Magnetic Decontamination and Water Valorization

M M Lopez Guerrero, I Morales Benitez, A. Doblao Onieva, E I Vereda Alonso

Mechanochemical Synthesis of Magnetic Graphene Oxide (MGO)

- **Mechanochemical synthesis** uses mechanical energy to drive reactions:
  - Shorter reaction times
  - Less catalyst required
  - Ball milling reduces particle size and increases surface area

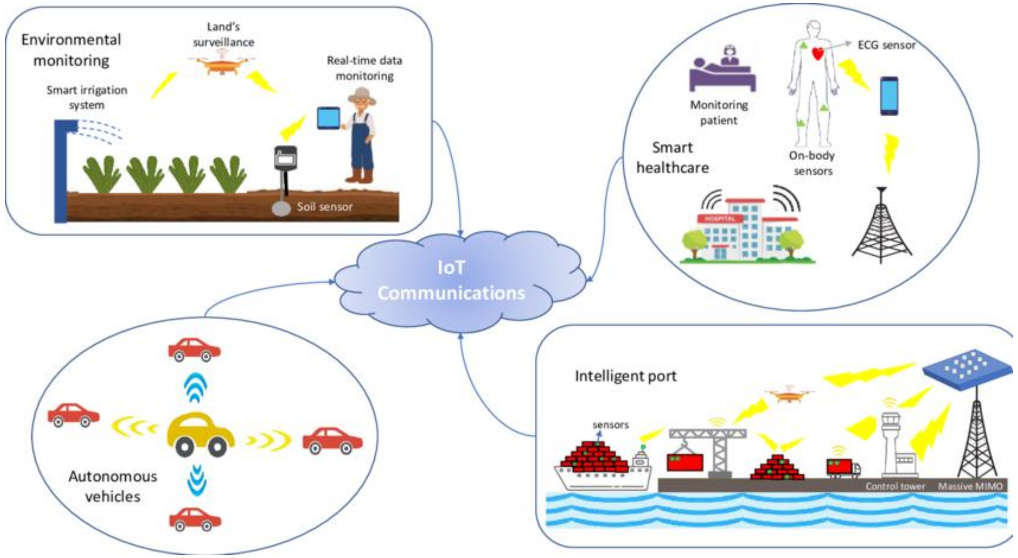
- **GO mechanochemical synthesis**:

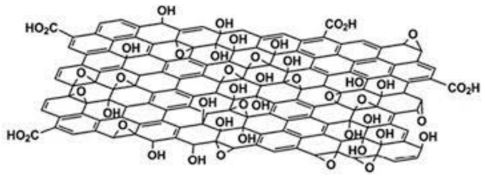
Uses oxidizing agents like $KMnO_4$, APS, Oxone®, or **atmospheric oxygen** (eco-friendly)

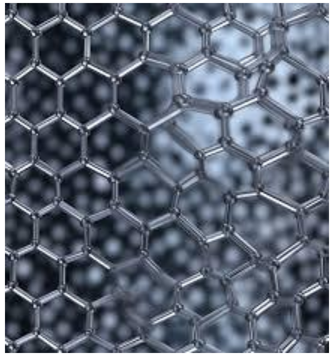
Milling parameters (speed, time, ball size) control GO properties

Environmental applications of GO:

- High surface area, low toxicity, excellent sorption capacity
- Useful for wastewater treatment and pollutant removal
- Difficult to separate from water → **solution: magnetization**

