Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Magnetic few-layers graphene nanocomposites for the highly efficient removal of benzo(a)pyrene from water

Joana Vaz-Ramos, Dominique Bégin, Paula Duenas-Ramirez Anaïs Becker, Mathieu Galmiche, Maurice, Millet, Sylvie Bégin, Stéphane Le Calvé**

Table S1. Previous studies reported in the literature using carbon based and/or magnetic materials for the adsorption of PAHs in water [19,26–32]

Adsorbent [a]	Adsorbent Conc. (mg L^{-1})	PAH [b]	PAH Conc. (µg L^{-1})	Co-solvent [c]	Method [d]	RE [e] (%)	q_{max} [f] (mg g^{-1})	Recovery [g] (%)	Ref.
Fe^0/iron oxide-oxyhydroxide/ graphene	300	Mix 16 EPA PAHs	1	n.m.	MSPE	-	-	~95	Karamani *et al.*
Fe^0/iron oxide-oxyhydroxide						-	-	~10	
graphene						-	-	80	
GO/ FeO•Fe_2O_3	100	NAP	$20x10^3$	n.m.	BA	-	337 (283K) 636 (303K) 733 (323K)	-	Yang *et al.*
MWCNTs/ FeO•Fe_2O_3						-	135 (283K) 445 (303K) 456 (323K)	-	
FeO•Fe_2O_3						-	73 (283K)	-	
m-G/CNF	1000	NAP	0.1 50	MeOH (residual)	Magn. SPE [h]	-	-	99.3 99.8	Rezvani-Eivari *et al.*
		FL	0.1 50			-	-	97.9 98.8	
		PHE	0.1 50			-	-	99.1 99.9	
Iron oxide nanoparticles	10 130	BaP	1	n.m.	BA	20 [i] 71.6 [i]	-	-	Hassan *et al.*
	90		1–4	n.m.	BA	99–79.5 [j]	0.029	-	
	10 130	PY	100	n.m.	BA	30 [i] 67.8 [i]	-	-	
	90		100–400	n.m.	BA	98–78.3 [j]	2.8	-	
C_{11}-Fe_3O_4	30 180	BaP	2	n.m.	BA	8.4 79.7	-	-	Yang *et al.*
	180		0.5–14	n.m.		-	$59.89x10^{-3}$	-	
CDs/C_{11}-Fe_3O_4	30 180		2	n.m.		14.7 93.9	-	-	
	180		0.5–14	n.m.		-	$76.23x10^{-3}$	-	
MMWCNT	5 100	PHE	50–800	DMSO (<0.1%)	BA	~10-20 ~100	-	-	Zhang *et al.*
	20		50–800			-	20.0 – 28.46	-	
MSWCNT	5 100		50–800			~80 ~100	-	-	
	20		50–800			-	74.61	-	
MGNS	5 100		50–800			~25 ~100	-	-	
	20		50–800			-	31.53	-	
MGO	20	PHE	10–1200	ACN (<0.1%)	BA	-	13.65	-	Huang *et al.*
MCRG	4.2					-	30.12	-	
MARG	12.5					-	26.18	-	
Graphene wool	1000 1250 1500 2500	16 EPA PAHs	400–500	MeOH (1 %)	BA	52.2–72.6 55.1–80 65.3–85.1 80–100	-	-	Adeola & Forbes
	1000	NAP	100–500	MeOH (1 %)	BA [k]	-	0.0489	-	
		ANT				-	12.2	-	
		BaA				-	2.35	-	
		BaP				-	1.52	-	
		BghiP				-	16.0	-	

FLG@TA@RSN	5	BaP	10	EtOH (1 %)	BA	99.95	1.27	-	This work
				EtOH (10 %)		95.42	-	-	
				EtOH (50 %)		31.70	-	-	
			10–5000	EtOH (50 %)		-	68.13	-	
FLG@TA			10	EtOH (50 %)		25.76	-	-	

[a)] Fe^0 – zero-valent iron, GO – graphene oxide, MWCNTs – multi-walled carbon nanotubes, m-G/CNF – magnetized graphene on carbon nanofibers, rGO – reduced graphene oxide, CDs/C_{11}-Fe_3O_4 – carbon dots/fatty acid-coated magnetic nanoparticles, MMWCNTs – magnetic multi-walled carbon nanotubes, MSWCNTs – magnetic single-walled carbon nanotubes, MGNS – magnetic graphene nanosheets, MGO – magnetic graphene oxide, MCRG – magnetic chemically-reduced graphene, MARG – magnetic annealing-reduced graphene; [b)] NAP – naphthalene, FL – fluorene, PHE – phenanthrene, ANT – anthracene, PY – pyrene, BaP – benzo(a)pyrene; [c)] n.m. – not mentioned, MeOH – methanol, DMSO – Dimethyl sulfoxide, ACN – acetonitrile, EtOH – ethanol; [d)] MSPE – micro solid-phase extraction, BA – batch adsorption, magn. SPE – magnetic solid phase extraction; [e)] RE – removal efficiency obtained for batch experiments; [f)] q_{max} – maximum adsorption capacity; [g)] recovery = (amount of PAH present in the solution after desorption of the adsorbent / amount of PAH present in the initial solution)×100 and is typically calculated in solid-phase extraction experiments; [h)] tap water samples spiked with the indicated PAHs; [i)] for adsorption time of 30 minutes; [j)] for adsorption time of 150 minutes; [k)] single solute experiments.

