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Supplementary Material

Sorptive Remediation of Perfluorooctanoic Acid (PFOA) Using Mixed Mineral and Graphene/Carbon-Based Materials

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Table of Contents

Text S1. Synthesis of graphene oxide (GO) and Fe-oxide-modified reduced GO composite (FeG).

A top-down approach based on an improved Hummer's method [1] which involves strong oxidative exfoliation of graphite using concentrated H_2SO_4, H_3PO_4 and $KMnO_4$ was used to synthesise GO. Unreacted $KMnO_4$ was reduced using 30% H_2O_2, and multiple wash cycles were performed with 30% HCl and distilled water to remove metal and acid residues. The material was dried (35 °C, 36 hours) to obtain the solid GO product, which was used as flakes. Based on a method reported by Cong et al. [2], GO was further modified by adding $FeSO_4.7H_2O$ to a stable suspension of well-exfoliated GO. After adjusting the pH to 3.5 using ammonia, the suspension was hydrothermally reduced at 90 °C for 6 hrs without stirring until a black 3D hydrogel monolith (FeG) was formed. The hydrogel was then separated, washed, freeze dried and crushed into the powdered FeG product.

Text S2. Sample preparation for characterisation of adsorbents.

SEM-EDX samples were prepared by applying the dried adsorbents directly onto aluminium stubs covered with adhesive carbon tape. Images were obtained using a spot size of 3, and an accelerating voltage of 10 kV. For TEM, adsorbents were ultra-sonicated in ethanol (20 min), after which the suspensions were drop-casted onto a Lacey copper grid and dried for a few hours before imaging at an accelerating voltage of 100 kV.

FTIR and XRD analyses were performed using powdered adsorbent samples. FTIR spectra were recorded at wavelengths ranging from 400 - 4000 cm^{-1}. XRD spectra were recorded using Fe-filtered Co Kα radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3 - 80° in steps of 0.017° 2 theta with a 0.5 second counting time per step for an overall counting time of approximately 35 minutes.

Specific surface area (SSA) of adsorbents were measured using the Methylene Blue (MB) dye absorption method commonly used for carbonaceous materials. 15 mg of each adsorbent was added to 150 mL of 20 mg/L MB solutions and shaken for 60 hrs at 100 rpm to allow the solutions to attain equilibrium and maximum absorption. After centrifugation, supernatants were analysed using UV-visible spectrophotometry (at 664 nm) and compared to controls to determine the amount of MB absorbed. The SSA was then calculated using the following equation:

$$SSA = \frac{N_A . A_{MB} . (C_i - C_e) . V}{M_{MB} . m_s}$$

where, N_A represents Avogadro number (6.023 x 10^{23} molecules/mole), A_{MB} is the area covered per MB molecule (1.35 nm^2), C_i and C_e are the initial and equilibrium MB concentrations, respectively, V is the volume of MB solution, M_{MB} is the molecular mass of MB, and m_s is the mass of the adsorbent.

Surface charge and point of zero charge (PZC) of adsorbents were determined by using 0.1 % w/v suspensions in Milli Q water, that were adjusted to pHs ranging from around 2 – 10. The suspensions were placed on a shaker for 48 hours to equilibrate pH before measuring zeta potential across the pH gradient using dynamic light scattering (Malvern Zetasizer NanoZS).

Table S1. Full names and abbreviations for the suite of PFASs measured in the field water sample.

