Adsorption of emerging contaminants by graphene related materi-als and their alginate composite hydrogels

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Content

1. X-Ray Photoelectron Spectroscopy (XPS)

High-resolution XPS was obtained by using a Phoibos 100 hemispherical energy analyser (Specs GmbH, Berlin, Germany) and Mg Kα photons (ħω = 1,253.6 eV; X-Ray power = 125W) in constant analyser energy mode, with analyser pass energies set to 10 eV. Overall resolution of 0.9 eV was measured on Ag 3d 5/2. Base pressure in the analysis chamber during analysis was 4.2x10-8 mbar. Spectra were fitted by using CasaXPS (www.casaxps.com) after Shirley background subtraction and all spectra were calibrated to the C 1s binding energy (285.0 eV). XPS samples were tablet composed by the dry powder of each material and grounded on the sample holder by conductive carbon tape.

Table S1. Atomic composition (% at.) and O/C ratio of GO, GO-Lys, rGO and GNP. *Data from Mantovani et al.[1]

Transition	GO*	GO-Lys*	rGO	GNP
C 1s 285 eV	70.4 ± 0.8	81.5 ± 0.8	98.8 ± 0.3	94.5 ± 0.8
O 1s 532 eV	27.0 ± 0.5	13.9 ± 0.5	1.1 ± 0.2	4.7 ± 0.4
N 1s 400eV	0.7 ± 0.3	3.1 ± 0.3	-	-
Na KLL KE 990 eV	-	1.2 ± 0.3	-	-
Cl 2p 200eV	0.8 ± 0.2	0.3 ± 0.1	0.3 ± 0.1	-
S 2p 168 eV	1.0 ± 0.2	-	0.11 ± 0.04	0.6 ± 0.1
Fe $2p_{3/2}$ 712 eV	-	-	-	0.16 ± 0.05
O/C ratio	0.38	0.17	0.01	0.05

