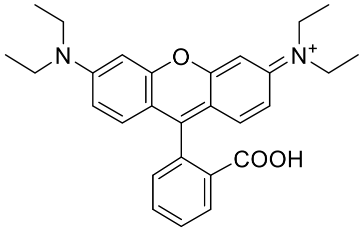
pKa = 13.9

Carbamazepine, CBZ

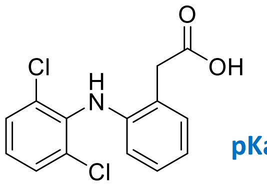


pKa = 9.6

Bisphenol A, BPA

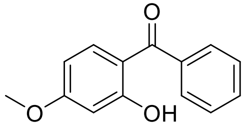


Rhodamine B, RhB



pKa = 4.15

Diclofenac, DCF



pKa = 7.1

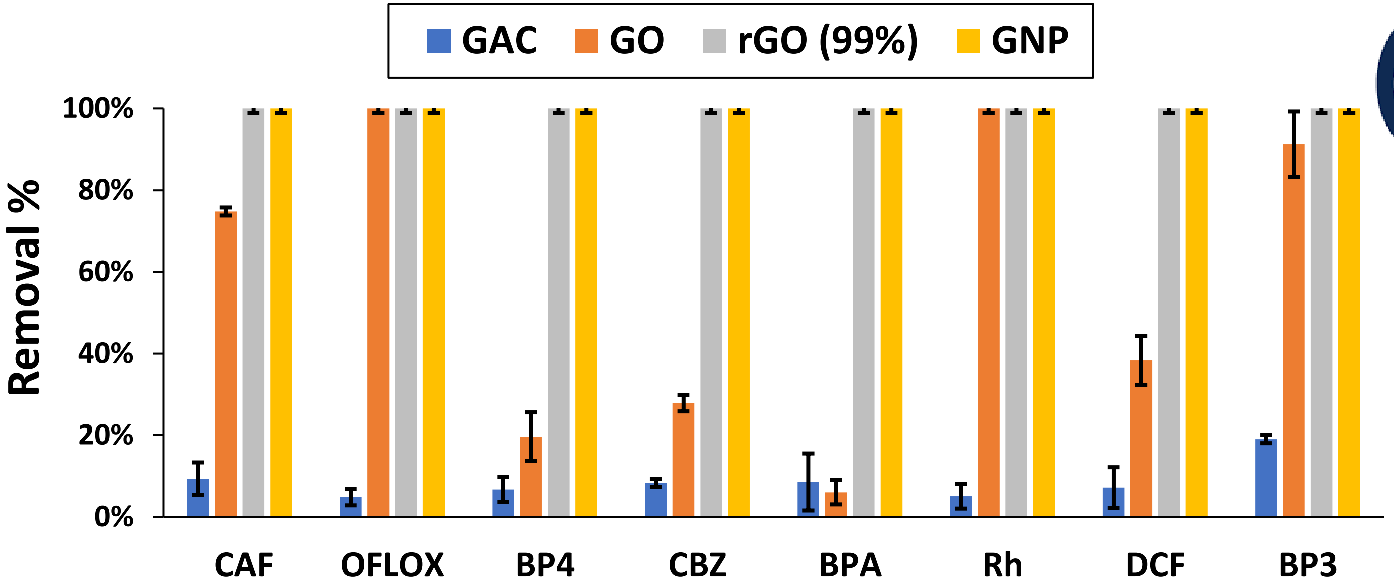
Benzophenone-3, BP3

Mix of Metals

Silver (**Ag**)	Lead (**Pb**)
Arsenic (**As**)	Antimony (**Sb**)
Cadmium (**Cd**)	Selenium (**Se**)
Chromium (**Cr**)	Uranium (**U**)
Copper (**Cu**)	Zinc (**Zn**)
Nickel (**Ni**)	

