Adsorption of perfluorooctanoic acid (PFOA) using graphene-based materials

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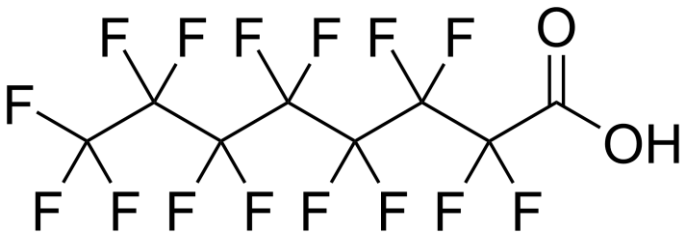
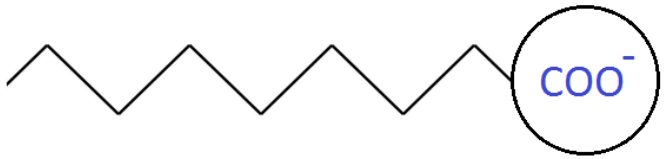
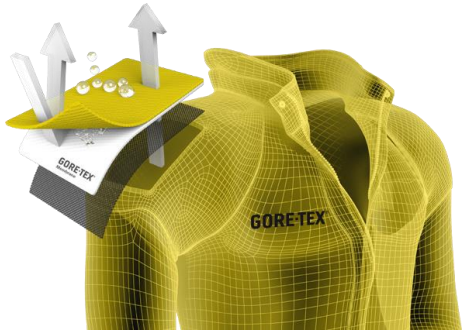
PFOA (Perfluorooctanoic acid)





hydrophobic fluorinated tail

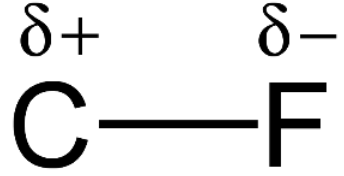
anionic polar head



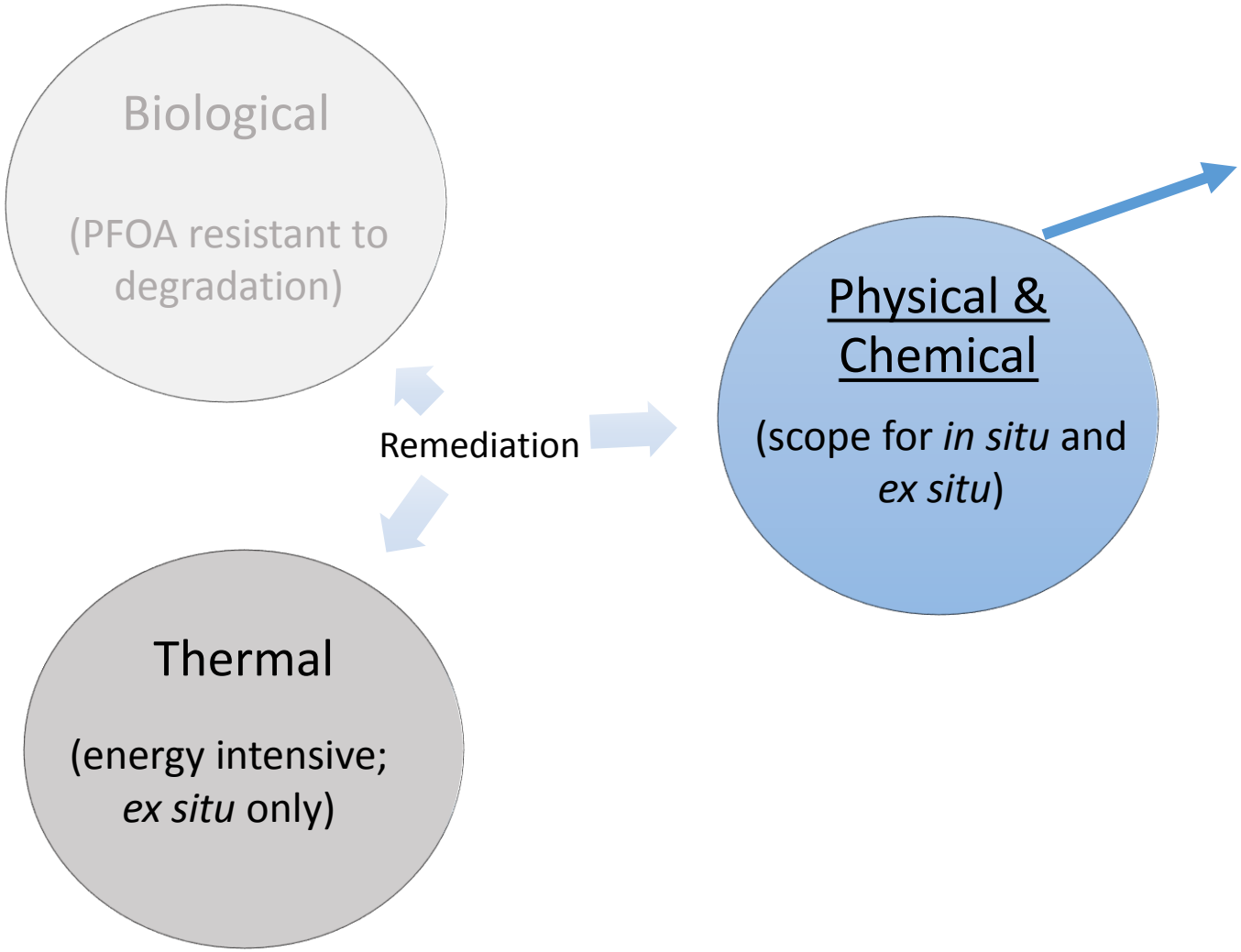
Applications

Concerns and Challenges

- Bioaccumulation; long-range transport
- Exposure through soil, water, dust
- Linked with human and animal health
- Phased out, but ubiquitous
- Resistant to degradation; stable