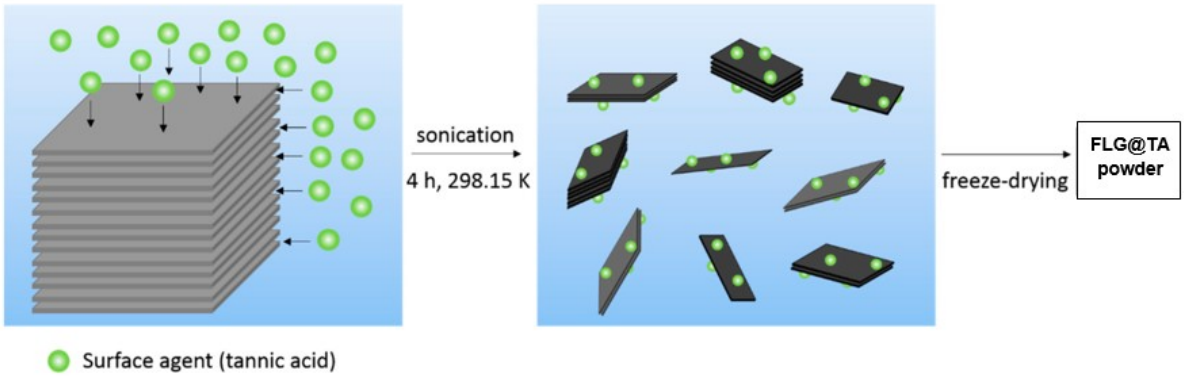

Figure S1. Illustration of the preparation of FLG@TA.

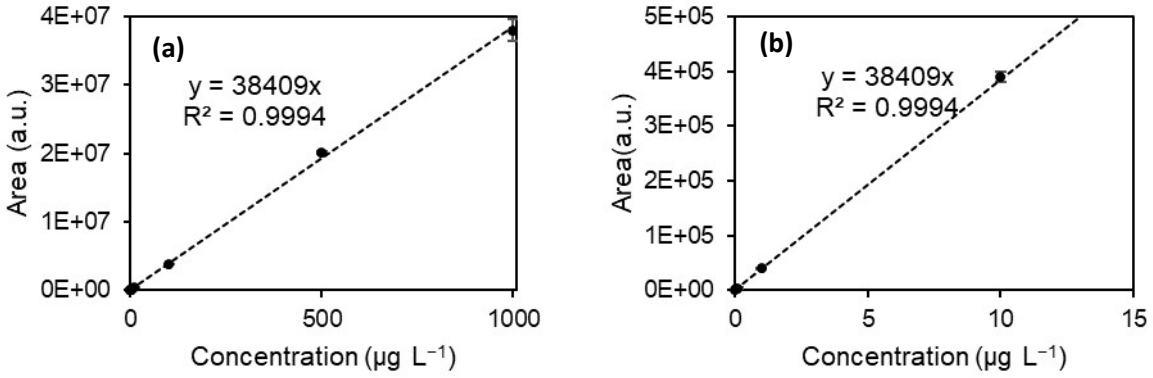

Figure S2. (a) 7-point calibration curve of benzo(a)pyrene (BaP) obtained by Ultra High-Performance Liquid Chromatography with Fluorescence Detection (UHPLC/FLD) in the range 0.010–1000 µg L^{-1} of BaP concentration in acetonitrile; **(b)** Zoom in on the calibration curve of BaP obtained by UHPLC/FLD in the range 0.010–10 µg L^{-1} in acetonitrile. The vertical error bars correspond to the standard deviation of peak area determined from triplicates.