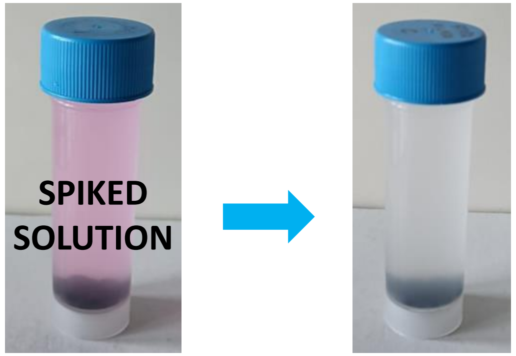
SELECTIVITY TEST IN BATCH CONDITION

ORGANIC CONTAMINANTS

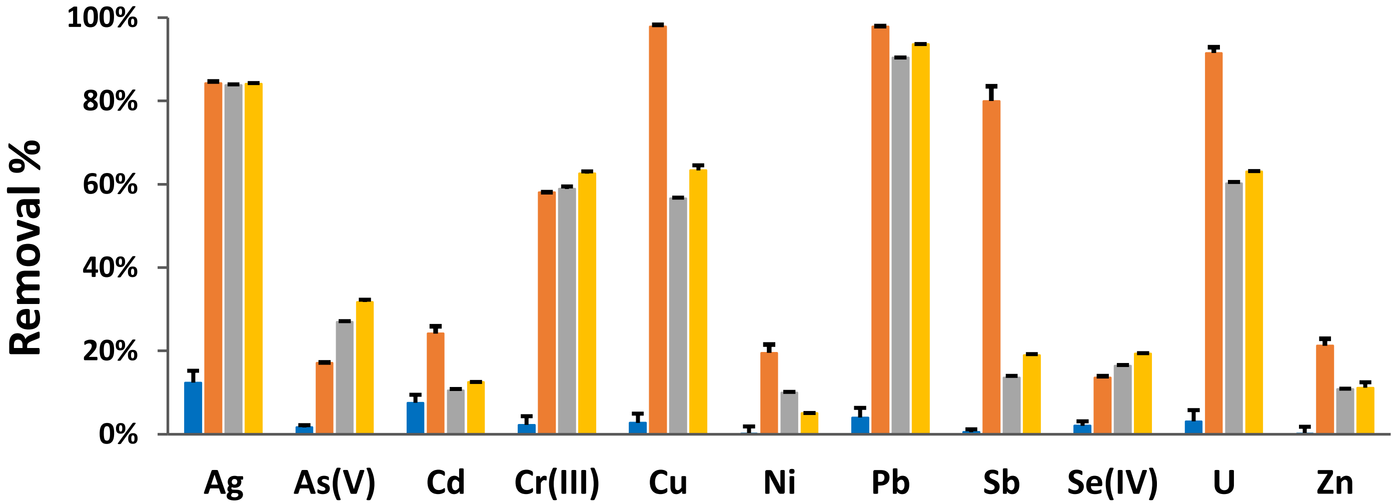


(C_{IN}= 0.5 mg/L each, $t_{CONTACT}$ = 15 min)

Batch experiments

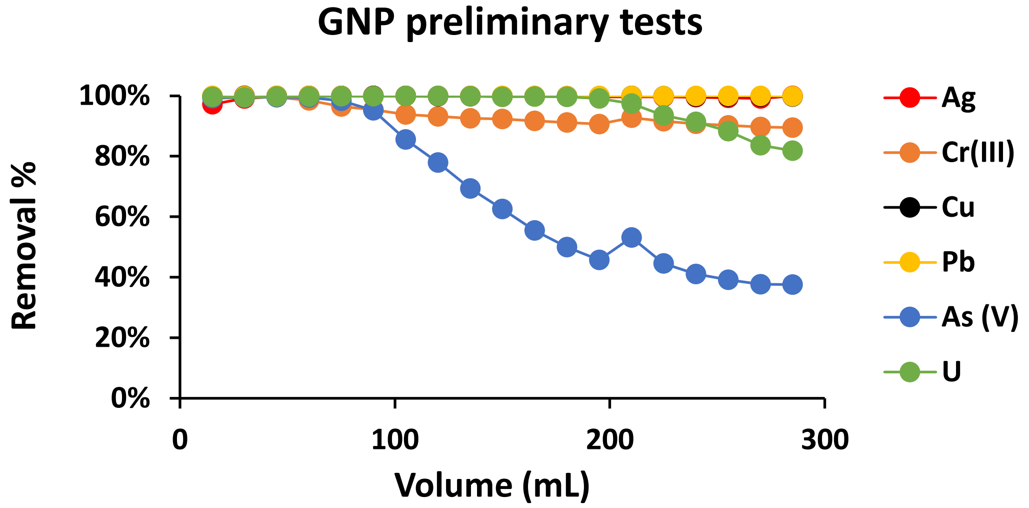


METAL CONTAMINANTS

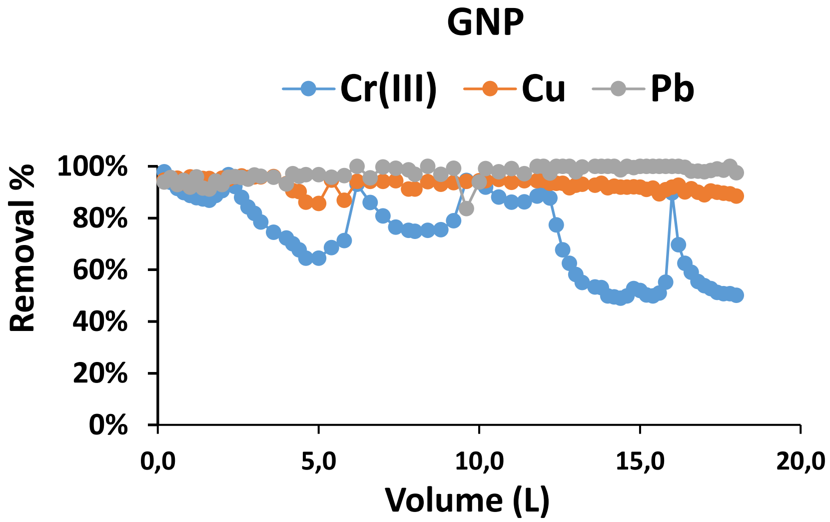


(C_{IN}= 100 µg/L each, $t_{CONTACT}$ = 1 h)

