Electronic Supplementary Information for:

Amino acid-driven adsorption of emerging contaminants in water by modified graphene oxide nanosheets

Contents:

1. Purification setup

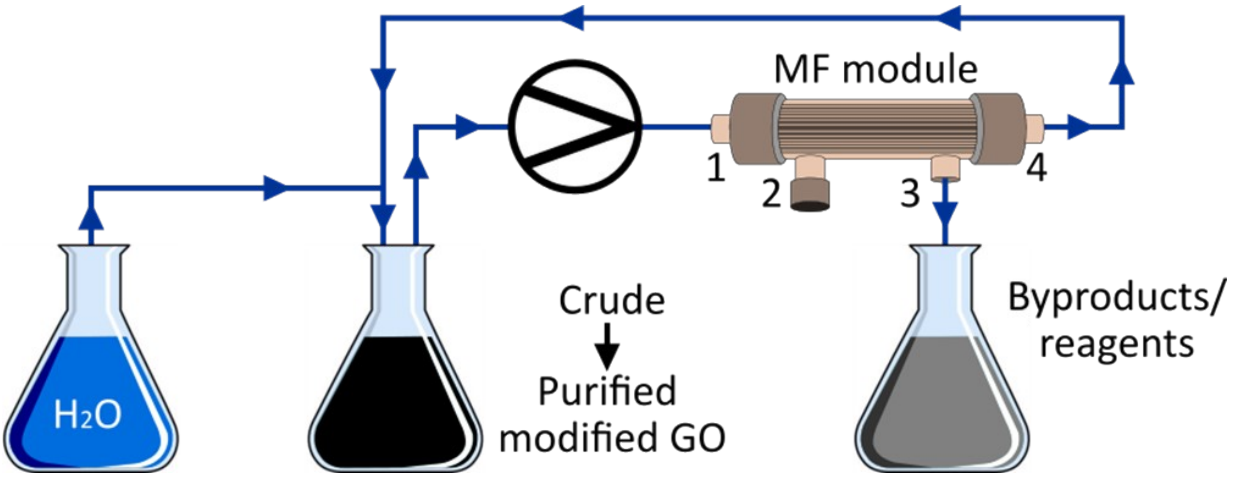

Fig. S1. Sketch of the purification set up. The crude is pumped into the microfiltration module (Plasmart 100, Versatile™ PES membranes, cut-off 150 nm) in tangential modality, i.e. input from nozzle 1, output from nozzle4. Nozzle 3 was opened to collect water with unreacted by-products, while modified GO could not pass through the membrane section, and it was recirculated 1→4. Ultrapure water was periodically added to the feed suspension to wash the GO nanosheets during the recirculation that was carried out until no amino acids residuals were detected into the washing water solution and until the pH was neutral.

2. Zeta potential

Z potential was measured in ultrapure water, using NanoBrook Omni Particle Size Analyzer Brookhaven Instruments Corporation, USA.

3. X-Ray Photoelectron spectroscopy (XPS)

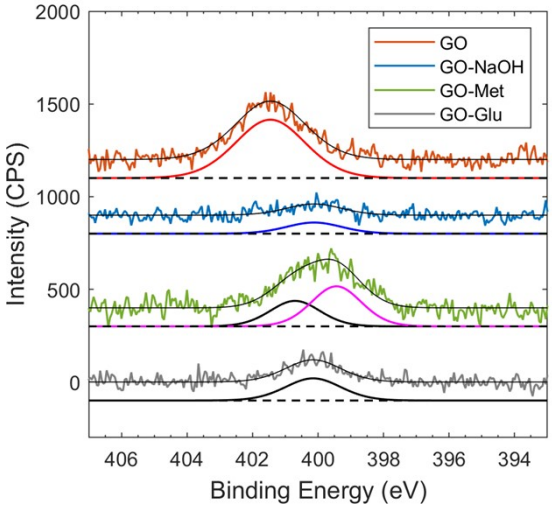

Fig. S2. N1s XPS signal of GO, GO-NaOH, GO-Met and GO-Glu. The fitted peaks were at: 401.5 eV for GO, 400.1 eV for GO-NaOH, 400.7 eV and 399.4 eV for GO-Met and 400.2 eV for GO-Glu.