Remediation Strategies for PFOA & PFASs

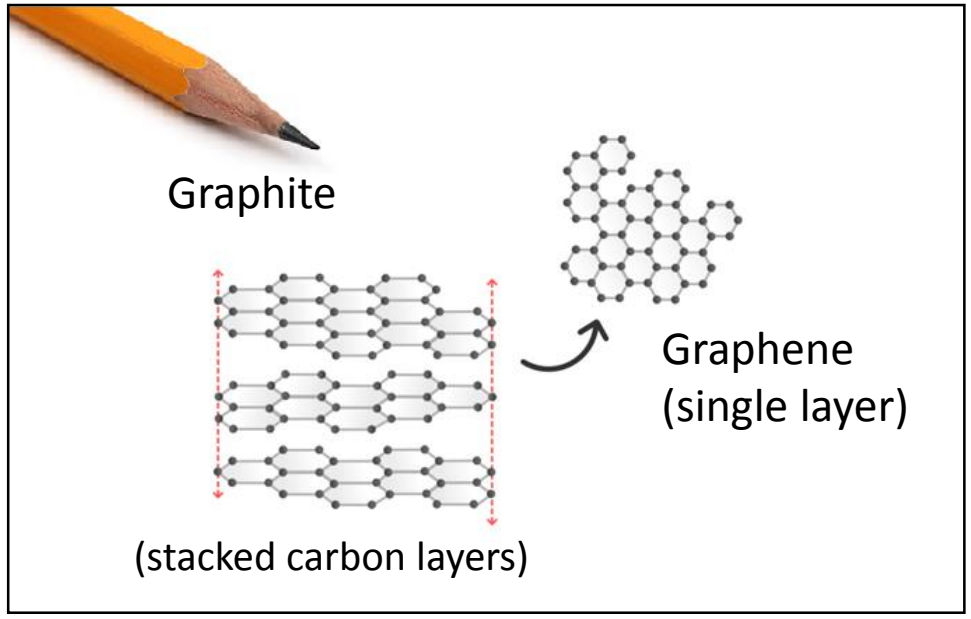


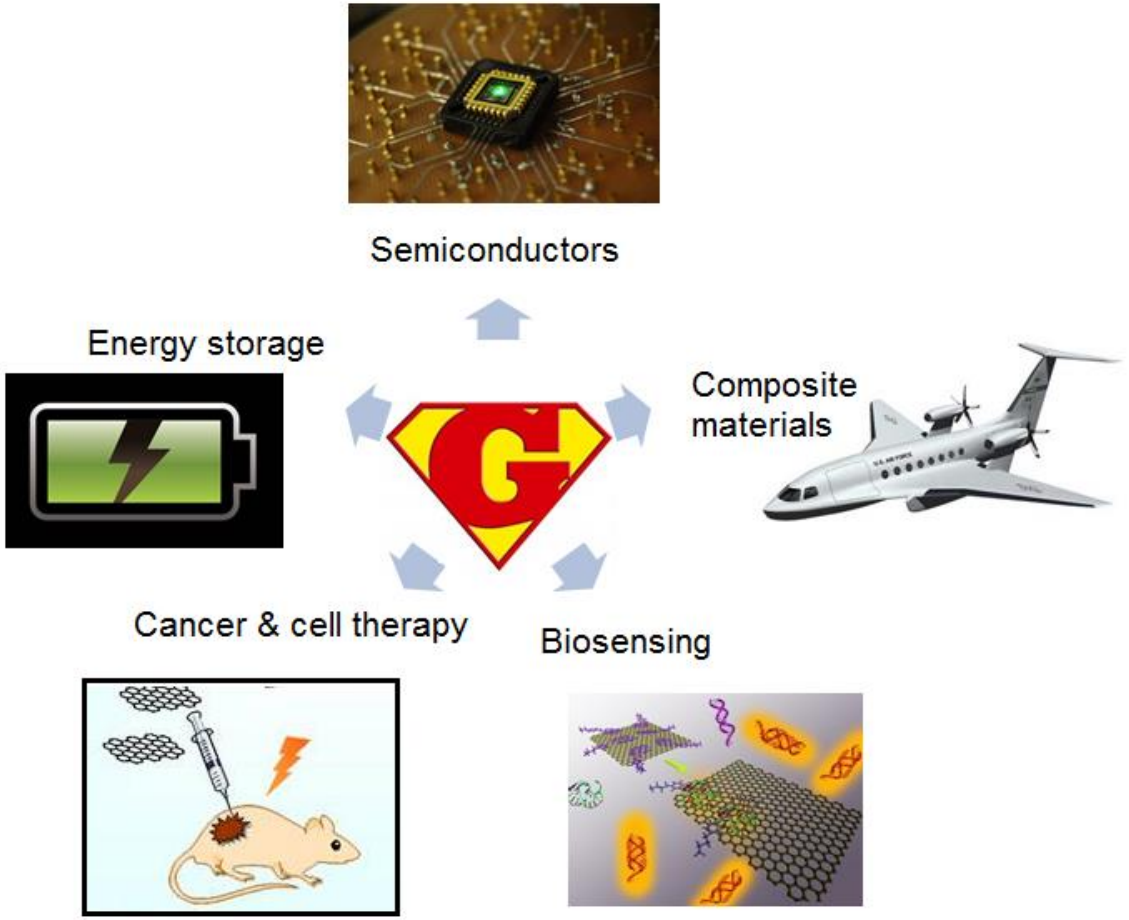
- Photocatalysis
- Sonochemical degradation
- Advanced oxidation