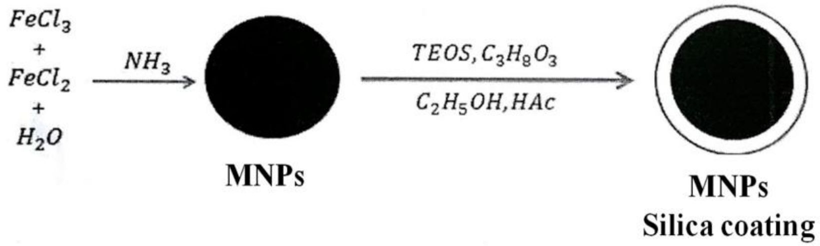


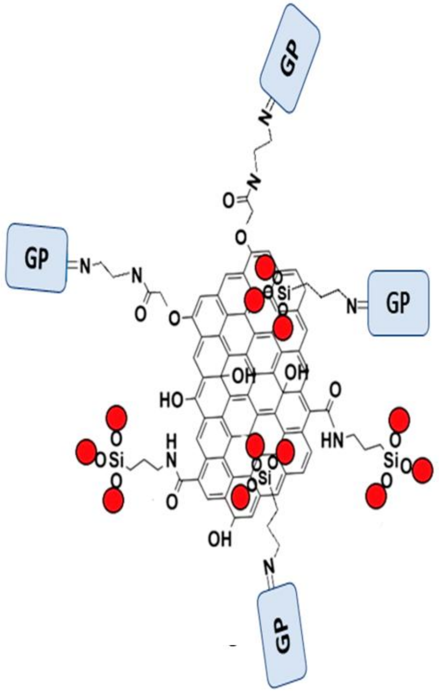




Magnetic Graphene Oxide (MGO):

- GO coupled with **magnetic nanoparticles (MNPs)** for easy recovery
- Synthesis methods for MNPs: coprecipitation, solvothermal, sol-gel
- Applications: heavy metal removal, dye adsorption, water disinfection, analytical sorbents, Magnetic Solid-Phase Extraction (MSPE)





Sustainability improvement

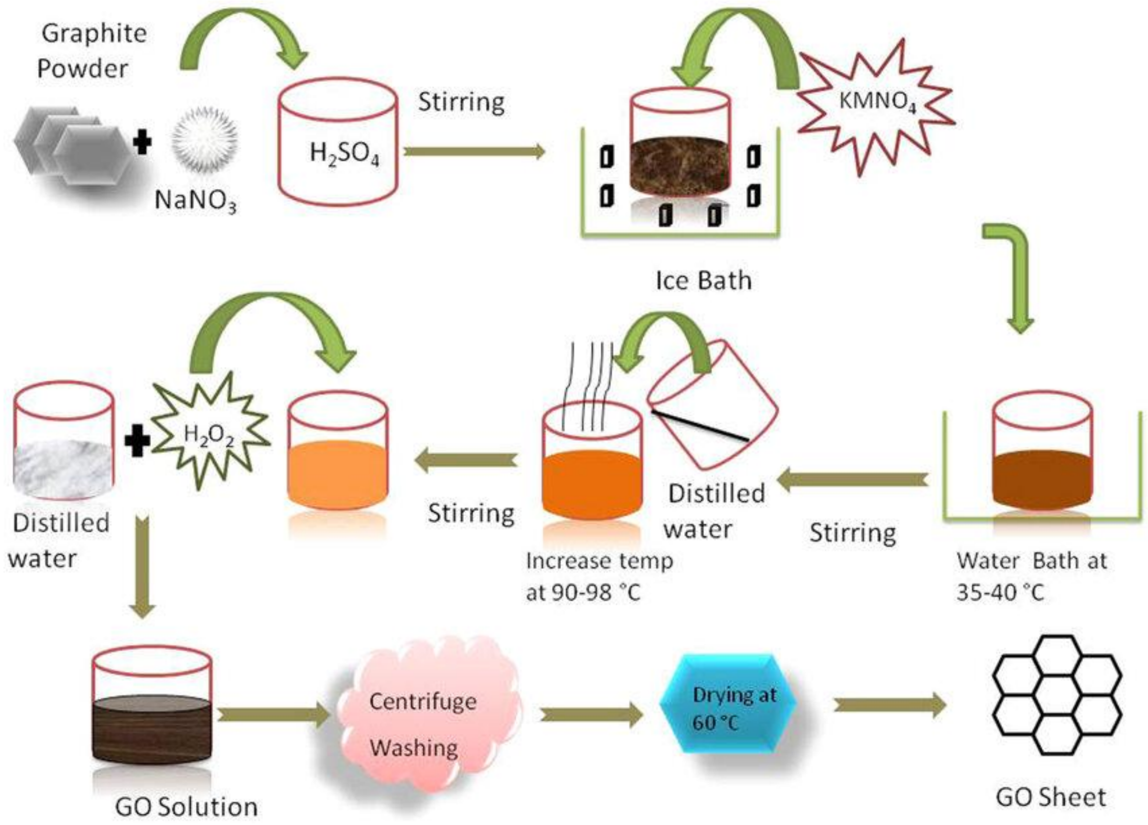
- Traditional M@GO used wet-synthesized GO (non-sustainable)
- New **mechanochemical GO synthesis** developed using air as oxidant
- Optimized parameters: rotation speed, ball size, synthesis time
- Produced **dry-synthesized GO (d-GO)** → combined with MNPs to make **d-M@GO**