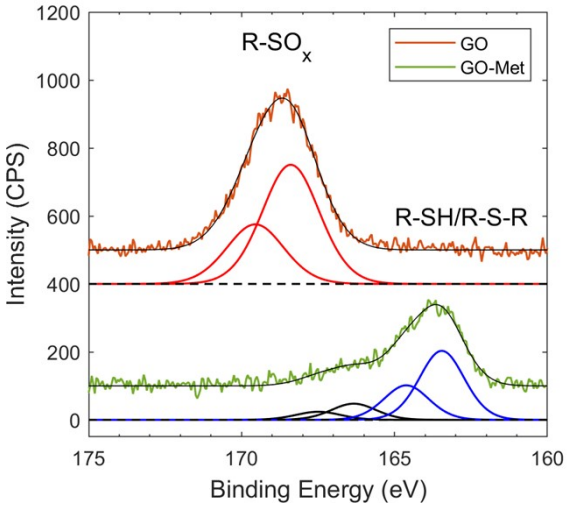

Fig. S3. S 2p XPS signal of GO and GO-Met. The fitted S 2p 3/2 were at 168.4 eV for GO, 163.4 eV and 166.3 eV for GO-Met.

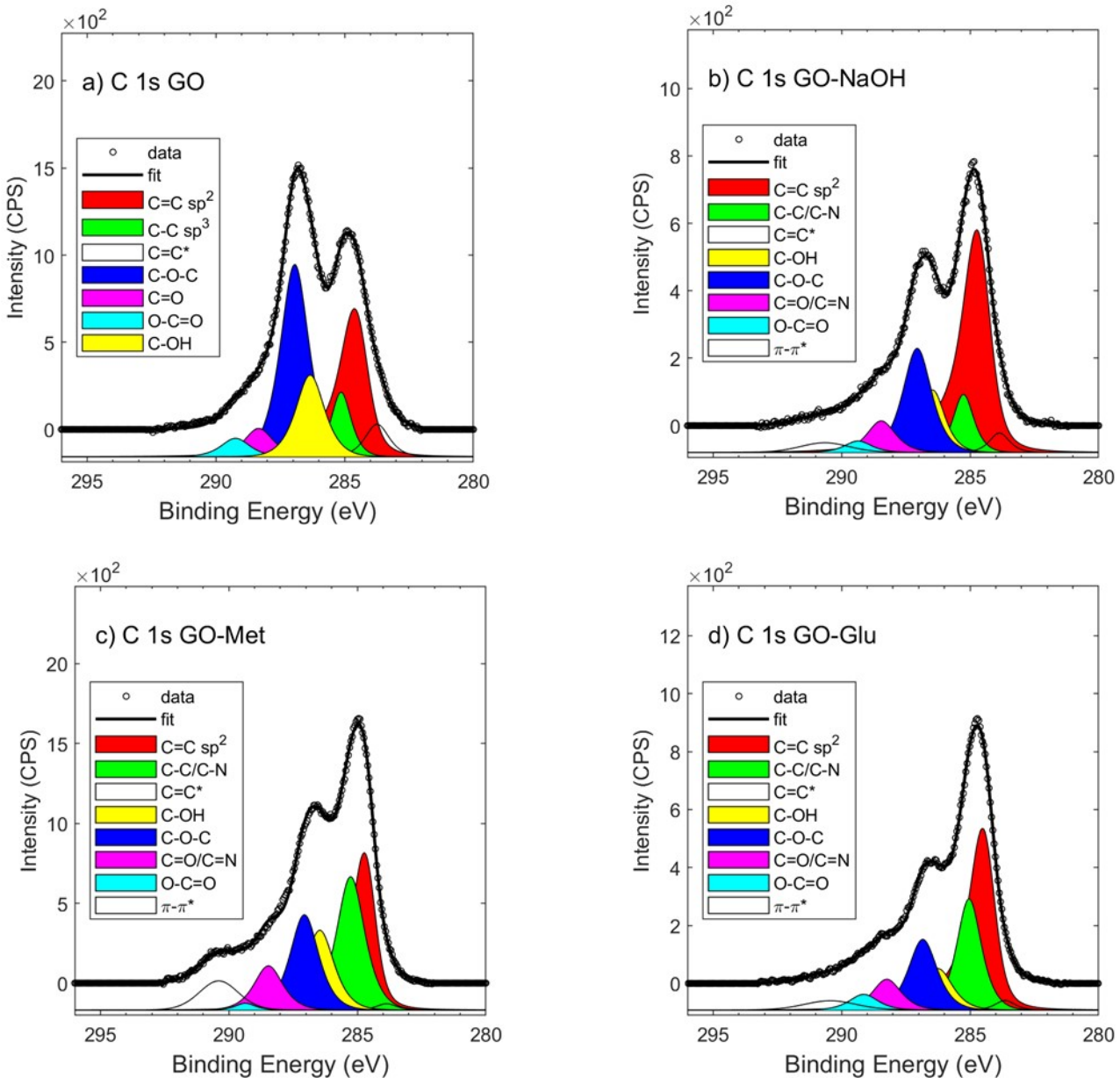

Fig. S4. C1s XPS signal of a) GO, b) GO-NaOH, c) GO-Met and d) GO-Glu.

Table S1. C1s deconvolution of GO, GO-NaOH, GO-Glu and GO-Met, expressed in %. Some groups present possible overlaps (i.e. C-OH and C-N).

Material	C 1s fit						
	C sp2	**C sp3**	**C=C***	**C-OH/C-N**	**C-O-C**	**C=O/C=N**	**O-C=O**
GO	31.2	7.9	4.8	14.3	33.7	5.0	3.2
GO-NaOH	51.2	8.0	2.6	10.1	19.9	6.0	2.1
GO-Glu	43.3	20.8	1.4	9.0	15.3	6.7	3.4
GO-Met	45.6	14.0	0.3	16.6	13.9	6.6	3.1

Table S2. Atomic ratios of modified GO compounds obtained by XPS.

Material	N/C	S/C	O/C
GO	0.01	0.014	0.38
GO-NaOH	0.003	-	0.36
GO-Met	0.011	0.010	0.19
GO-Glu	0.009	-	0.26
GO-Lys	0.04	-	0.14

4. Elemental Analysis

Table S3. Atomic ratios of amino acids. Expected values between parentheses.

Amino acid	formula	H/C	N/C	S/C	O/C
Met	$C_6H_{13}NO_2S$	2.4 (2.7)	0.17 (0.17)	0.17 (0.17)	0.36 (0.33)
Glu	$NaC_5H_8NO_4$	2.0 (1.6)	0.20 (0.20)	<0.002	1.01 (0.80)
Lys	$C_6H_{14}N_2O_2$	2.5 (2.3)	0.33 (0.33)	<0.001	0.43 (0.33)

Table S4. Atomic ratios of modified GO materials.

Material	H/C	N/C	S/C	O/C
GO	0.71	0.002	0.010	0.77
GO-NaOH	1.07	0.001	0.003	0.92
GO-Met	0.74	0.020	0.012	0.49
GO-Glu	0.95	0.008	-	0.67
GO-Lys	0.96	0.06	-	0.62