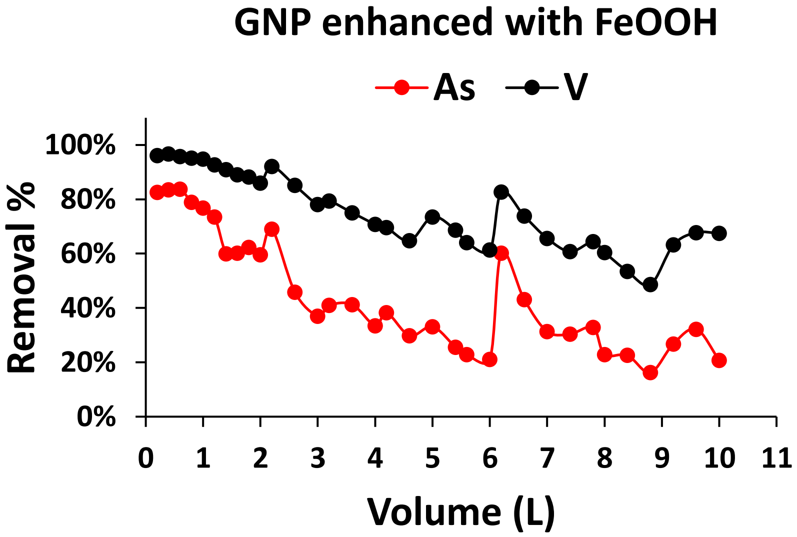
SELECTIVITY TEST IN FLOW CONDITION



8 Metals mix in natural water
Cin1 mg/L
Flow 2,5 mL/min
GNP 1.2 g
No sand

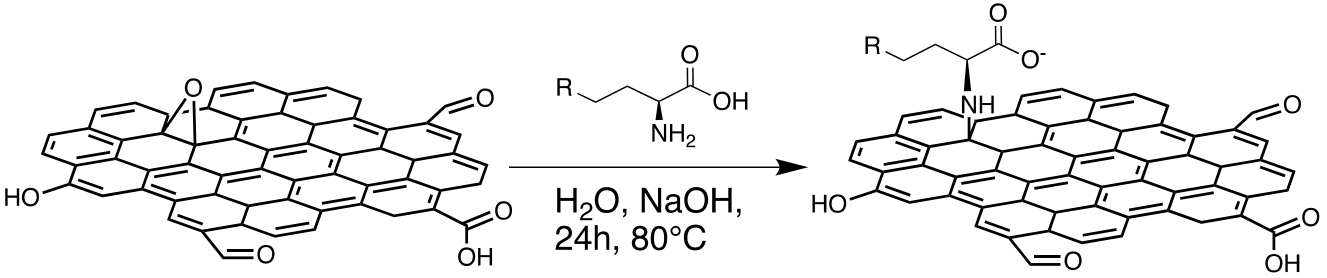


Natural water
Spiked Cr(III), Pb and Cu 50 µg/L
Flow 5 mL/min
GNP modified with Fe 1.4 g
Mixed with sand 1:5



Natural Volcanic Groundwater
As and V 30-35 µg/L
Flow 5 mL/min
GNP modified with Fe 1.4 g
Mixed with sand 1:5

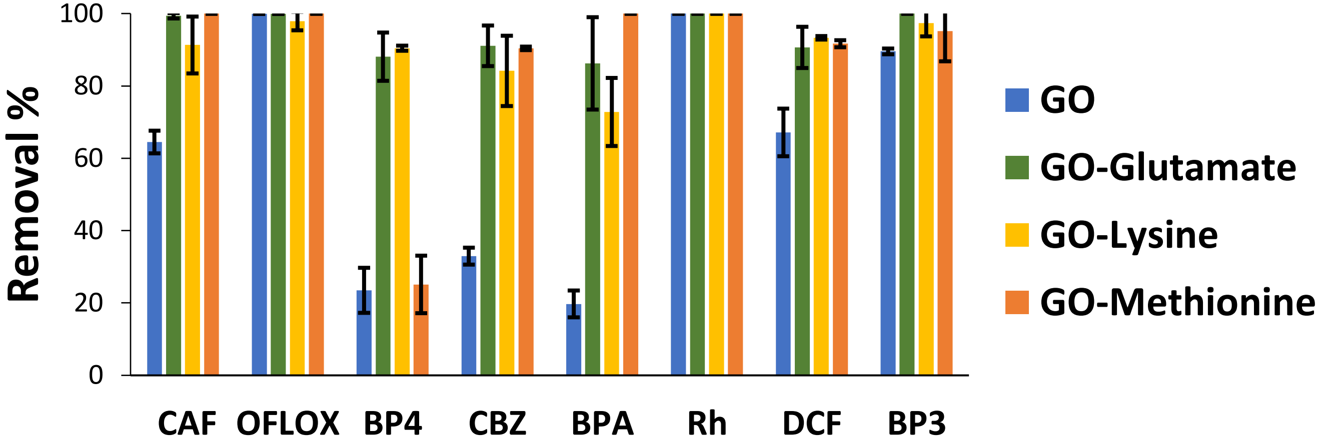
COVALENTLY MODIFIED GO FOR SELECTIVE SORPTION: AMINOACID MODIFIED GO



GO

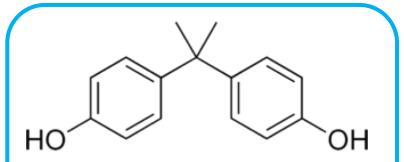
R= $-CH_2CH_2NH_2$ **GO-Lysine**
R= -COOH **GO-Glutamate**
R= $-SCH_3$ **GO-Methionine**

ENHANCED SELECTIVITY AND EFFINCENCY



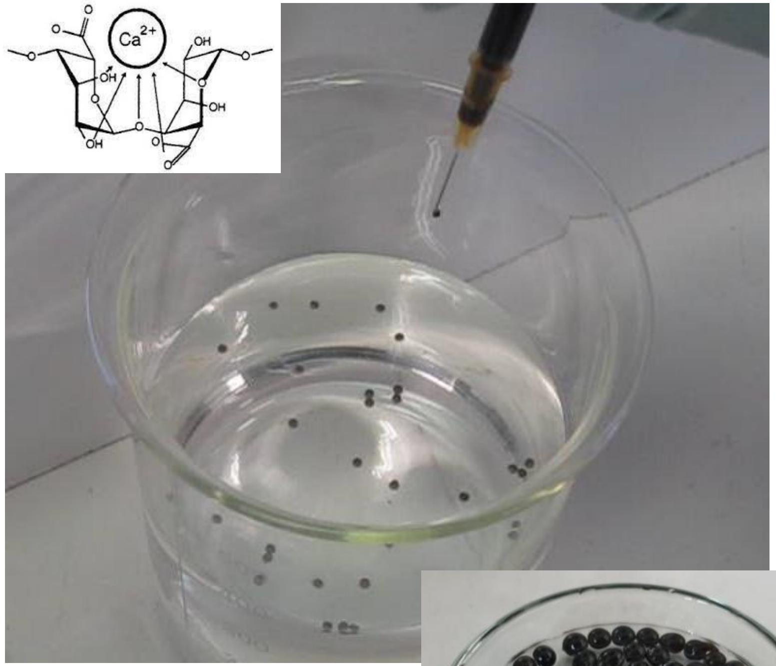
(C_{IN}= 5 mg/L, 25 mg sorbent, V_{tot}=10 mL, $t_{CONTACT}$ = 1 h)