Pollutant Selection for Adsorption Studies

- **Goal**: Evaluate and compare adsorption performance of
  - **d-M@GO** (dry-synthesized magnetic graphene oxide)
  - **w-M@GO** (wet-synthesized magnetic graphene oxide)
- **Pollutants selected**:
  - **PFAS compounds**: PFOS, PFOA, PFBS
    - Regulated/proposed under **EU Water Framework Directive** and **US EPA**
    - Persistent, bioaccumulative, toxic
  - **Metal ions**: As, Cd, Pb, Hg, Sb
    - Listed as **priority substances** in EU & US regulations
    - Common in industrial effluents

Preparation of w-GO

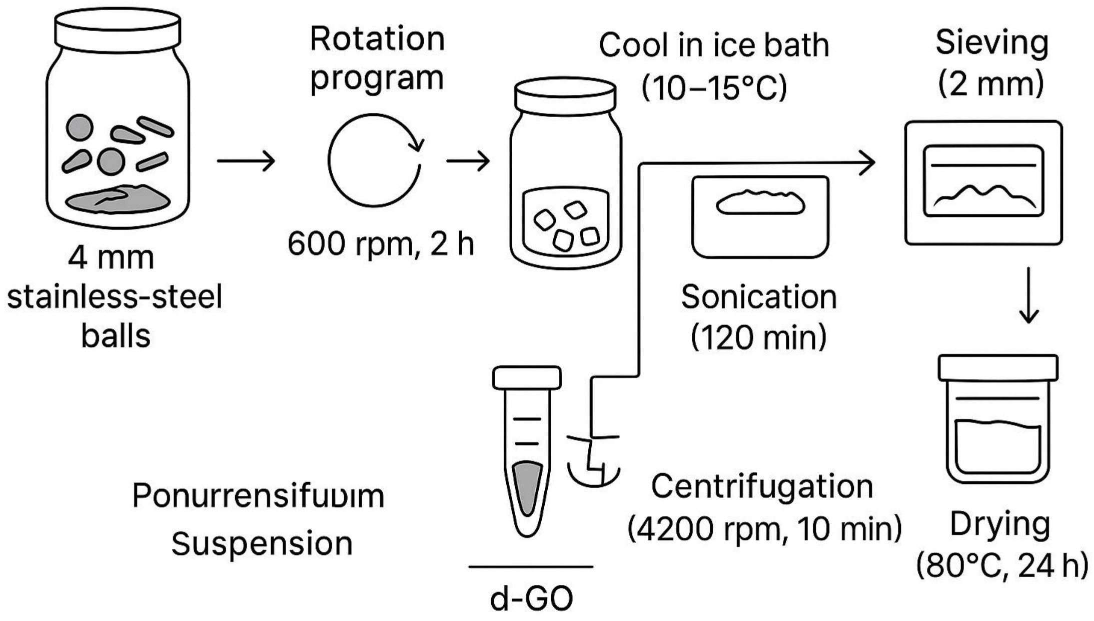
- A modified Hummers´ method described by Diagboya et al. was followed for the synthesis of w-GO from natural graphite, purified by centrifugation multicycles.