5. Adsorption selectivity and kinetic experiments

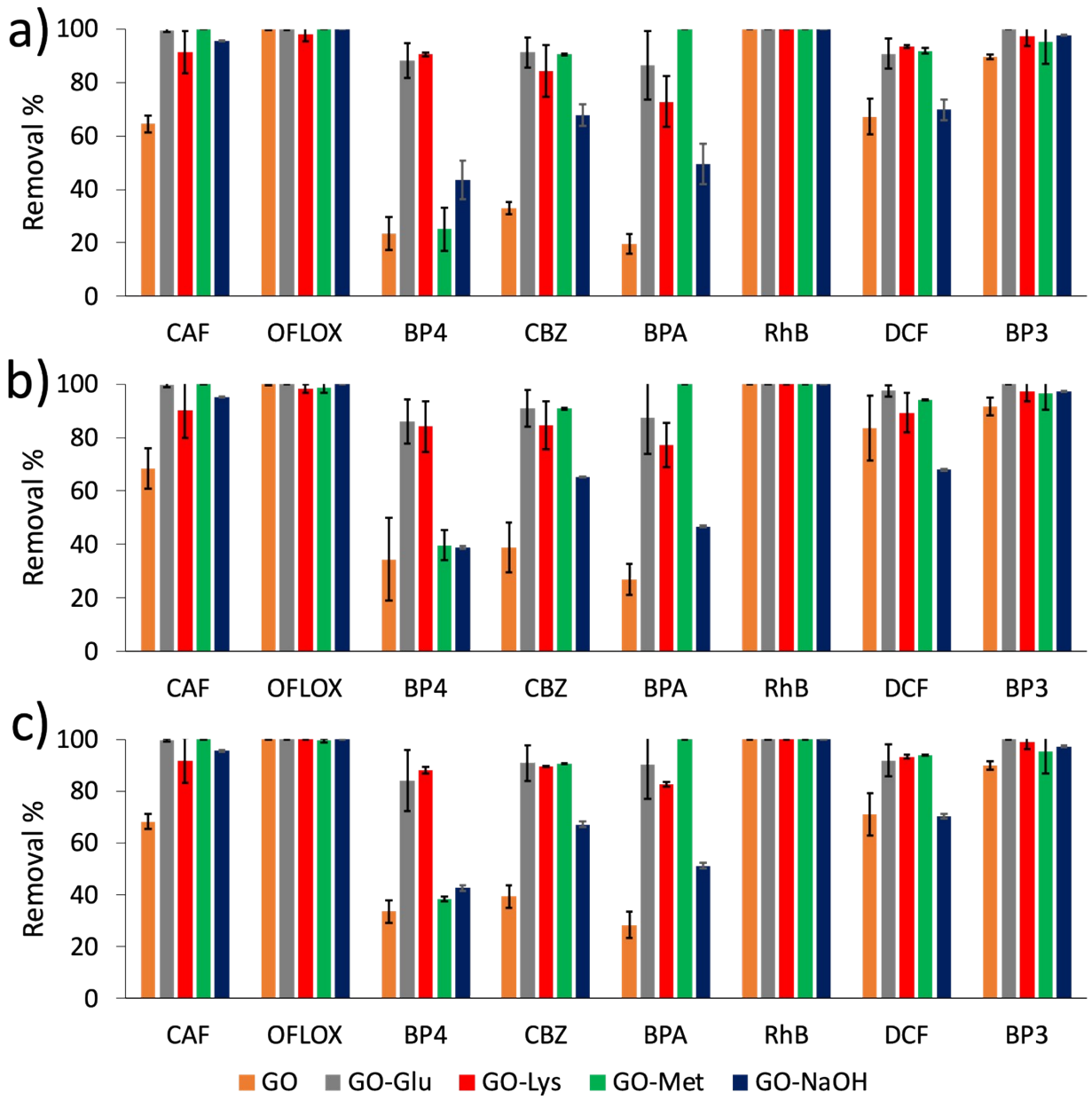

Figure S5. Removal at different contact time of each contaminant from the mixture in tap water (total volume=10 mL, sorbent amount= 25 mg, C_{IN}=5 mg/L of each contaminant) by GO (orange), GO-NaOH (dark blue), GO-Glu (grey), GO-Met (green) and GO-Lys (red). a) contact time 1 h, b) contact time 4h and c) contact time 24 h. Values of GO, GO-NaOH and GO-Lys from ref[1].

6. Adsorption isotherms

Table S5. Experimental parameters of material and solutions used for GO-Met isotherms on BP4, BPA and CBZ.

GO-Met								
Sample	**C_0 BP4 (mg/mL)**	**GO-Met (mg)**	**Sample**	**C_0 BPA (mg/mL)**	**GO-Met (mg)**	**Sample**	**C_0 CBZ (mg/mL)**	**GO-Met (mg)**
1	0.5	7	1	0.27	2	1	0.09	1
2	0.5	5	2	0.15	5	2	0.09	0.5
3	0.5	2	3	0.15	2	3	0.08	3
4	0.25	5	4	0.09	2	4	0.06	1
5	0.25	2	5	0.06	3	5	0.06	1
6	0.1	3	6	0.06	2	6	0.05	3
7	0.1	1				7	0.05	1
8	0.1	2				8	0.025	5

Table S6. Experimental parameters of material and solutions used for GO-Glu isotherms on BP4, BPA and CBZ.