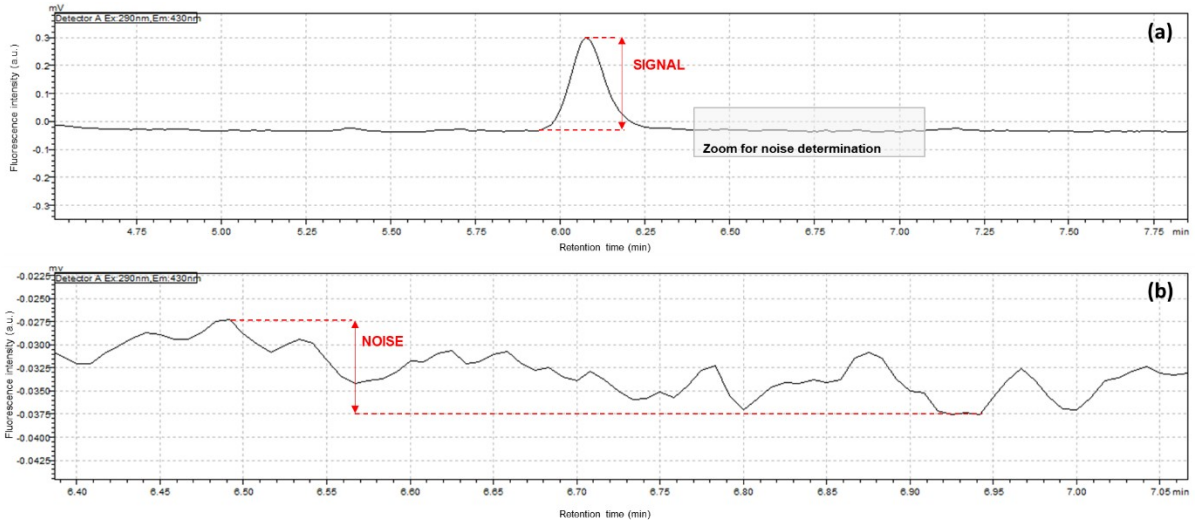

Figure S3. Example of signal and noise determinations for Limit of Detection (LOD) and Limit of Quantification (LOQ) calculations for the quantification of BaP by UHPLC/FLD: **(a)** signal determined from the chromatogram corresponding to a standard solution of BaP at a concentration of 0.05 µg L^{-1} in acetonitrile; **(b)** noise experimentally determined from the baseline obtained in the same chromatogram, here, just after the peak of BaP.

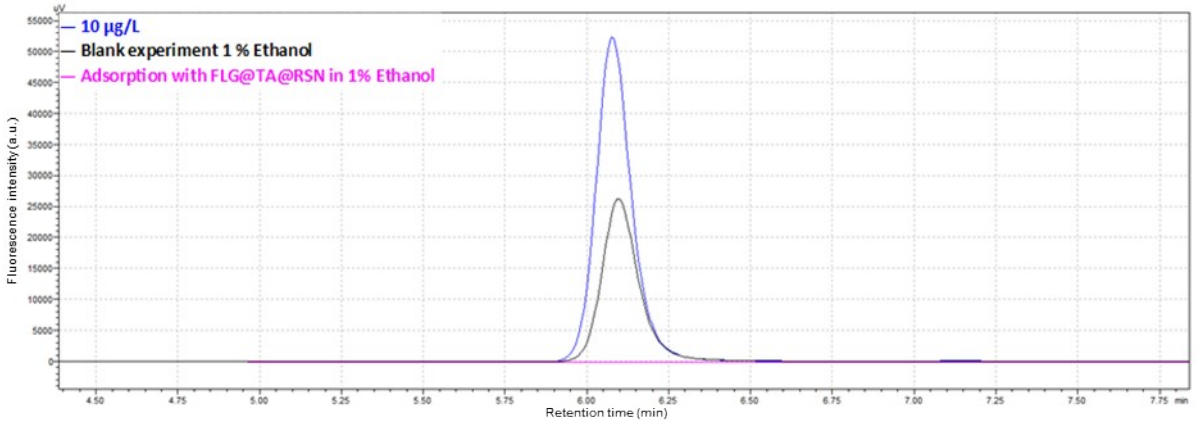

Figure S4. Examples of chromatograms obtained for a standard solution of BaP at a concentration of 10 µg L^{-1} in acetonitrile (blue); at the end of the blank experiment with an initial concentration of BaP of 10 µg L^{-1} in 1% ethanol : 99% water (black); at the end of the adsorption experiment with an initial concentration of BaP of 10 µg L^{-1} in 1% ethanol : 99% water (pink).