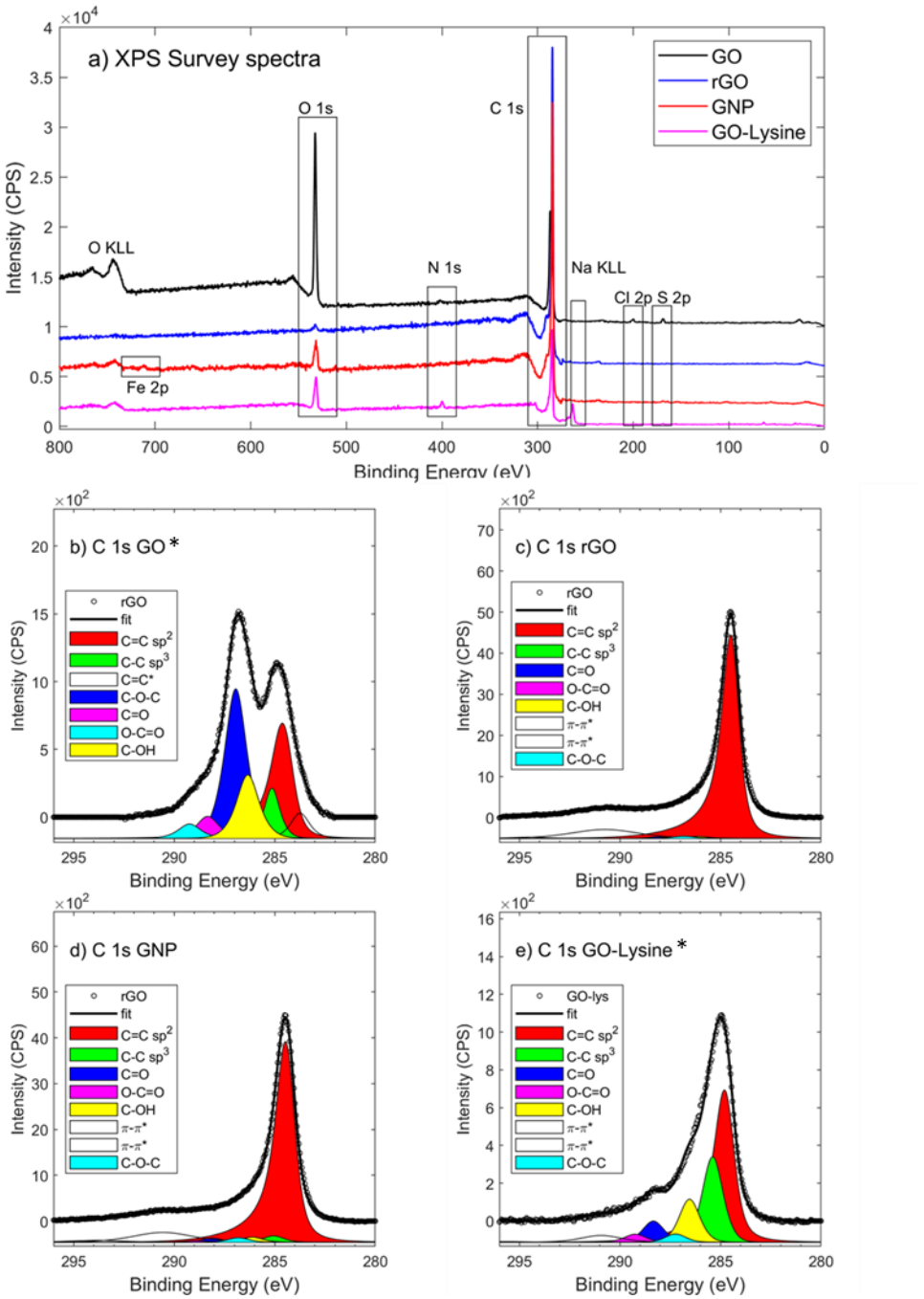

Fig. S1. Survey (a) and C 1s spectra of (b) GO, (c) rGO, (d) GNP and (e) GO-Lysine. C=C sp^2 relative abundance obtained from C 1s fit (red component) was 36 %, 98%, 92% and 52 %, respectively. * Data reported from Mantovani et al.[1]