GO-Glu								
Sample	**C_0 BP4 (mg/mL)**	**GO-Glu (mg)**	**Sample**	**C_0 BPA (mg/mL)**	**GO-Glu (mg)**	**Sample**	**C_0 CBZ (mg/mL)**	**GO-Glu (mg)**
1	0.5	7	1	0.24	3	1	0.09	1
2	0.5	5	2	0.24	1	2	0.08	3
3	0.5	2	3	0.15	5	3	0.08	1
4	0.25	5	4	0.15	2	4	0.05	5
5	0.25	2	5	0.09	5	5	0.05	3
6	0.1	5	6	0.09	2	6	0.05	1
7	0.1	2	7	0.06	2	7	0.025	5
						8	0.025	2

Table S7. Experimental parameters of material and solutions used for GO-Glu isotherms on BP4, BPA and CBZ

rGO								
Sample	**C_0 BP4 (mg/mL)**	**rGO (mg)**	**Sample**	**C_0 BPA (mg/mL)**	**rGO (mg)**	**Sample**	**C_0 CBZ (mg/mL)**	**rGO (mg)**
1	0.8	3	1	0.24	3	1	0.09	1
2	0.8	1	2	0.24	1	2	0.07	2
3	0.5	5	3	0.18	5	3	0.05	5
4	0.5	3	4	0.18	1	4	0.05	3
5	0.25	5	5	0.06	3	5	0.05	1
6	0.1	5	6	0.06	1	6	0.025	5
7	0.1	3				7	0.01	3
8	0.05	3				8	0.01	1
9	0.05	1						
10	0.01	3						
11	0.01	1						

Table S8. Adsorption model and complete fitting for BP4 isotherm. *Values from ref.[1]

Langmuir $Q_e = Q_m \cdot \frac{C_e \cdot K_L}{1 + K_L \cdot C_e}$				**BET** $Q_e = \frac{Q_m \cdot C_{BET} \cdot x}{(1-x) \cdot (1 + C_{BET} \cdot x - x)}$,			
	Q_m (mg/g)	**K_L** (mL/mg)	**R^2**	**Q_m** (mg/g)	**C_s** (mg/mL)	**C_{BET}**	**R^2**
GO*	45	4	0.311	11	0.6	18	0.7724
GO-NaOH*	62	22	0.9891	21	1	46	0.8841
rGO	115	10	0.9686	33	1	30	0.9145
GO-Met	205	265	0.9836	102	0.7	98	0.9325
GO-Lys*	292	8.1	0.9859	117	1	85	0.779

GO-Glu	248	3.8	0.7094	77	0.7	16	0.9684

Table S9. Adsorption model and complete fitting for BPA isotherm. *Values from ref.[1]

Langmuir $Q_e = Q_m \cdot \frac{C_e \cdot K_L}{1 + K_L \cdot C_e}$				**BET** $Q_e = \frac{Q_m \cdot C_{BET} \cdot x}{(1-x) \cdot (1 + C_{BET} \cdot x - x)}$,			
	Q_m (mg/g)	**K_L** (mL/mg)	**R^2**	**Q_m** (mg/g)	**C_s** (mg/mL)	**C_{BET}**	**R^2**
GO*	33.3	30	0.2	14	0.22	70	0.8186
GO-NaOH*	48	19	0.9702	16	0.3	63	0.8967
rGO	78	151	0.9483	30	0.3	33	0.8149
GO-Met	147	17	0.9443	47	0.29	21	0.9425
GO-Lys*	295	43	0.9809	142	0.3	70	0.9552
GO-Glu	237	16.8	0.956	74	0.3	68	0.9206

Table S10. Adsorption model and complete fitting for CBZ isotherm. * Values from ref.[1]