- **Adsorptive immobilisation (*in situ*)**
  e.g. activated carbon

Graphene Materials

- Single layer of graphite
- 2-D carbon sheet
- High surface area
- Versatile surface chemistry



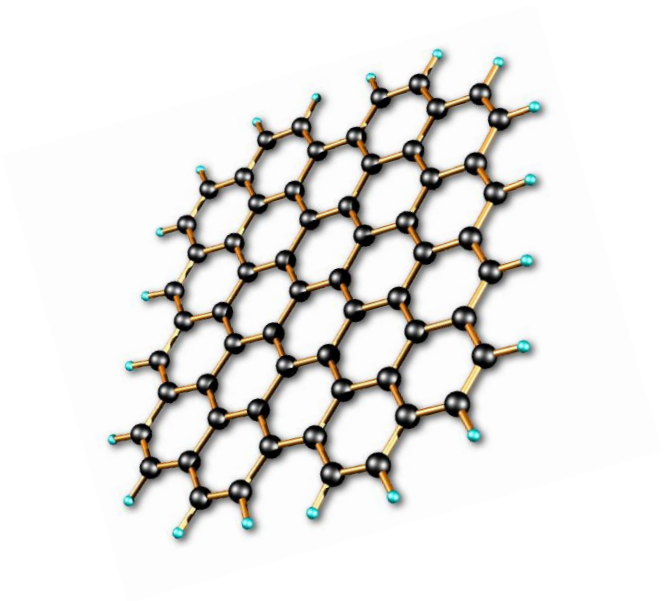


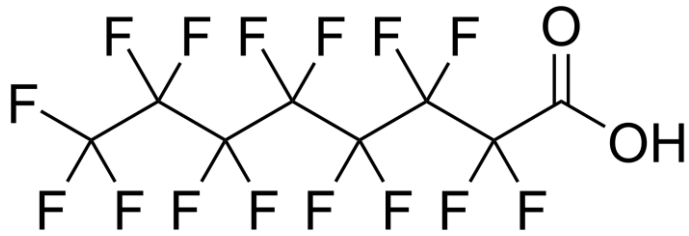
Project Aims

- Develop graphene-based materials with capabilities for immobilisation of PFOA.

- Evaluate efficiency of prepared materials for PFOA-sorption, and compare with a commercial remediation agent.

    - effect of pH
    - effect of ionic strength
    - effect of PFOA concentration





Materials Used

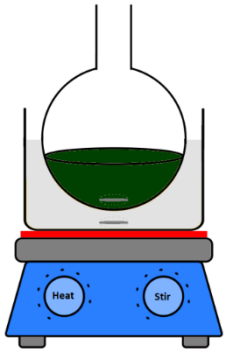
Commercial adsorbent:

- RemBind™ (mixture of activated C, gibbsite and kaolinite) — RemB

Prepared graphene adsorbents:

- Graphene oxide — GO
- Iron-modified graphene — FeG

Synthesis of GO & FeG



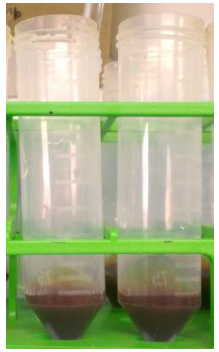
Graphite + $KMnO_4$ + conc. H_2SO_4 : H_3PO_4 (9:1)

Δ 50^{0}C , 15 hrs

Ice + 30% H_2O_2

Multiple wash cycles with HCl, water & ethanol

(centrifuge, decant)

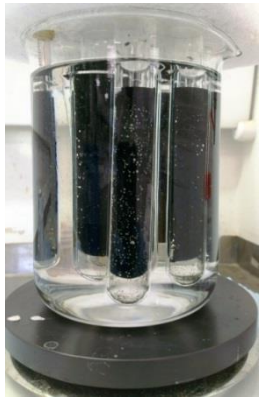


GO, oven dry at 30^{0}C

Well-exfoliated GO suspension (2 mg/mL)