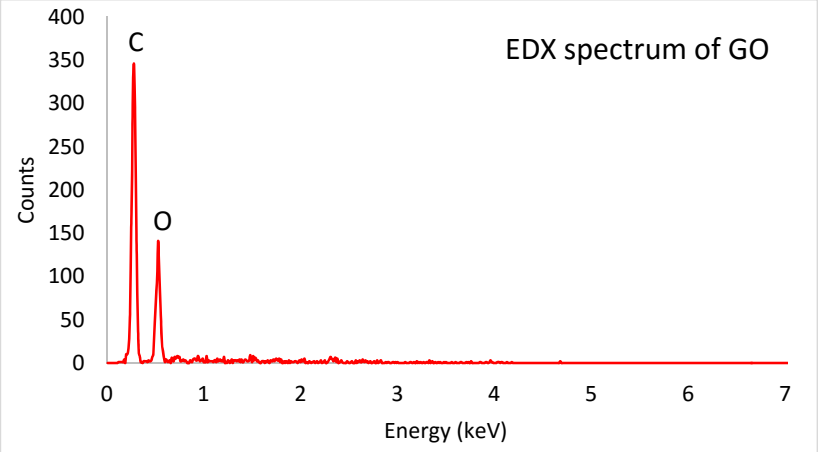
PFAS name	Abbreviation and CAS No.
Perfluoroalkyl carboxylates (increasing order of chain length)	
Perfluoro-n-butyrate	PFBuA (375-22-4)
Perfluoro-n-pentanoate	PFPeA (2706-90-3)
Perfluoro-n-hexanoate	PFHxA (307-24-4)
Perfluoro-n-heptanoate	PFHpA (375-85-9)
Perfluoro-n-octanoate	PFOA (335-67-1)
Perfluoro-n-nonanoate	PFNA (375-95-1)
Perfluoro-n-decanoate	PFDA (335-76-2)
Perfluoroalkyl sulphonates (increasing order of chain length)	
Perfluoro-n-butanesulfonate	PFBS (375-73-5)
Perfluoro-n-hexanesulfonate	PFHxS (432-50-7)
Perfluoro-n-octanesulfonate	PFOS (1763-23-1)
Fluorotelomers and perfluoroalkylsulphonamides	
1H,1H,2H,2H-perfluoro-n-octane sulfonate	6:2 FTS (27619-97-2)
1H,1H,2H,2H-perfluoro-n-decane sulfonate	8:2 FTS (39108-34-4)
Perfluorooctanesulfonamide	PFOSA (754-91-6)

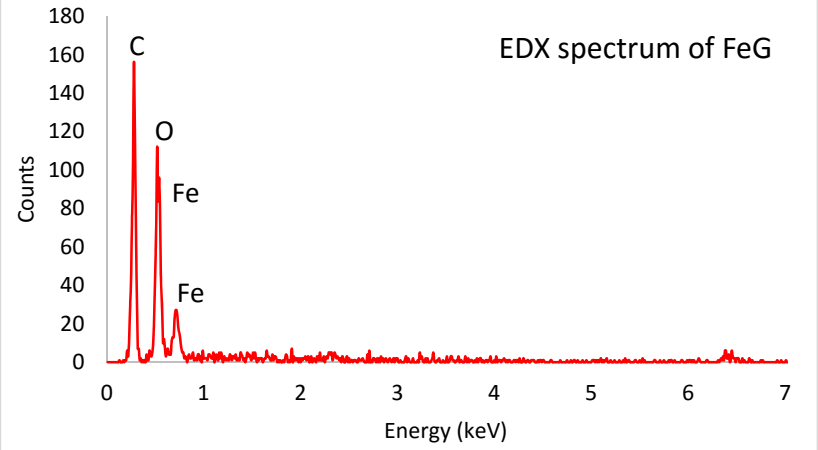
92 Table S2. Elemental composition of adsorbents graphene oxide (GO), Fe-oxide-modified
93 reduced GO composite (FeG) and RemBind™ (RemB), as determined by energy dispersive
94 X-ray (EDX) detector coupled to a scanning electron microscope. See Figure S1 for EDX
95 spectra.
96

Adsorbent	Element (series)	Weight %	Atomic %
GO	C (K)	65.88	72.01
	O (K)	34.12	27.99
FeG	C (K)	37.19	56.39
	O (K)	28.48	32.42
	Fe (K)	34.34	11.20
RemB	C (K)	22.42	34.37
	O (K)	27.70	31.89
	Si (K)	38.63	26.36
	Al (K)	11.26	7.38

97

Figure S1. Energy dispersive X-ray (EDX) spectra collected for adsorbents graphene oxide (GO), Fe-oxide-modified reduced GO composite (FeG) and RemBind™ (RemB) to elucidate elemental composition. All adsorbents exhibited signals for carbon and oxygen. FeG displayed an additional signal for iron, and RemB displayed additional signals for aluminium and silicon.