2. Kinetic experiments (15 min-4 h)

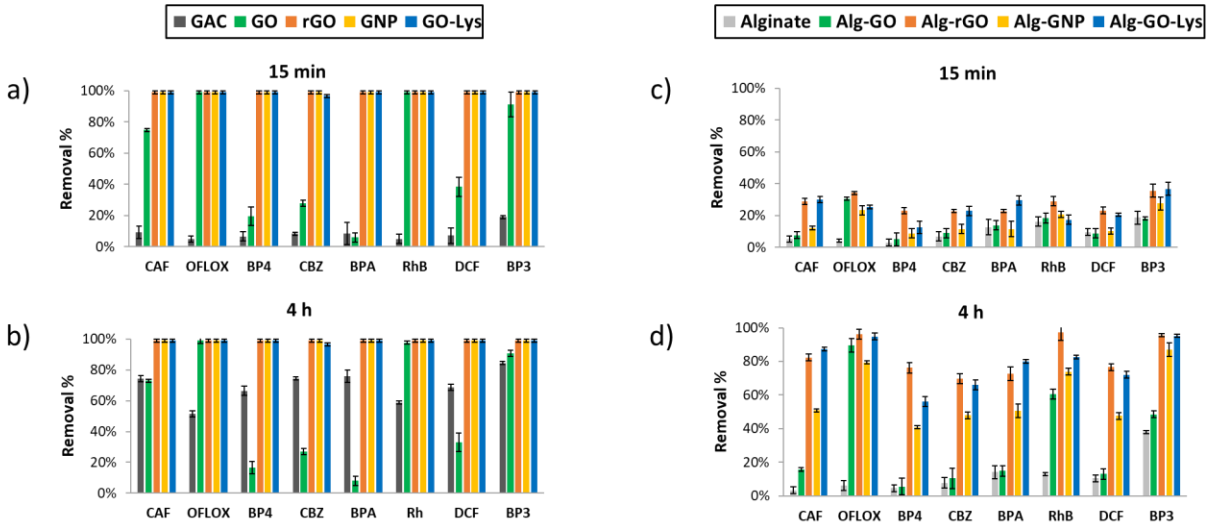

Fig. S2. Removal of ECs mix (0.5 mg/L each in tap water, V_{tot}= 25 mL, 25 mg of sorbent material). On the left, graphene nanosheets removal compared with GAC obtained after contact time of (a) 15 min, and (b) 4 h. On the right, alginate-graphene beds removal compared with pristine alginate beads after contact time of (c) 15 min, and (d) 4 h.