Langmuir $Q_e = Q_m \cdot \frac{C_e \cdot K_L}{1 + K_L \cdot C_e}$				**BET** $Q_e = \frac{Q_m \cdot C_{BET} \cdot x}{(1-x) \cdot (1 + C_{BET} \cdot x - x)}$,			
	Q_m (mg/g)	**K_L** (mL/mg)	**R^2**	**Q_m** (mg/g)	**C_s** (mg/mL)	**C_{BET}**	**R^2**
GO*	7	86	0.9398	125	0.08	52	0.9078
GO-NaOH*	80.8	12	0.8471	12.8	0.1	26	0.8275
rGO	43	127	0.9682	9	0.1	102	0.7776
GO-Met	131	760	0.997	54	0.1	183	0.9175
GO-Lys*	172	102	0.952	73	0.1	34	0.8643
GO-Glu	121	94	0.968	36	0.08	55	0.8845

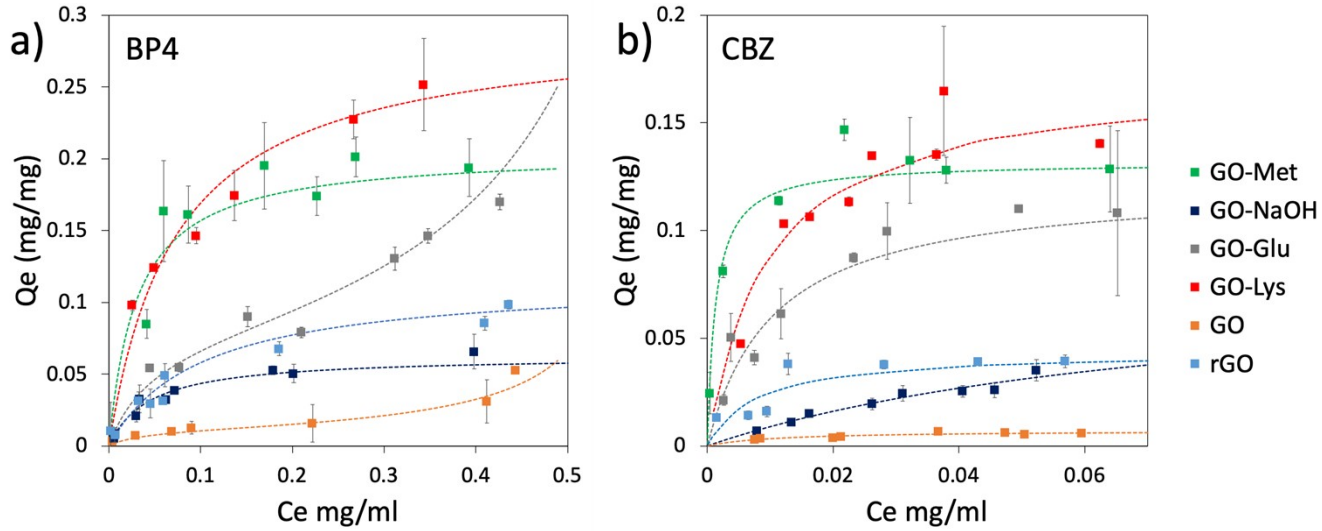

Fig. S6. Adsorption isotherm for a) BP4, b) CBZ. GO-Met (green line), GO-NaOH (dark blue line), GO-Lys (red line), GO-Glu (grey line), GO (orange line) and rGO (light blue line). Values of GO, GO-NaOH and GO-Lys from ref[1].