Sample	Qmax (mg/g)
GO Abalonyx	14 ± 5 (BET)
GO NaOH	48 ± 15 (Langmuir)
GO-Lysine	295 ± 50 (Langmuir)
GO-Glutamate	237 ± 40 (Langmuir)
GO-Methionine	147 ± 30 (Langmuir)

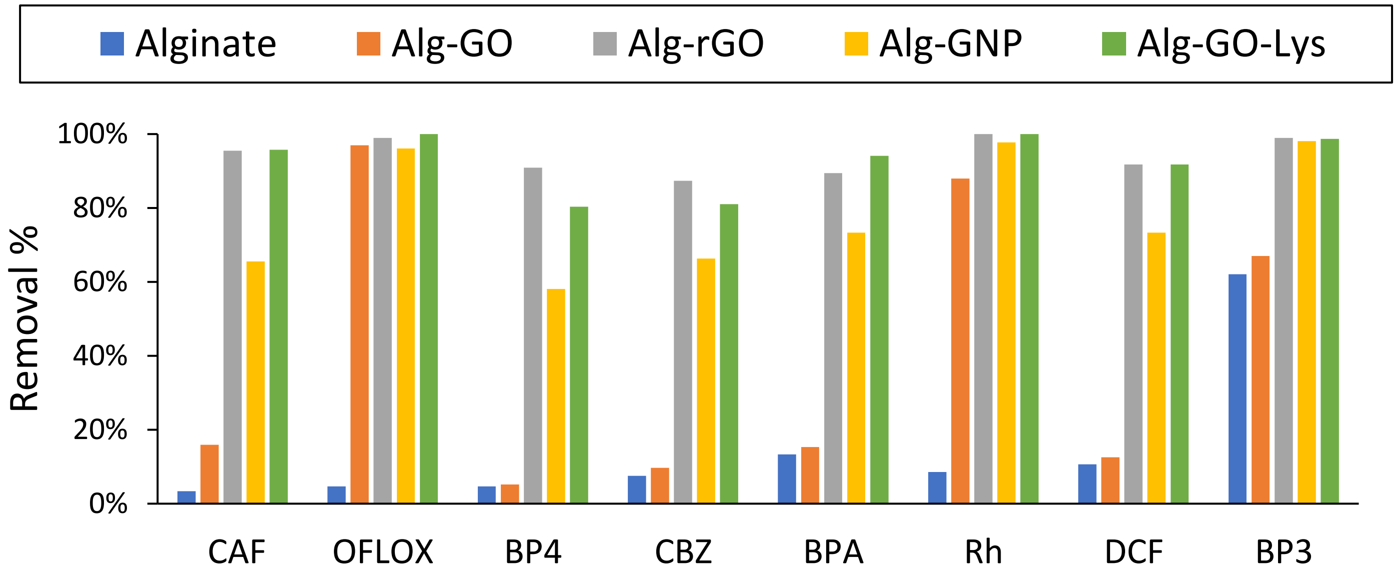


Bisphenol A, BPA

ALGINATE-GRAPHENE BEADS



Batch experiments



(C_{IN}= 0.5 mg/L, 25 mg sorbent, V_{tot}=25 mL, $t_{CONTACT}$ = 4 h)

Composites show **same selectivity** of 2D nanosheets

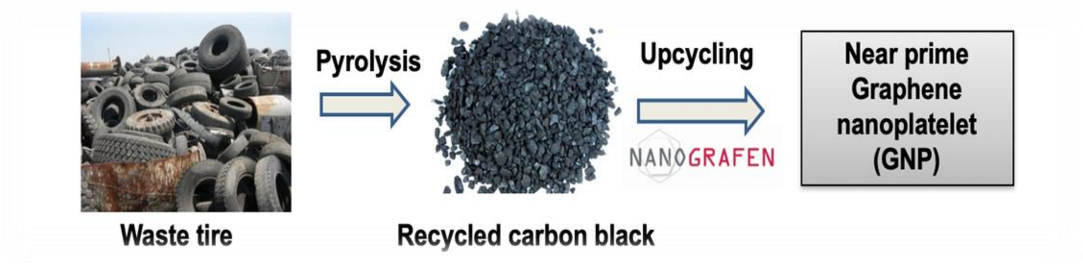
↓

Next step: test in **flow condition**

FABRICATION OF COMPOSITE MEMBRANES

GNP synthesis pathway

Step 1. Waste tire driven graphene nanoplatelets (GNP) production in pilot scale

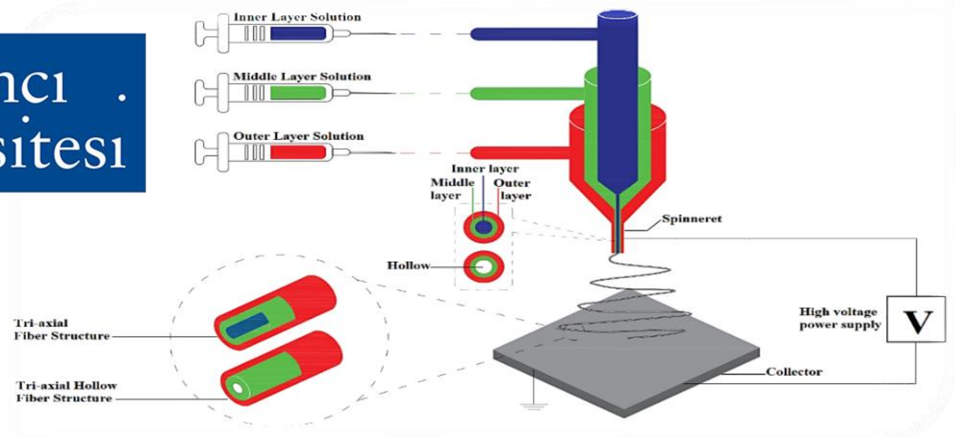


Step 2. Encapsulation GNP in electrospun structures and polymeric GNP-based membranes are developed for water treatment application.