$FeSO_4.7H_2O$

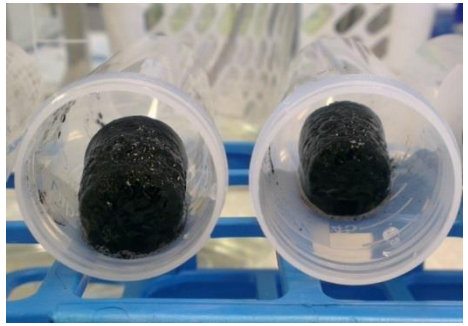
Δ 90^{0}C
8 hrs



Hydrothermal reduction

Self-assembly

FeG hydrogel



Freeze-dry

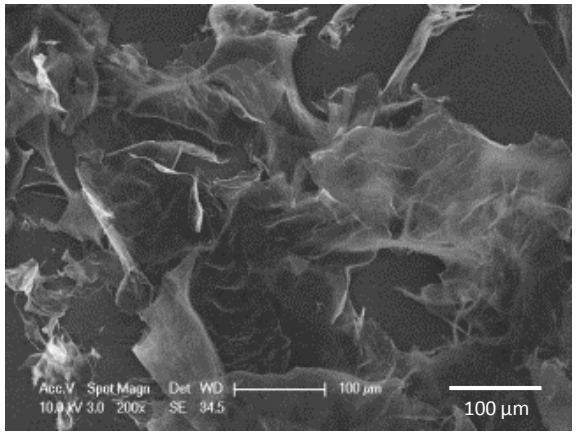
FeG aerogel

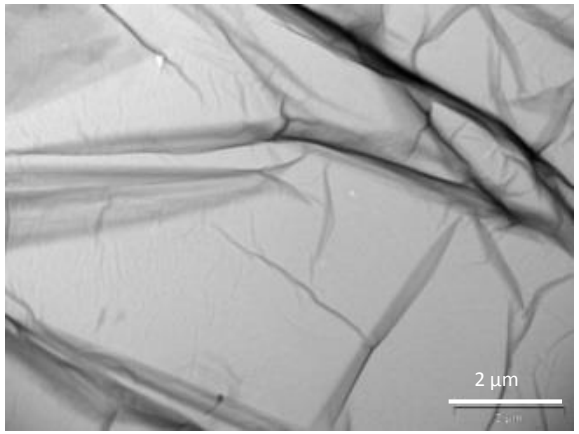
Marcano, D. C., et al. (2010). "Improved Synthesis of Graphene Oxide." ACS Nano 4(8): 4806-4814.

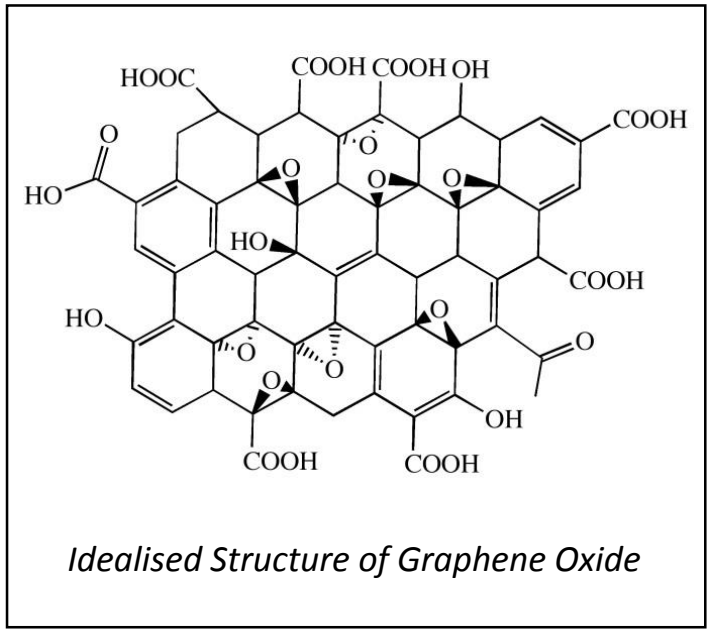
Cong, H.P., et al. (2012). "Macroscopic Multifunctional Graphene-Based Hydrogels and Aerogels by a Metal Ion Induced Self-Assembly Process." ACS Nano 6(3): 2693-2703.

Structural Characterisation

GO: SEM and TEM images

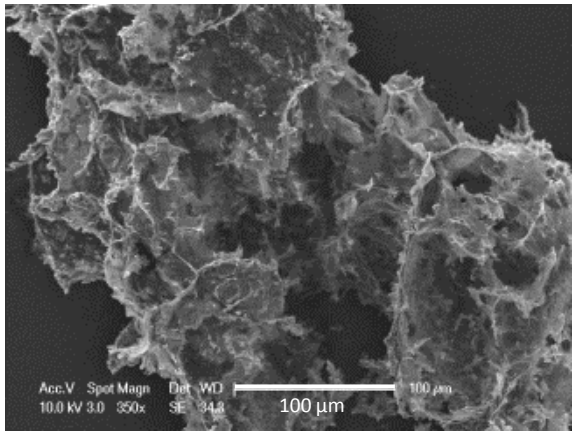


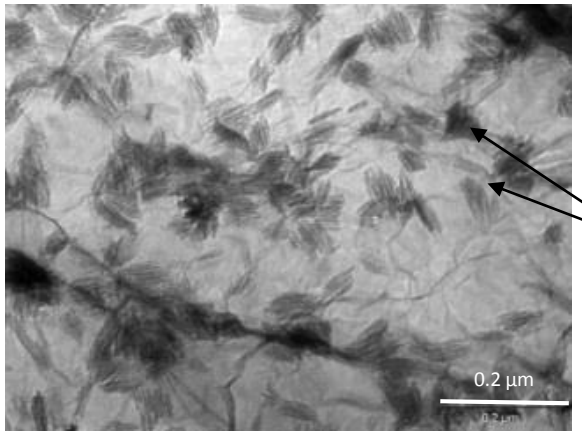




Idealised Structure of Graphene Oxide

FeG: SEM and TEM images





iron oxide particles (goethite mineral)

Additional characterisation:

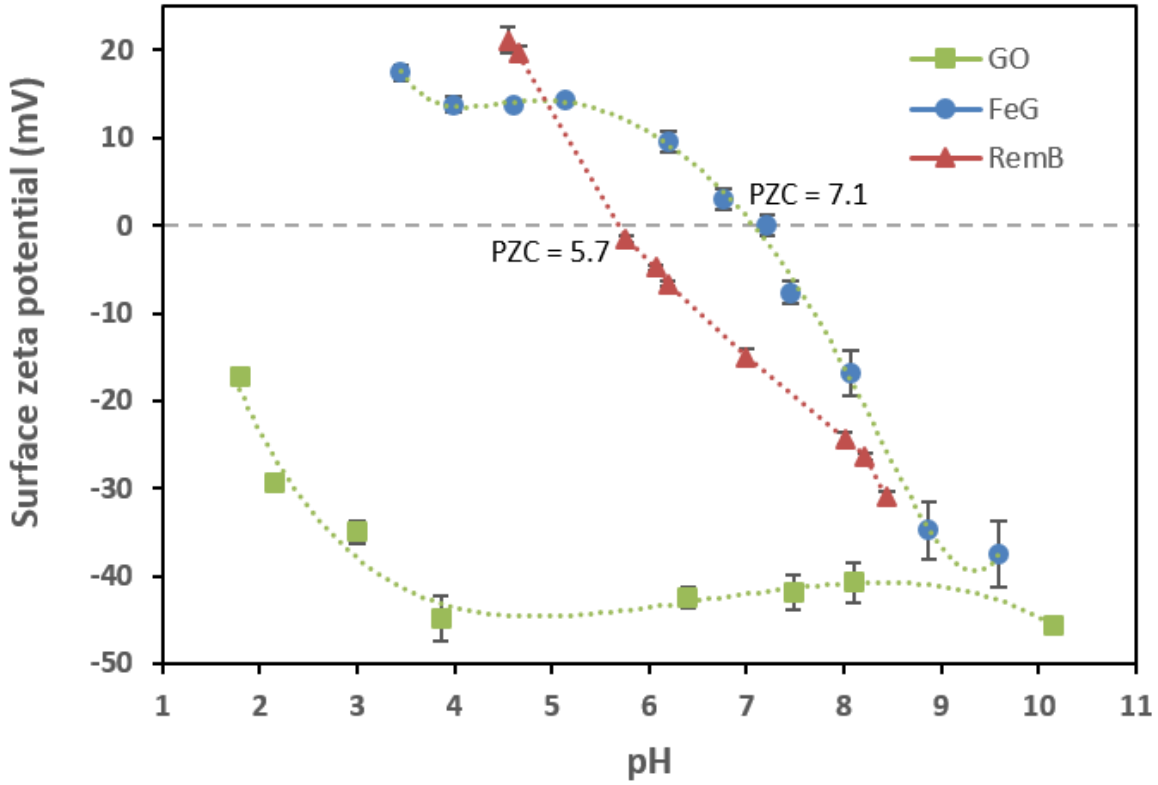
- XRD spectra
- FTIR spectra

Surface Characterisation

Specific surface area (25 °C)

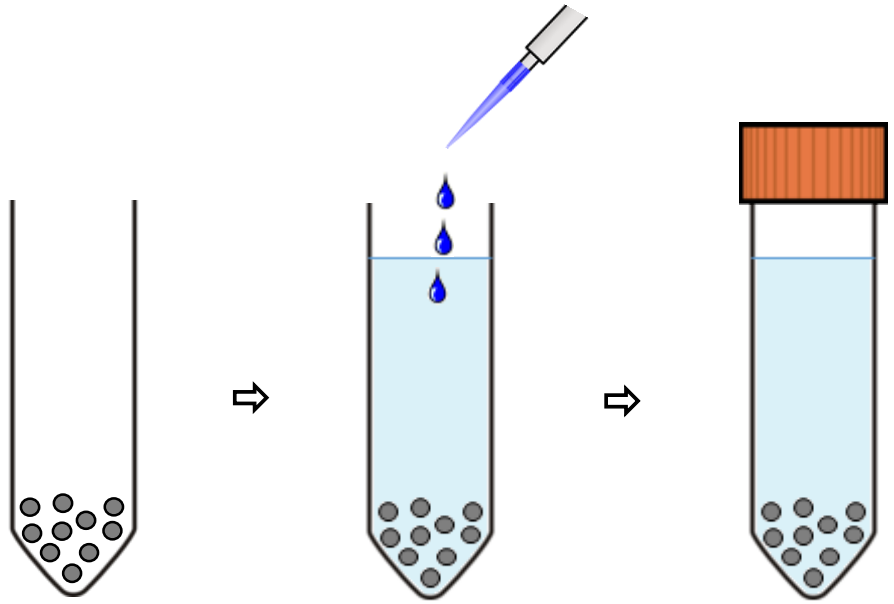
Adsorbent	Specific surface area
GO	434.6 m^2/g
FeG	242.4 m^2/g
RemB	123.4 m^2/g
Kaolinite[1]	~ 25 m^2/g

Surface zeta potential (25 °C)



[1]*Avena, Marcelo J., et al. (2001). "Methylene blue dimerization does not interfere in surface-area measurements of kaolinite and soils." Clays and clay minerals 49.2: 168-173.*

Experimental methods & PFOA analysis



Weigh adsorbents

Spike PFOA solutions (10 mM $CaCl_2$ background electrolyte)

Shake (48 hrs), centrifuge, remove aliquot for analysis

Radiochemical Analysis:

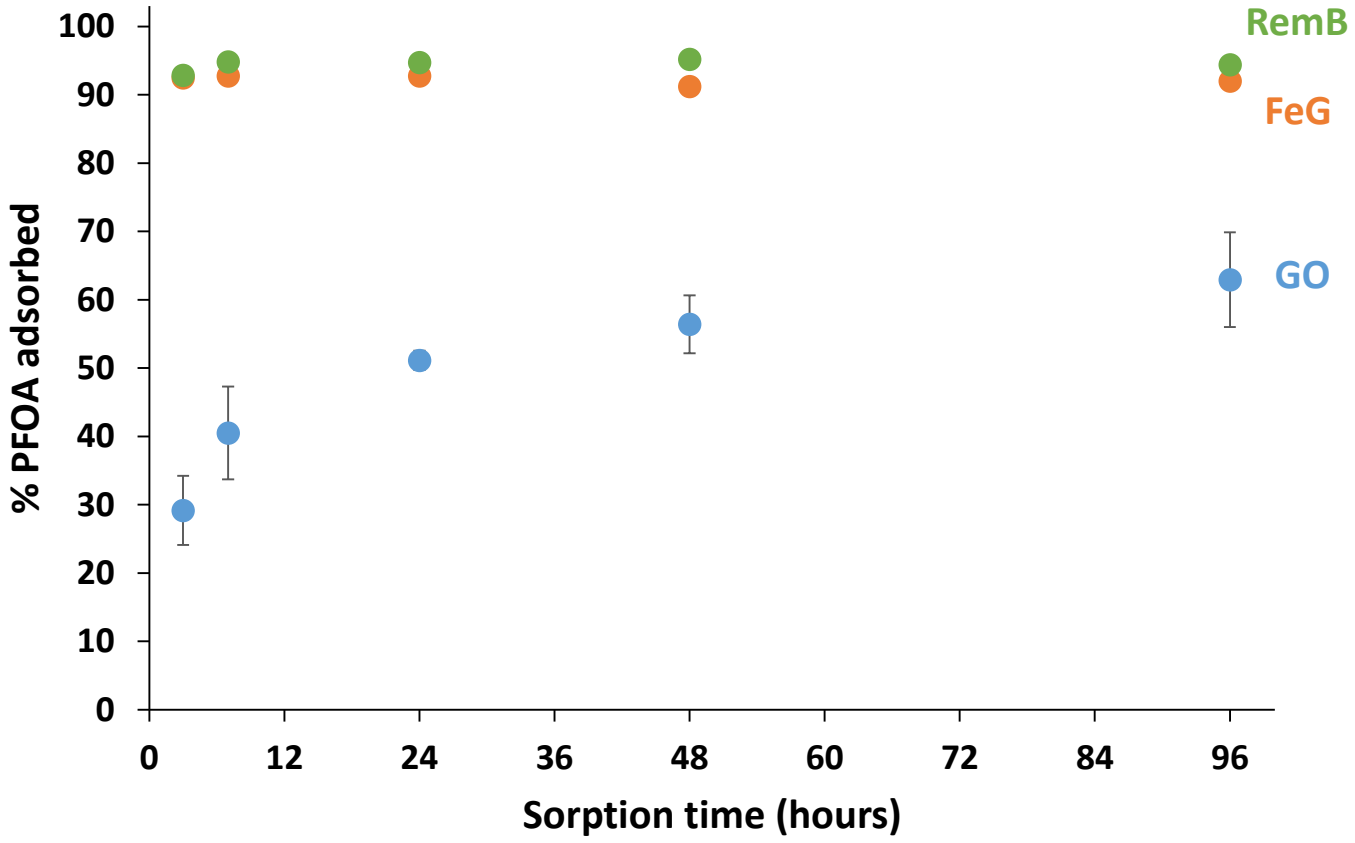
Isotopically labelled (^{14}C) PFOA, (ARC Inc., USA)

Liquid scintillation β-counting measures ^{14}C activity.