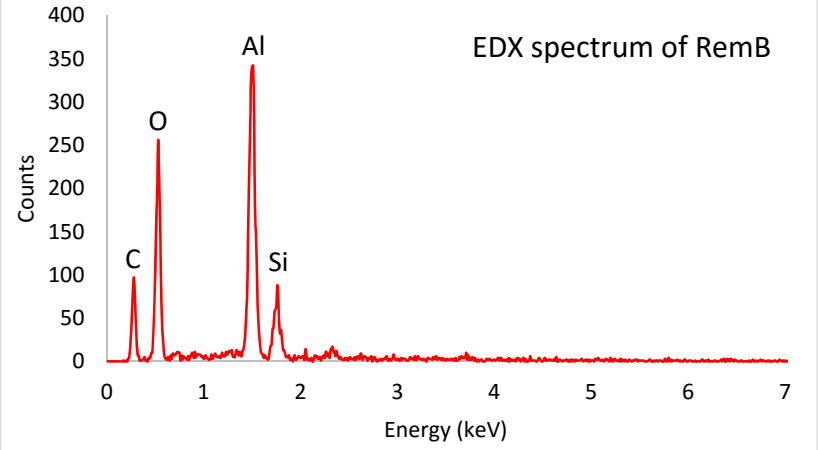


Figure S2. X-ray diffraction (XRD) spectra of adsorbents graphene oxide (GO), Fe-oxide-modified reduced GO composite (FeG) and RemBind™ (RemB)