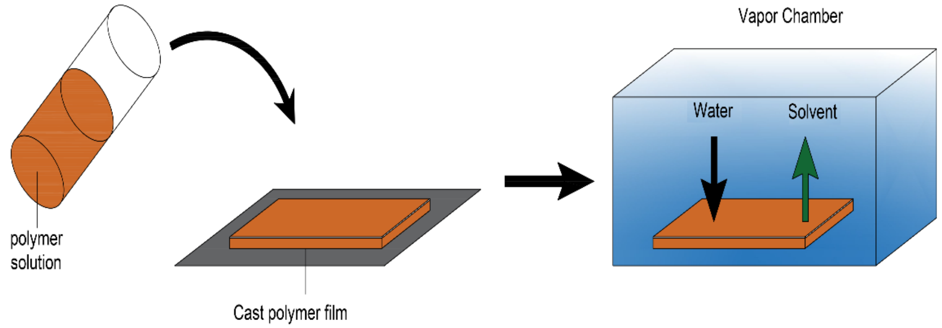
PCL and PLA polymers used as backbone structure.
GNP, TEGO, GO, and rGO are used as carbon-based materials.

2-1. Tri-axial Hollow Fibers by Core-shell Electrospinning:

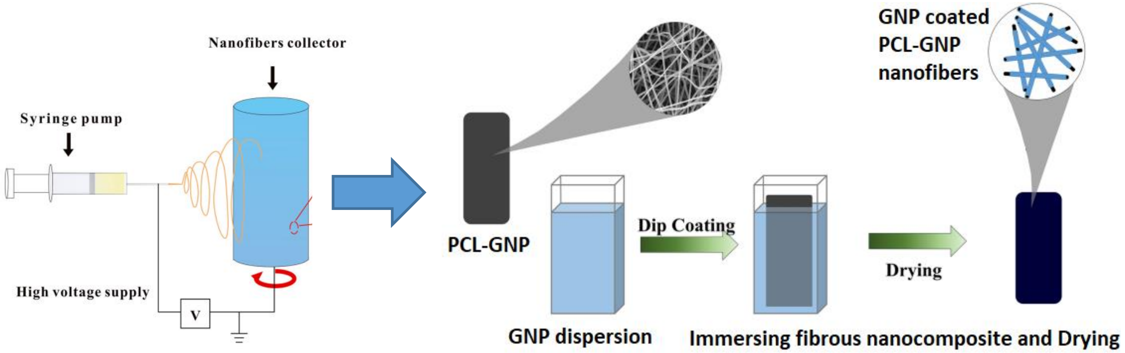
Sabancı Universitesi



2-2. Polymer solution Casting:



2-3. Coating of electrospun nanocomposite:



FABRICATION OF COMPOSITE MEMBRANES

Sabancı Üniversitesi

Tri-axial Hollow Fibers by Core-shell Electrospinning

Layers Set1:

Electrospun hollow fiber

1-PCL 15 wt%-GNP 0.25 wt%

2-PCL 15 wt%-GNP 0.5 wt%

Layers Set2:

Electrospun hollow fiber

1-PCL15%-TEGO 0.25%

2-PCL15%-TEGO 0.5%

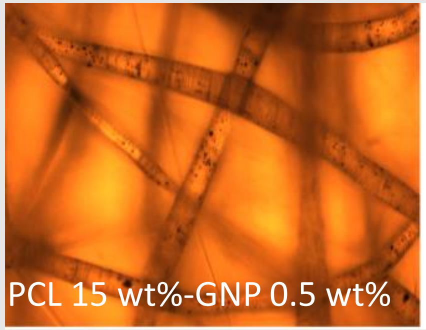
3-PCL15%-TEGO 1%

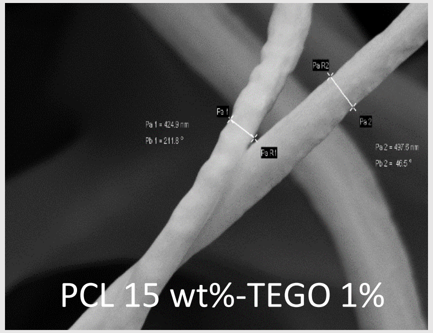
Layers Set3:

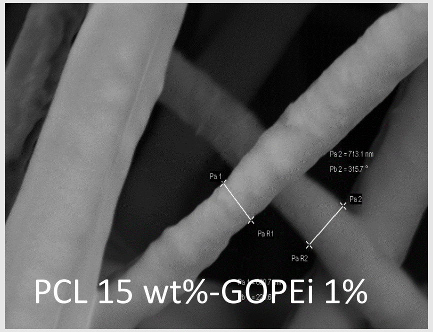
PCL-GOPEi Membranes

1-PCL15%- GOPEi 0.5%

2-PCL15%- GOPEi 1%

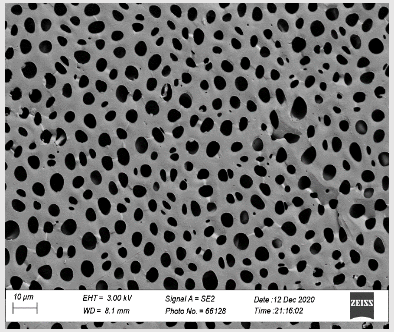


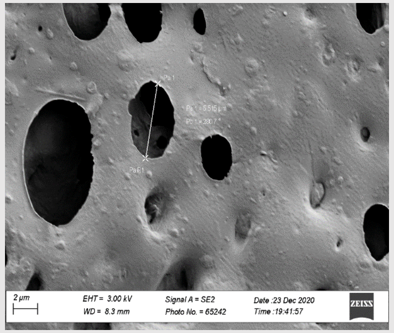




Polymer solution Casting

PCL:PLA porous casted film

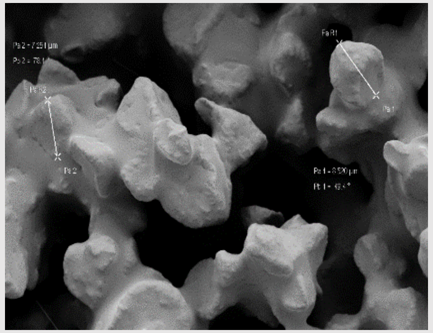




Layers Set4:

Electrospun

PCL 1wt%-GNP 0.25wt% (foam)



Coating of electrospun nanocomposite

Coating 1 - CNT ✘

PCL 15%-GNP 1% Nanofibrous web was dipped in CNT-Water dispersion for 2h and then dried.

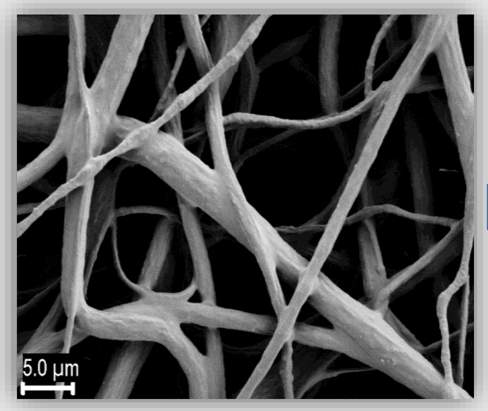
Coating 2 - rGO ✔

PCL 15%-GNP 1% Nanofibrous web was dipped in GO-Water dispersion for 2h and then reduced by using hydrazine hydrate (20%) evaporation in a desiccator for 24 h in 40°C.

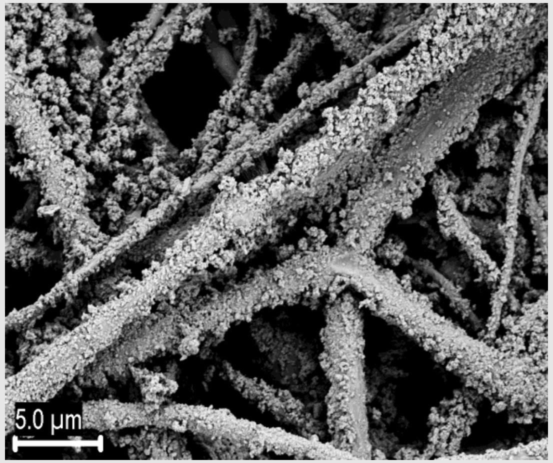
Coating 3 - GNP ✔

PCL 15%-GNP 1% Nanofibrous web was dipped in GNP-Methanol dispersion for 2h and then dried.

PCL 15%-**GNP 1**%



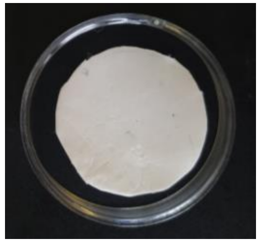
Dip Coated in GNP



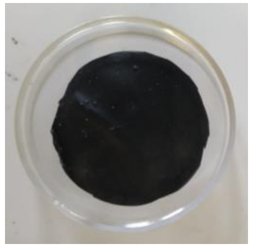
ADSORPTION TEST: FIRST REMOVAL TESTS WITH METALS

Enhanced GNP membranes did not show significantly higher removal if compared to pristine membrane (PCL15%)

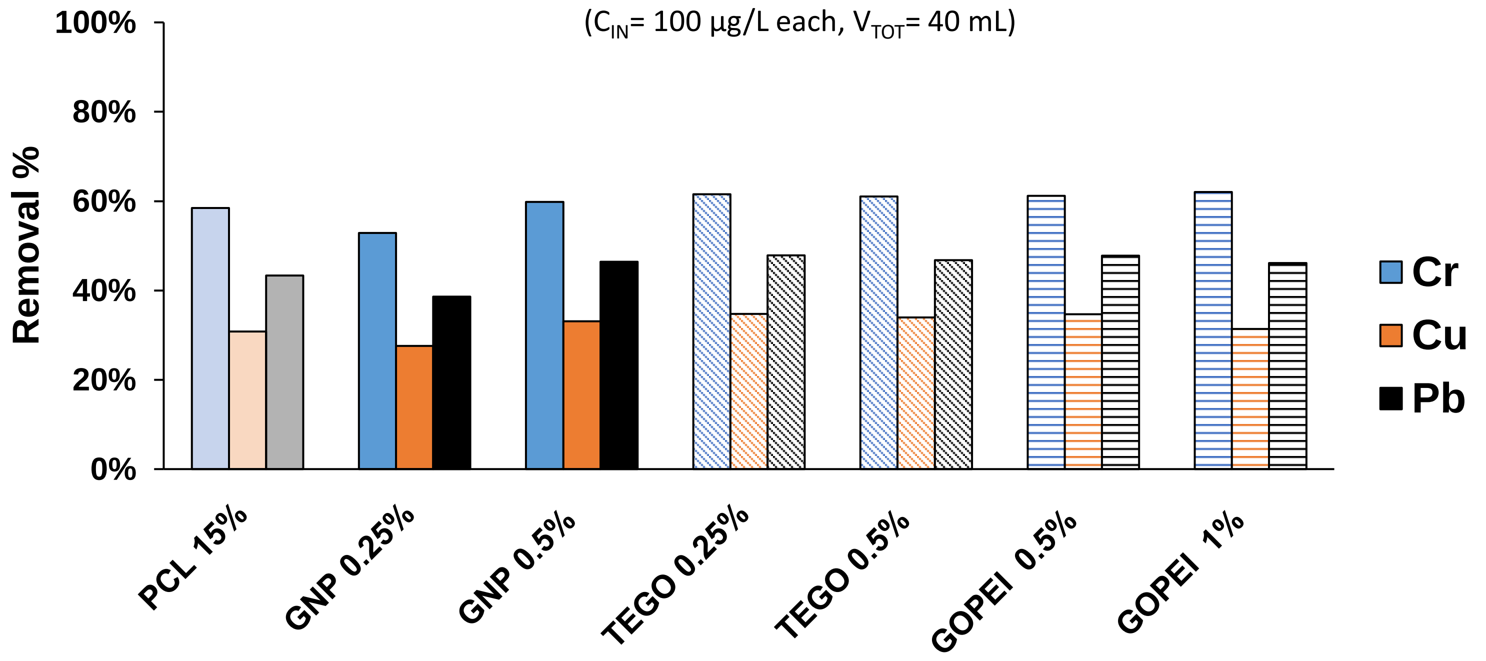
→ Next step: **enhance GNP concentration** (< 1% was too low) and **render more available graphene** by coating or fabricating membranes in a different composition.