Specific activity = 2035 MBq/mmol

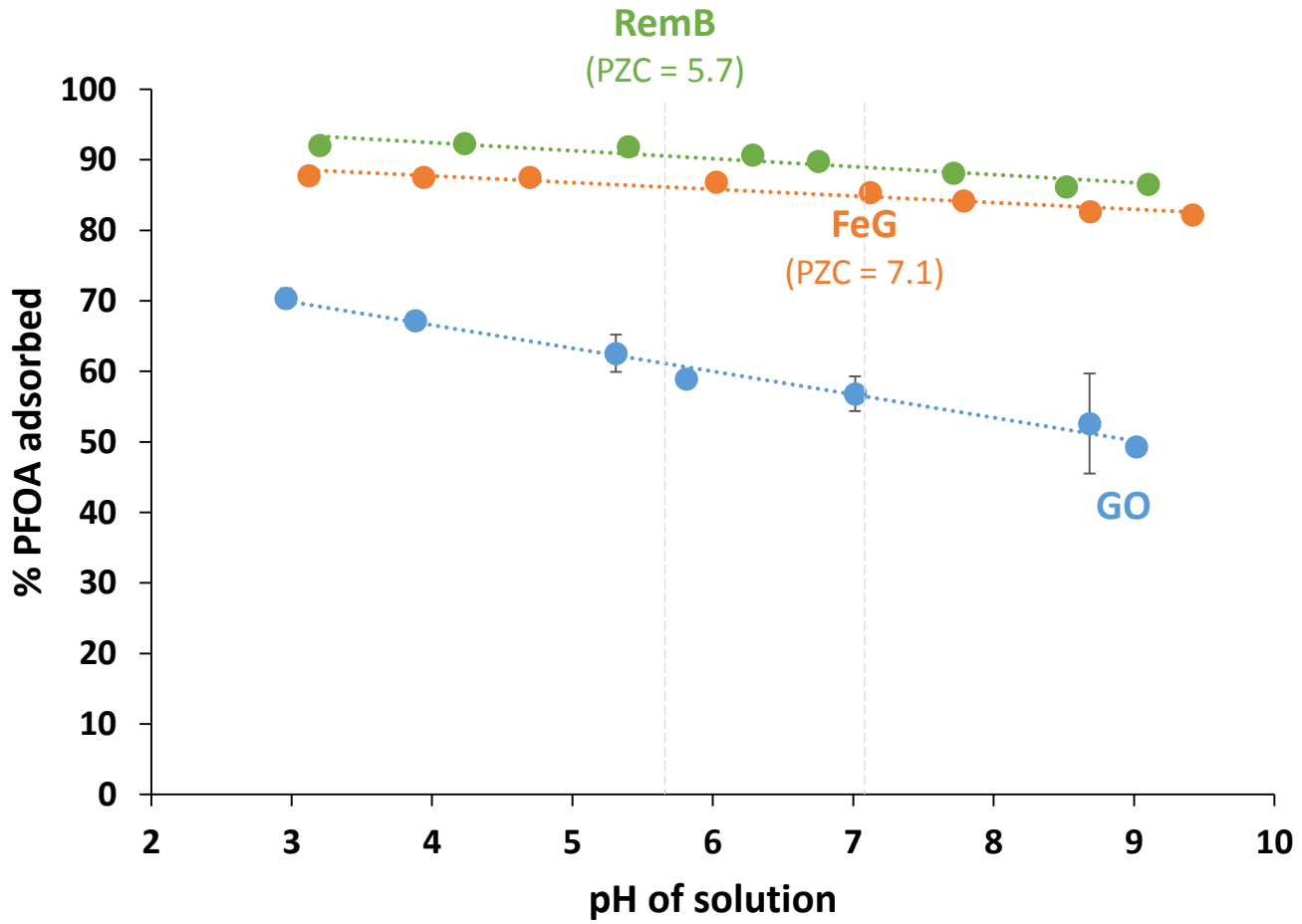
Note: PFOA concentration calculations were corrected for any sorption that occurred on the reaction vessels during batch sorption.

PFOA sorption: equilibrium time



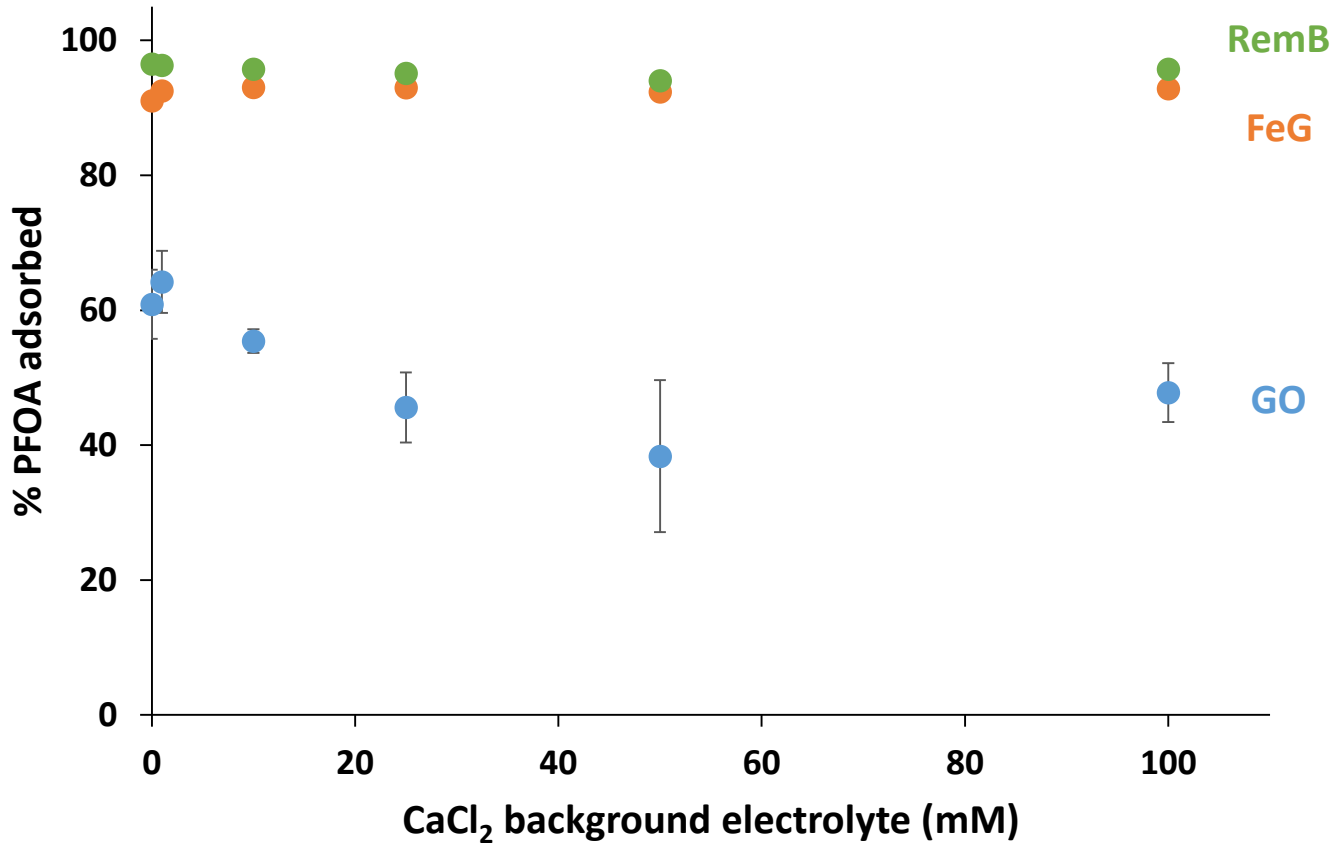
- Time: 0 – 96 hrs
- Initial [PFOA] ~ 30 ng/mL
- pH 5.5
- 10 mM $CaCl_2$ background
- 25 °C