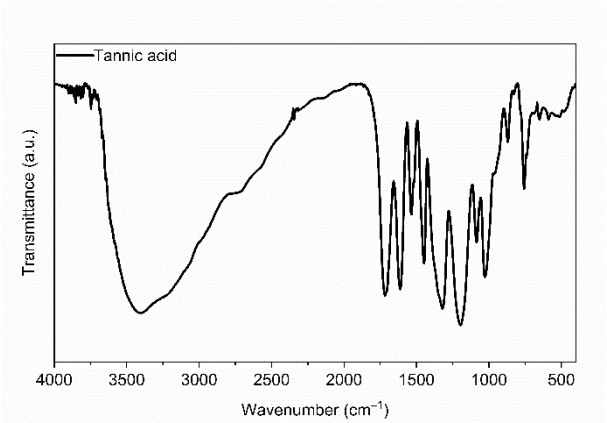

Figure S5. IR spectrum of tannic acid.

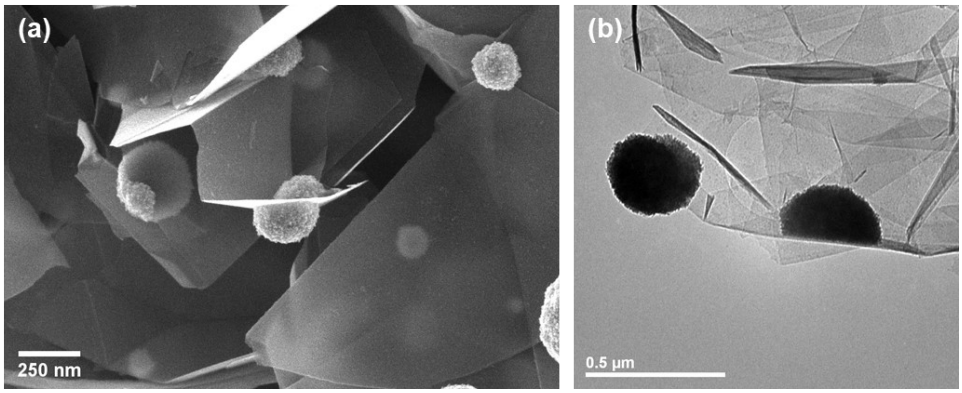

Figure S6. (a) Scanning Electron Microscopy (SEM) image and **(b)** Transmission Electron Microscope **(**TEM) image of FLG@TA@RSNs CNs.

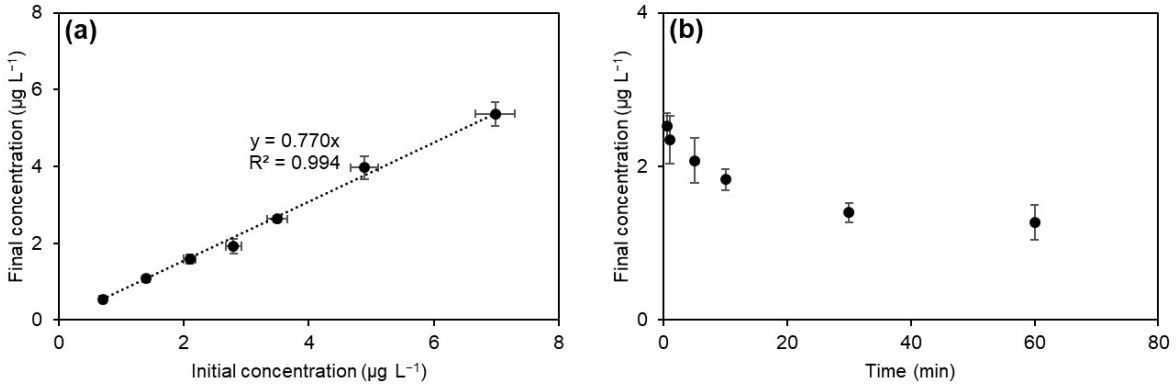

Figure S7. Blanks experiments in 1% Ethanol to quantify adsorption by glassware at room temperature: **(a)** isotherm experiments; **(b)** kinetics experiments. The vertical error bars correspond to the standard deviation of final concentration of BaP in solution determined from triplicates, while the horizontal ones in Figure S7(a) are based on the standard deviation of concentration of BaP in the fresh working solution prepared immediately before the experiments.

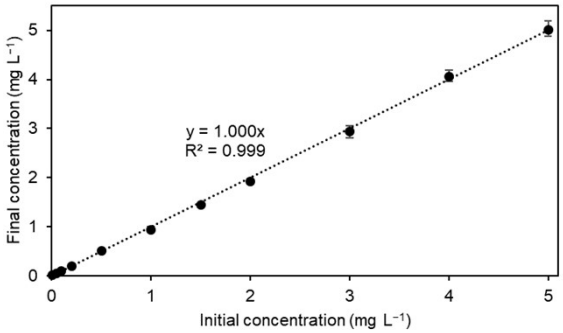

Figure S8. Blank experiments in 50% Ethanol to quantify BaP adsorption by glassware at room temperature. The vertical error bars correspond to the standard deviation of final concentration of BaP in solution determined from triplicates.