Pristine Membrane (PCL15%)



Composite Membrane (GNP 0.5%)



FABRICATION OF PCL/PLA-GRAPHENE AEROGELS

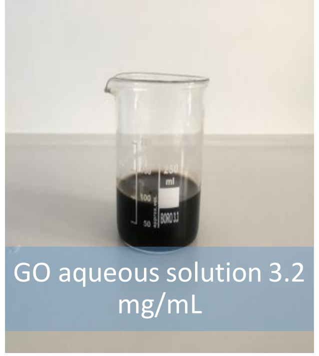
Freeze Drying

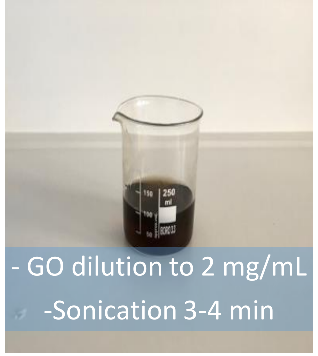
Water removal from a material that entails the freezing of the material followed by pressure reduction combined with the supply of heat, in order to allow the sublimation of the frozen water.

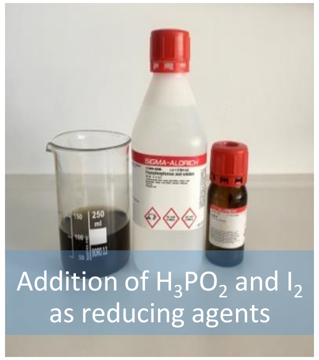
01	Pre-freezing	Reduces drying time by 30% Freezer, chilled bath or shelf on freeze-dryer
02	Primary Drying Phase	Stage of sublimation Removal of 95% of moisture Pressure and temperature of sample higher than ice collector's
03	Secondary Drying Phase	Higher temperature than in primary drying Formation of porous structure 7-8% residual moisture