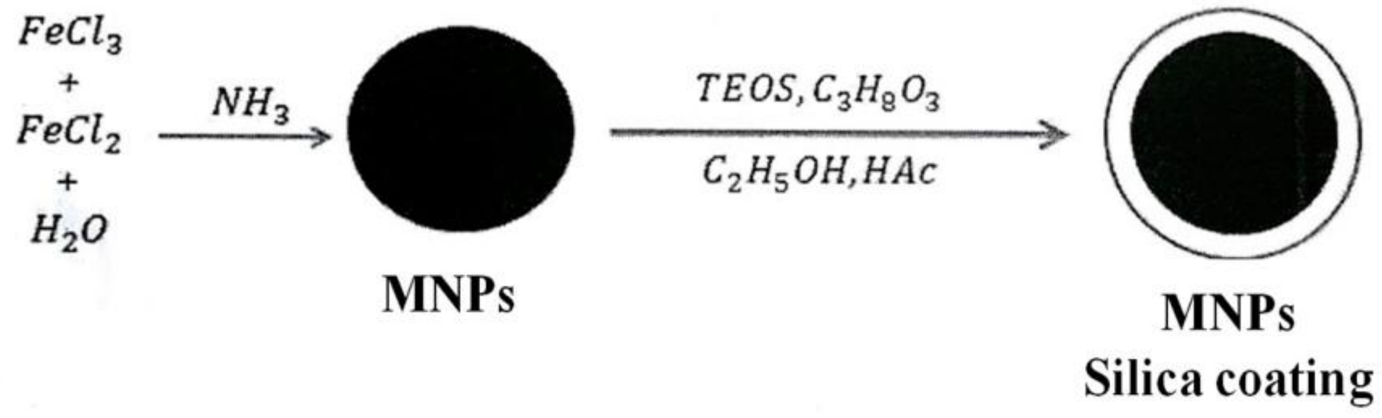
Preparation of d-GO

- In a 500-mL stainless-steel jar, 4 mm diameter stainless-steel balls and graphite powder are introduced. The jar with the content was subjected to a constant rotation program of 600 rpm for 2 hours.
- Then, the collected powder was sonicated for 120 minutes in deionized water using an ultrasonic bath at room temperature to achieve layer separation.
- Once the exfoliation process was completed, the resulting suspension was centrifuged for 10 min at 4200 rpm.
- Finally, the d-GO was dried at 80 ^{0}C 24 h.

Optimized protocol for the preparation of d-GO



Preparation of silica coating MNPs and M@GO



For coupling MNPs and GO, 500 mg of GO and 500 mg of functionalized MNPs were mixed in water and stirred for 10 min. The mix was incubated at 65 °C for 8 h. The coupling Fe3O4–GO suspension was cooled to room temperature and separated from the solution with the aid of external permanent magnet

Preparation of silica coating MNPs and M@GO

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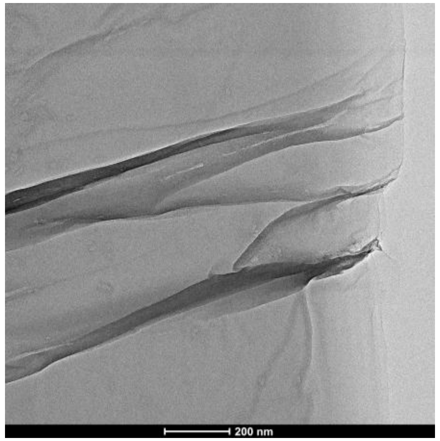
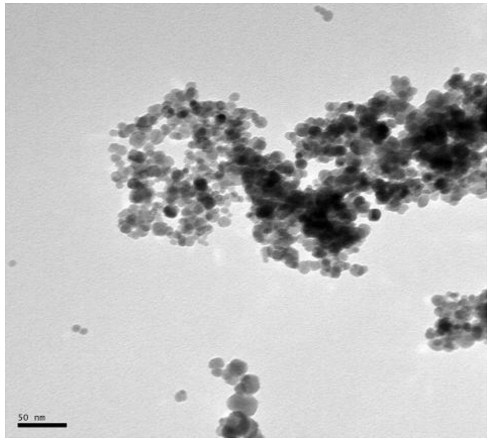
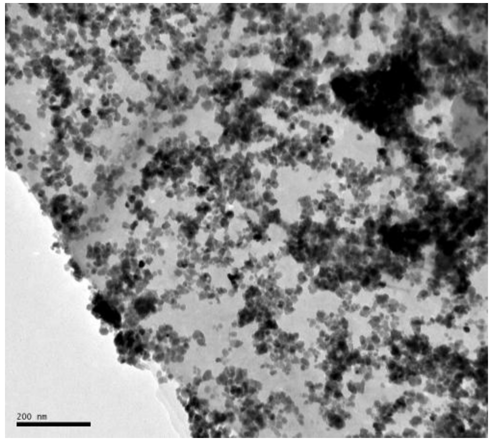
Sheets of **GO**