3. Release test on alginate beads

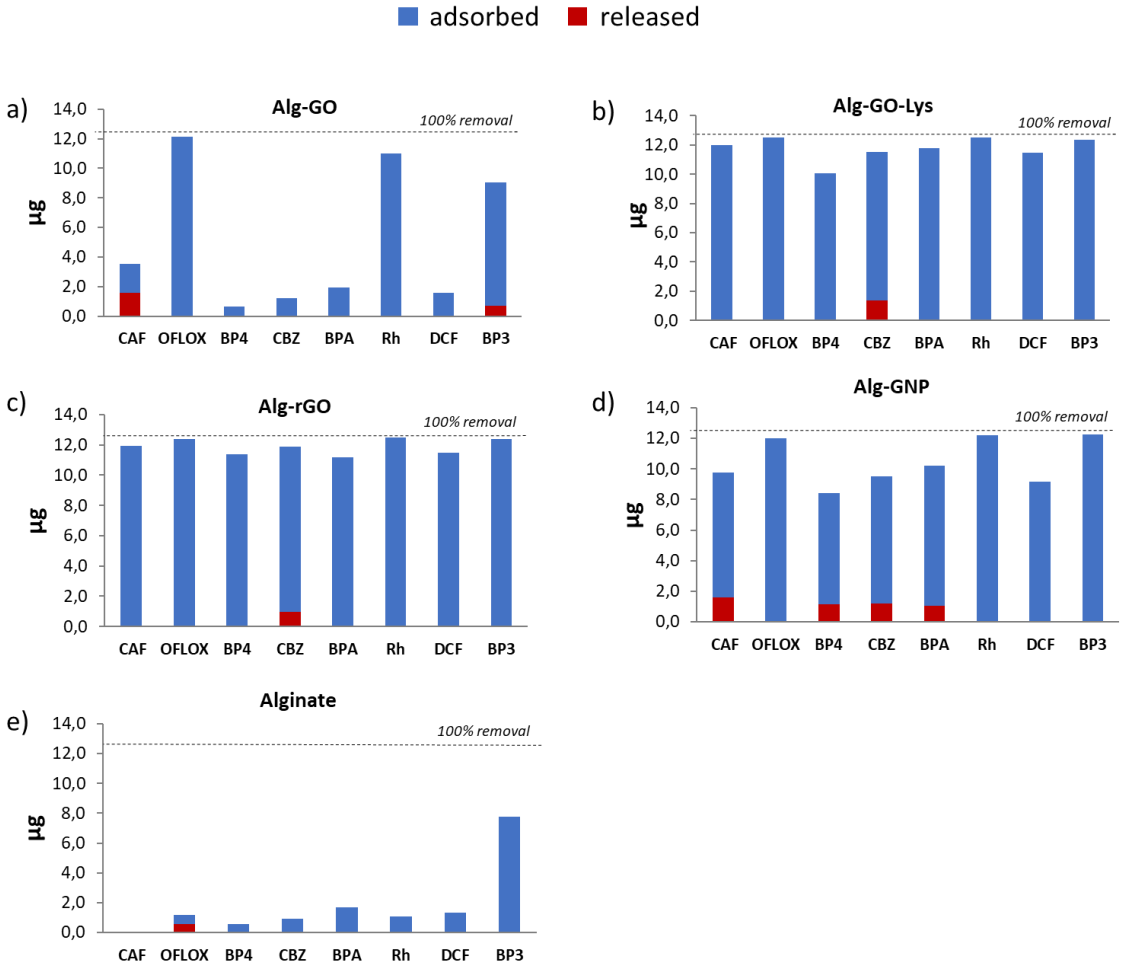

Fig. S3. Release test on (a) Alg-GO, (b) Alg-GO-Lys, (c) Alg-rGO, (d) Alg-GNP, and (e) Alginate. Blue bars show the mass in µg adsorbed during kinetic test, red bars correspond to the mass in µg of contaminants released in fresh tap water (25 mg of beads used for kinetic test, V_{tot}=25 mL of tap water, contact time= 4 h).

4. Adsorption isotherm

The adsorption isotherm on different graphene powder materials and alginate-graphene beads were performed on rhodamine B at fixed amount of adsorbent material by varying the contaminant concentration. In a total volume of 5 mL of mQ water, RhB at different concentration was added to 0.5 mg of samples (powder materials were previously sonicated 2 h in mQ water). The solutions were kept in darkness under gentle stirring for 24 h and then analyzed by UV-vis spectroscopy. The

experimental data, the plots, the equation and the R^2 referred to GO and rGO were reported in a previous work.[2]

Table S2-S8. Experimental parameters of solutions used for isotherms studies.

Table S2: GO-Lys			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	GO-Lys (mg)
1	5	1	7
2	5	1	5
3	5	1	2
4	5	0.5	10
5	5	0.5	5
6	5	0.5	2
7	5	0.2	5
8	5	0.2	2

Table S3: GNP			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	GNP (mg)
1	5	0.2	10
2	5	0.2	7
4	5	0.2	5
5	5	0.1	7
6	5	0.1	5
7	5	0.1	2
8	5	0.05	5
9	5	0.05	2

Table S4: Alginate			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	Alginate (mg)
1	5	0.0005	1
2	5	0.0025	4
4	5	0.005	3

5	5	0.01	2
6	5	0.015	4
7	5	0.015	3
8	5	0.04	4
9	5	0.04	4
10	5	0.05	4

Table S5: Alg-GO			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	Alg-GO (mg)
1	5	0.0025	0.5
2	5	0.005	0.5
4	5	0.010	0.5
5	5	0.015	0.5
6	5	0.020	0.5
7	5	0.025	0.5
8	5	0.030	0.5
9	5	0.040	0.5
10	5	0.050	0.5
11	5	0.060	0.5
12	55	0.070	0.5

Table S6: Alg-GO-Lys			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	Alg-GO-Lys (mg)
1	5	0.010	0.5
2	5	0.015	0.5
4	5	0.020	0.5
5	5	0.040	0.5
6	5	0.050	0.5
7	5	0.100	0.5
8	5	0.300	0.5
9	5	0.500	0.5

10	5	0.750	0.5

Table S7: Alg-rGO			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	Alg-rGO (mg)
1	5	0.005	0.5
2	5	0.010	0.5
4	5	0.015	0.5
5	5	0.020	0.5
6	5	0.025	0.5
7	5	0.040	0.5
8	5	0.050	0.5
9	5	0.100	0.5
10	5	0.200	0.5
11	5	0.300	0.5
12	5	0.500	0.5

Table S8: Alg-GNP			
SAMPLE	Volume (mL)	C_0 RhB (mg/L)	Alg-GNP (mg)
1	5	0.0005	0.5
2	5	0.0010	0.5
4	5	0.0025	0.5
5	5	0.005	0.5
6	5	0.010	0.5
7	5	0.025	0.5
8	5	0.030	0.5
9	5	0.040	0.5
10	5	0.050	0.5
11	5	0.060	0.5

Table S9-S10. Fit parameters of the adsorption isotherms on rhodamine B (RhB).