Synthesis Method

Based on: *J.-Y. Hong et al. / Chemical Engineering Journal 269 (2015) 229–235*


GO aqueous solution 3.2 mg/mL


- GO dilution to 2 mg/mL
-Sonication 3-4 min

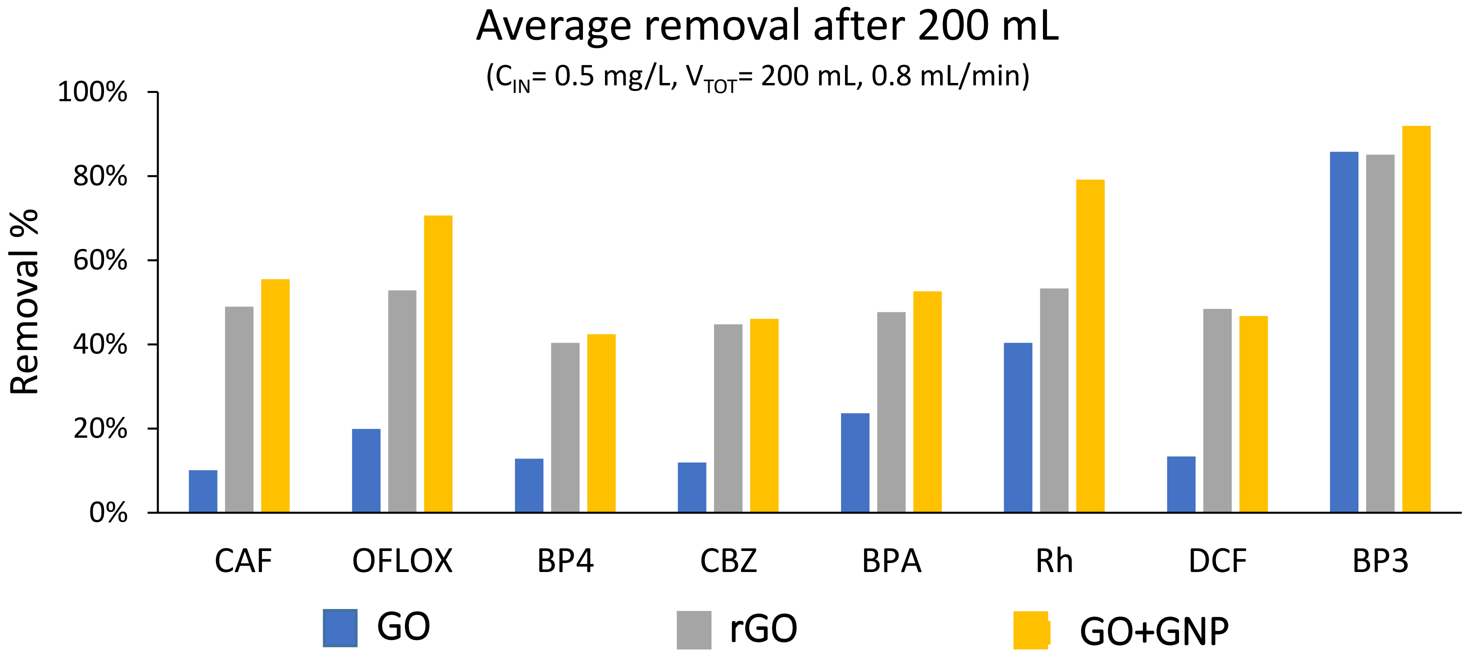

Addition of H_3PO_2 and I_2 as reducing agents

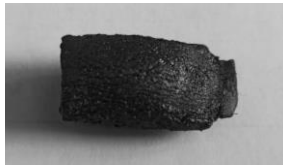

Oven
(80°C, 8 h)


Graphene Hydrogels


Graphene Aerogels with freeze-drying

ADSORPTION TEST: FIRST REMOVAL TESTS WITH ORGANICS





FLOW TEST

Graphene aerogels show same selectivity of 2D nanosheets in flow condition

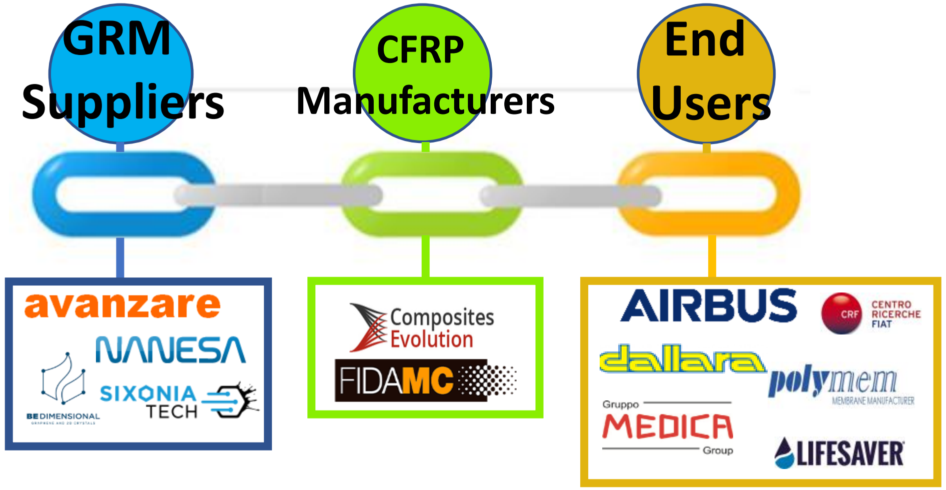
Next step: test **composite aerogels** (with PCL and PLA) in flow condition

INTERACTION WITH THE GRAPHENE FLAGSHIP

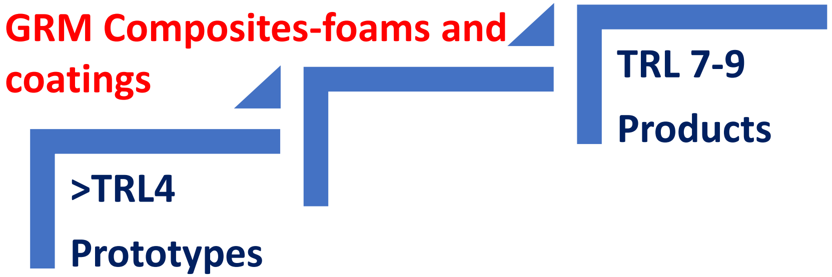
- *FORTH/ICEHT* is leader of the **WP14** of the Graphene Flagship. *University of Patras* has direct interaction with FORTH/ICEHT.
- CNR and FORTH are involved in **WP13**
- CNR, CUT are involved in **SH1-GRAPHIL**

Interaction between Flagera and Graphene Flagship

✓ Enhance further *the value chain established for automotive, aerospace, filters industries by combing excellent research facilities and industrial partners/ end users.*



✓ Optimize promising applications developed in Core2 to produce new prototypes and products, for aerospace, automotive, buildings, power transmission industries, water filters



GO-FOR-WATER Gantt chart

Task	Description	Partner	Year 1	Year 2	Year 3
			1 2 3 4 5 6 7 8 9 10 11 12	13 14 15 16 17 18 19 20 21 22 23 24	25 26 27 28 29 30 31 32 33 34 35 36
WP1: Project management and dissemination					
Task 1.1	S&T coordination	CNR			
Task 1.2	Administrative project management	CNR			
Task 1.3	Dissemination of results and IP issues	all			
WP2: Synthesis and structure-property relationships of GRM					
Task 2.1	Semindustrial synthesis of graphene precursors	UP, SU			
Task 2.2	Synthesis and chemo-physical characterization of GRM	CNR,CUT			
Task 2.3	Selectivity-efficiency tests of GRM (batch)	CNR			
WP 3: GRM deposition/processing in 3D structures and characterization					
Task 3.1	Fabrication of core-shell fibers, membranes	SU			
Task 3.2	Fabrication of aerogel	UP			
Task 3.3	Coatings	UP, CUT			
Task 3.4	Multiscale, chemo-physical characterization	CUT, UP, SU			
WP 4: Performances in small scale filters					
Task 4.1	Operation conditions/Removal efficiency (continuous)	CNR, UP			
Task 4.2	Materials stability/ integrity	UP, CUT			
WP 5: Scale up-Pilot tests					
Task 5.1	Scale up (materials/filters)	CNR, UP, SU			
Task 5.2	Filters validation in pilot POU	CNR,UP			

D3.1	M24	3D GRM composites and coatings for water purification
D3.2	M24	Removal efficiency of selected GRM composites in multicontaminated real matrices

Thank you

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