MNPS of Fe3O4 (Ø = 13 nm)



M@GO



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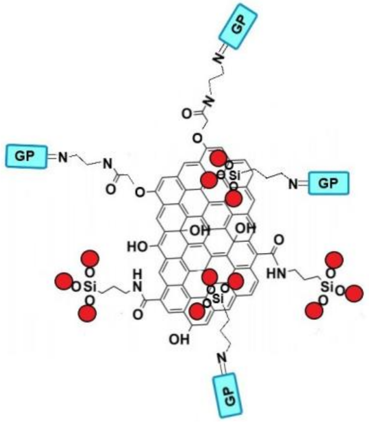

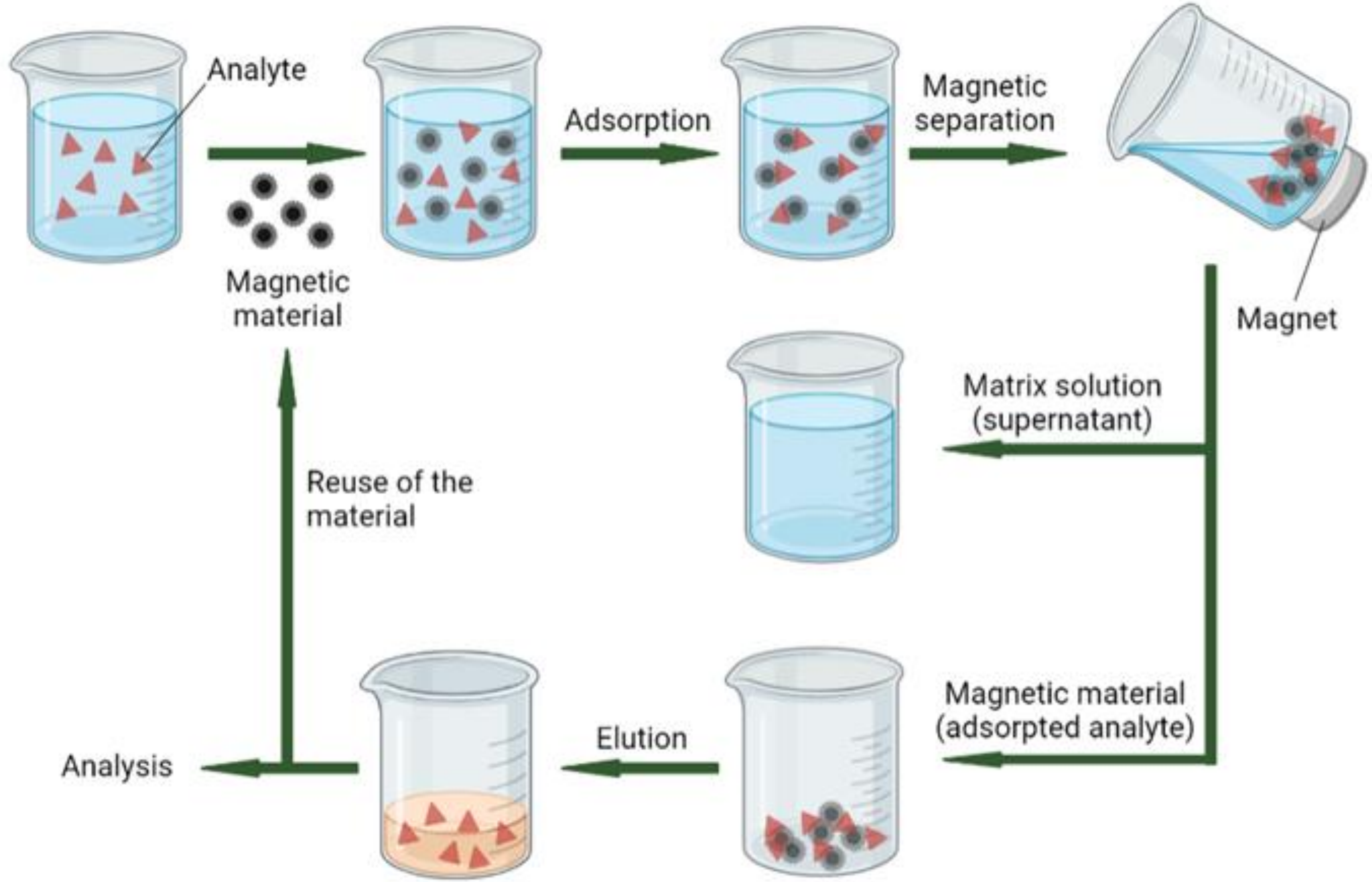
Analyte
Magnetic material
Adsorption
Magnetic separation
Magnet
Matrix solution (supernatant)
Reuse of the material
Magnetic material (adsorpted analyte)
Elution
Analysis