PFOA sorption: effect of pH



- **pH: 3 – 9**
- **Initial [PFOA] 100 ng/mL**
- **10 mM $CaCl_2$ background**
- **48hrs**
- **25 °C**

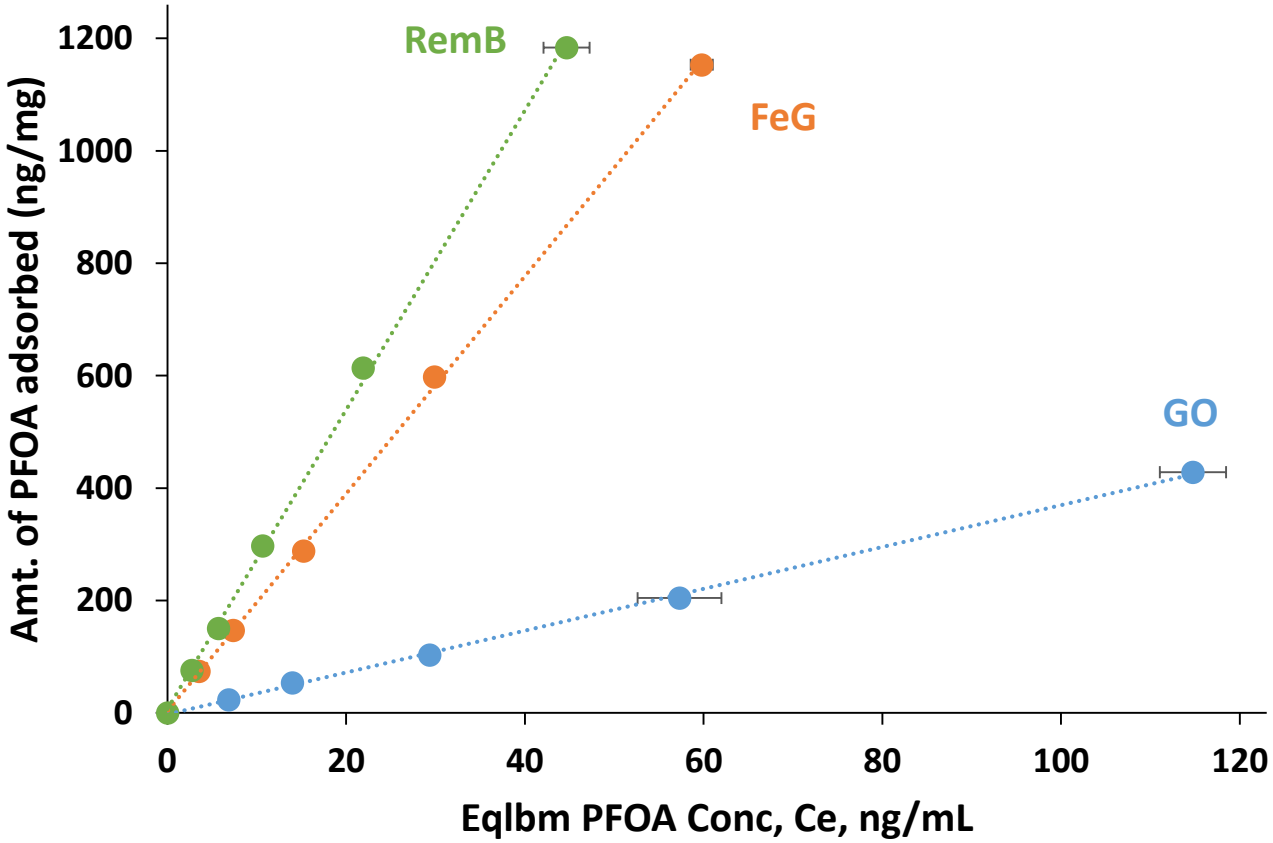
PFOA sorption: effect of ionic strength



- 0 – 100 mM $CaCl_2$ background
- Initial [PFOA] 20 ng/mL
- pH 5.5
- 48hrs
- 25 °C

Background electrolyte	Elec. conductivity mS/cm = dS/m
10 mM $CaCl_2$	2.11 (non-saline soil)
25 mM $CaCl_2$	4.93 (saline soil)
50 mM $CaCl_2$	9.24 (landfill leachate)

PFOA sorption: effect of concentration (isotherm)



- Initial [PFOA] 0 – 650 ng/mL
- 10 mM $CaCl_2$ background
- pH 5.5
- 48hrs
- 25 °C

Summary

✓ GO & FeG successfully adsorbed PFOA FeG > GO

✓ Surface area did not correlate with sorption performance

✓ Effect of pH and ionic strength
- Efficiency of GO ↓ with ↑ in pH
- FeG & RemB resistant to changes

✓ No saturation of binding sites to concentrations up to 650 µg/L PFOA

✓ Binding related to non-ionic interactions with surfaces
- Hydrophobic interactions
- Possible role of Important role of minerals Fe, Al, Si

Acknowledgements

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