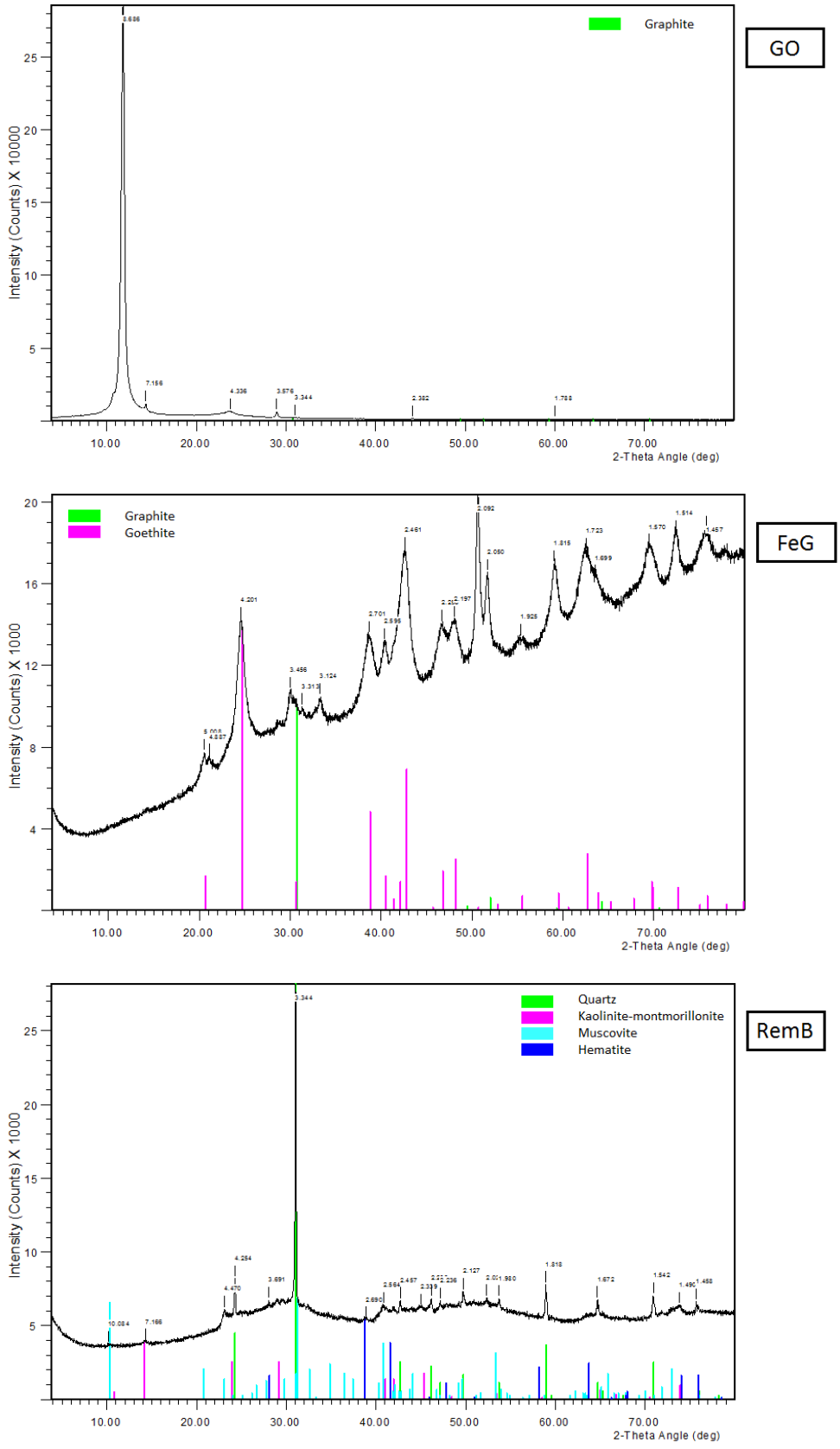


Figure S3. Fourier-transform infrared (FTIR) spectra of adsorbents graphene oxide (GO), Fe-oxide-modified reduced GO composite (FeG) and RemBind™ (RemB)