Evaluation of adsorption performance

	w-M@GO		d0-M@GO	
Compounds	Acid pH	Basic pH	Acid pH	Basic pH
Ag^{I}	93	100	100	100
Cu^{II}	55	92	58	94
Cd^{II}	25	100	20	100
Mn^{II}	--	98	--	98
Ni^{II}	12	98	11	100
Rh^{II}	--	83	--	88
Co^{II}	--	100	--	100
Cr^{III}	43	100	36	100
Os^{IV}	--	--	--	--
Pb^{IV}	100	100	100	100
Pt^{IV}	--	--	--	--
As^{V}	3	14	4	15
Sb^{V}	40	45	35	47
V^{V}	81	25	74	27

Evaluation of adsorption performance

	w-M@GO		d0-M@GO	
Compounds	Acid pH	Basic pH	Acid pH	Basic pH
PFOA	89	71	100	100
PFOS	96	76	100	100
PFDA	98	78	100	100
PFNA	93	60	100	100
PFBS	66	71	85	76
PFOSA	96	77	100	100
PFHxS	84	48	100	89
PFPeA	64	63	74	67
PFHpA	50	14	94	69
PFHxA	27	29	60	32
PFBuA	23	90	18	100
PFHpS	27	71	93	70
H4PFOS	90	92	100	100

Conclusions

A sustainable approach was developed for the preparation of graphene oxide using mechanochemistry, with atmospheric oxygen identified as the most effective and greener oxidizing agent. The resulting material, d-GO, exhibited a laminar structure, hydrophilic character, and formed stable aqueous suspensions. Both d-GO and classical wet-prepared GO (w-GO) were coupled with magnetic nanoparticles to produce magnetic sorbents, d-M@GO and w-M@GO, respectively.

The mechanochemical synthesis eliminates the need for strong acids and hazardous oxidants, reduces energy and water consumption, and allows easy, low-cost scalability. This aligns with principles of green chemistry and circular economy, highlighting the potential for real-world applications in sample preparation and wastewater remediation.

The adsorption performance of these materials was evaluated for 14 metal ions and 13 PFAS at acidic and basic pH values. In many cases, removal efficiencies approached 100% after only ten minutes of contact. d-M@GO showed higher adsorption efficiency for several organic compounds, suggesting that an intermediate oxidation grade can favour pollutant removal depending on the interactions with the sorbent.

Thank you very much for your attention. I would be happy to answer any questions