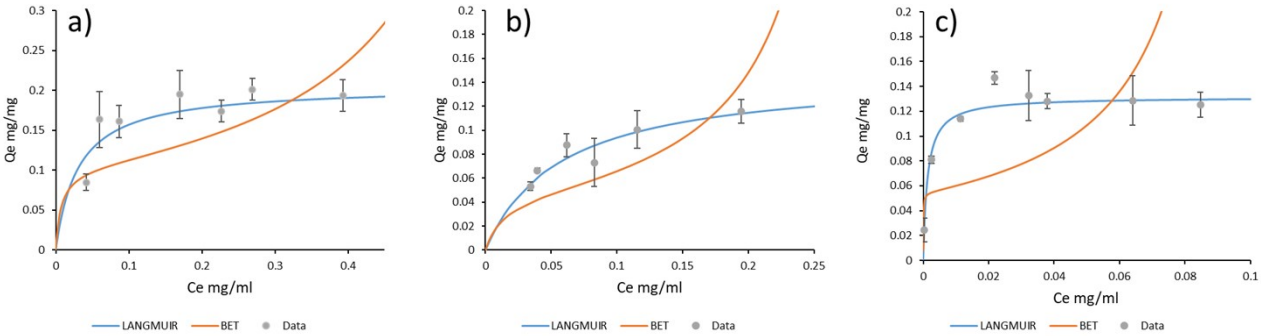

Fig. S7. Adsorption isotherm of GO-Met toward a) BP4, b) BPA and c) CBZ.

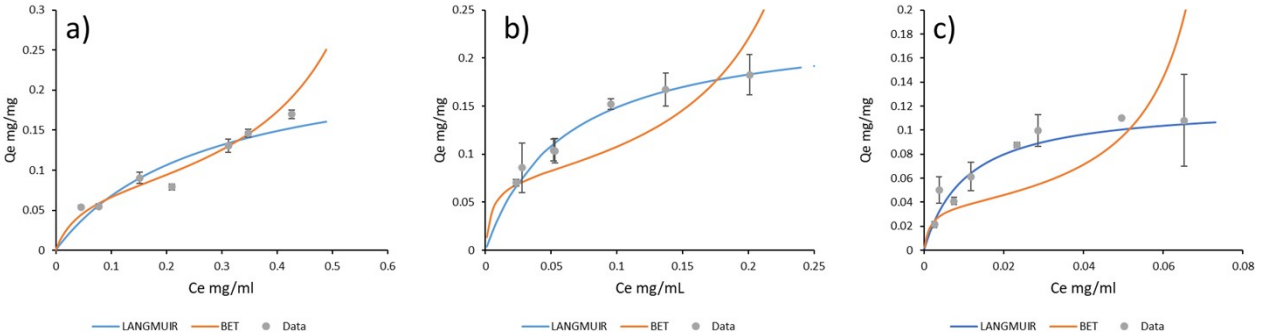

Fig. S8. Adsorption isotherm of GO-Glu toward a) BP4, b) BPA and c) CBZ.

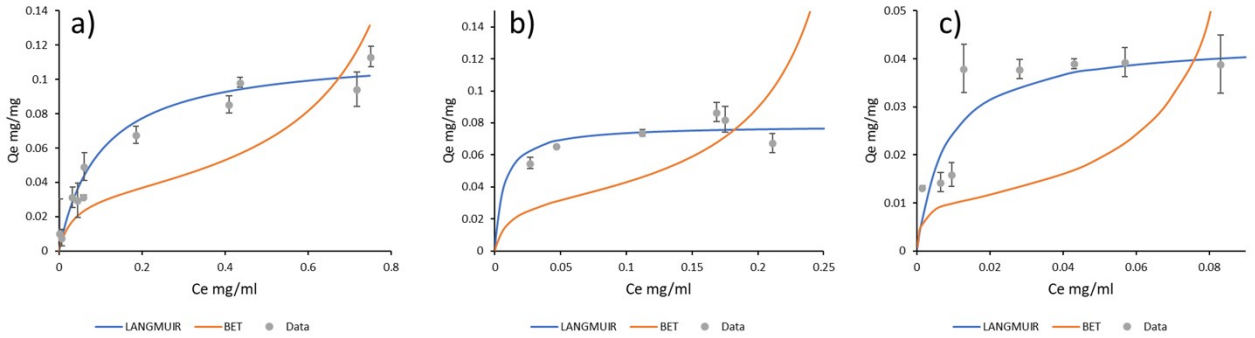

Fig. S9. Adsorption isotherm of rGO toward a) BP4, b) BPA and c) CBZ.