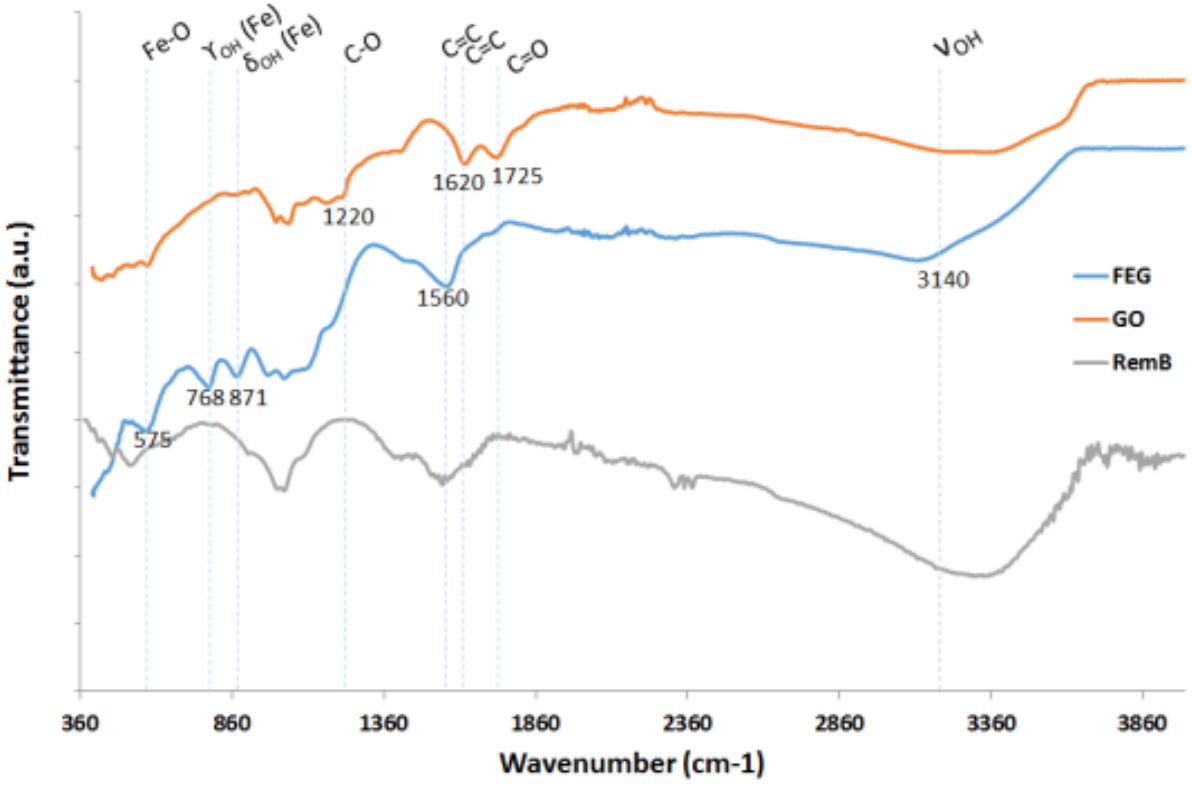
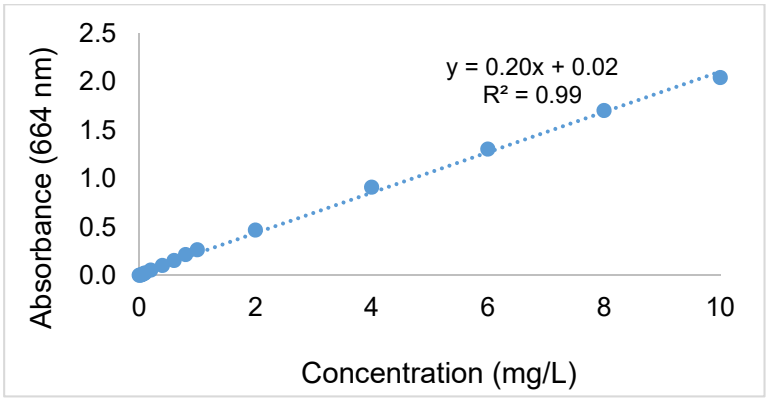
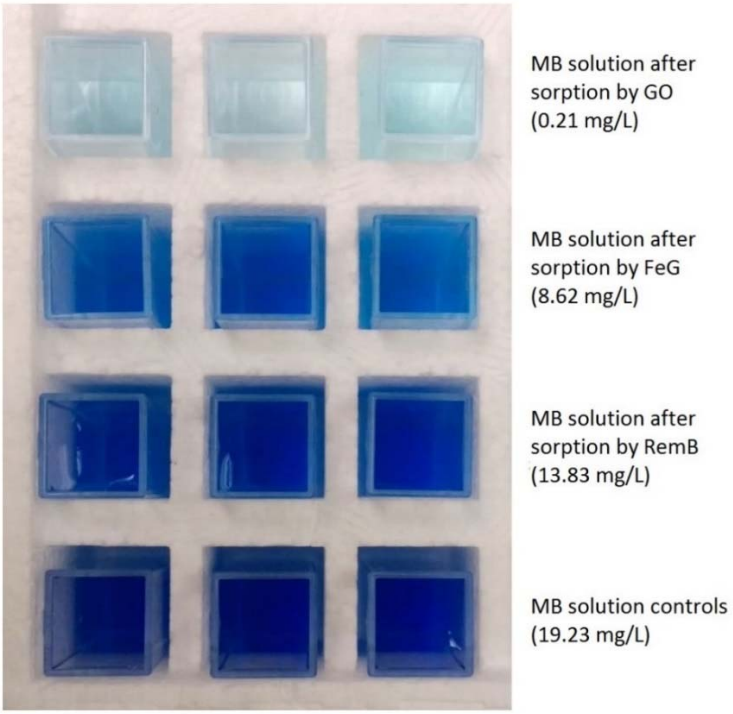


Figure S4. Methylene Blue standard calibration curve (664 nm) and sample analysis for measurement of surface areas of adsorbents graphene oxide (GO), Fe-oxide-modified reduced GO composite (FeG) and RemBind™ (RemB).





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2. H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, Macroscopic multifunctional graphene-based hydrogels and aerogels by a metal ion induced self-assembly process. *ACS Nano*, **2012**. *6(3)*: 2693-2703.