7. Molecular dynamic simulation

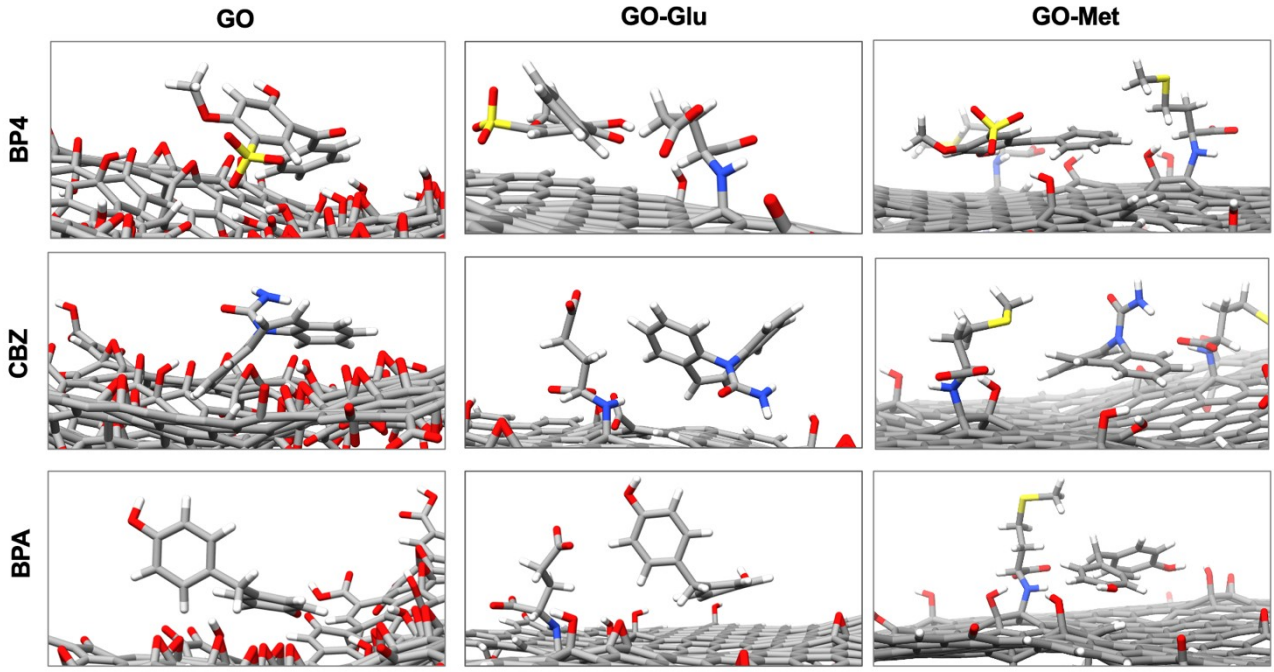

Fig. S10. Representative snapshots from MD simulations of the favourite adsorption sites of BP4, CBZ, and BPA on GO (left column), GO-Glu (inner column), and GO-Met (right column) sheets. Results on GO-Lys are report in ref [1].

Table S11. Variation of the solvent accessible surface area (DSASA) of BP4, CBZ, BPA and GO, Go-Glu and GO-Met nanosheets, upon binding. ΔΔSASA is the variation of ΔSASA of amino acid modified GO nanosheets, compared to GO.

Contaminant	Material	ΔSASA [Å^2]	ΔΔSASA [Å^2]
BP4	GO	372.7	-
	GO-Glu	686.3	313.6
	GO-Met	704.8	332.1
CBZ	GO	298.9	-
	GO-Glu	612.5	313.6
	GO-Met	657.7	358.8
BPA	GO	317.3	-
	GO-Glu	538.7	221.4
	GO-Met	631.0	313.7

References

1. Mantovani, S.; Khaliha, S.; Marforio, T. D.; Kovtun, A.; Favaretto, L.; Tunioli, F.; Bianchi, A.; Petrone, G.; Liscio, A.; Palermo, V.; Calvaresi, M.; Navacchia, M. L.; Melucci, M., Facile high-yield synthesis and purification of lysine-modified graphene oxide for enhanced drinking water purification. *Chem. Commun.* **2022,** *58* (70), 9766-9769.