Table S9: Nanosheets

	Langmuir $Q_e = Q_m \cdot \frac{C_e \cdot K_L}{1+K_L \cdot C_e}$			BET $Q_e = \frac{Q_m \cdot C_{BET} \cdot x}{(1-x) \cdot (1+C_{BET} \cdot x-x)}$, $x = \frac{C_e}{C_s}$			
	Q_m [mg/g]	K_L [mL/mg]	R^2	Q_m [mg/g]	C_s [mg/mL]	C_{BET}	R^2
GO-Lys	312	107	0.9704	167	1	600	0.5855
GNP	68	1519	0.9969	57	1	1763	0.9945

Table S10: Alginate-graphene composites

	Langmuir $Q_e = Q_m \cdot \frac{C_e \cdot K_L}{1+K_L \cdot C_e}$			BET $Q_e = \frac{Q_m \cdot C_{BET} \cdot x}{(1-x) \cdot (1+C_{BET} \cdot x-x)}$, $x = \frac{C_e}{C_s}$			
	Q_m [mg/g]	K_L [mL/mg]	R^2	Q_m [mg/g]	C_s [mg/mL]	C_{BET}	R^2
Alginate	0.6	229	0.9784	0.2	0.07	828	0.8268
Alg-GO	61	42	0.6035	15	0.07	226	0.99
Alg-GO-Lys	158	507	0.9975	113	1	44	0.841
Alg-rGO	449	22	0.8144	178	0.7	242	0. 9995
Alg-GNP	15	661	0.9877	7	0.1	1326	0.9576

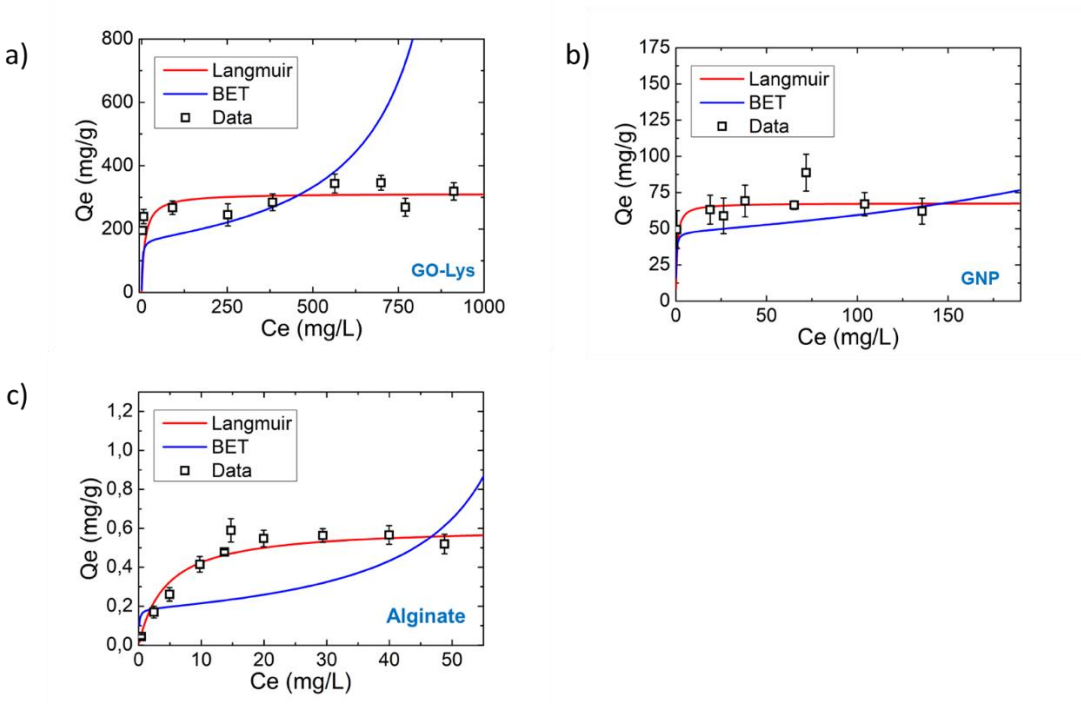

Fig. S4. Adsorption isotherm of (a) GNP, (b) GO-Lys, (c) alginate.

5. Regeneration test

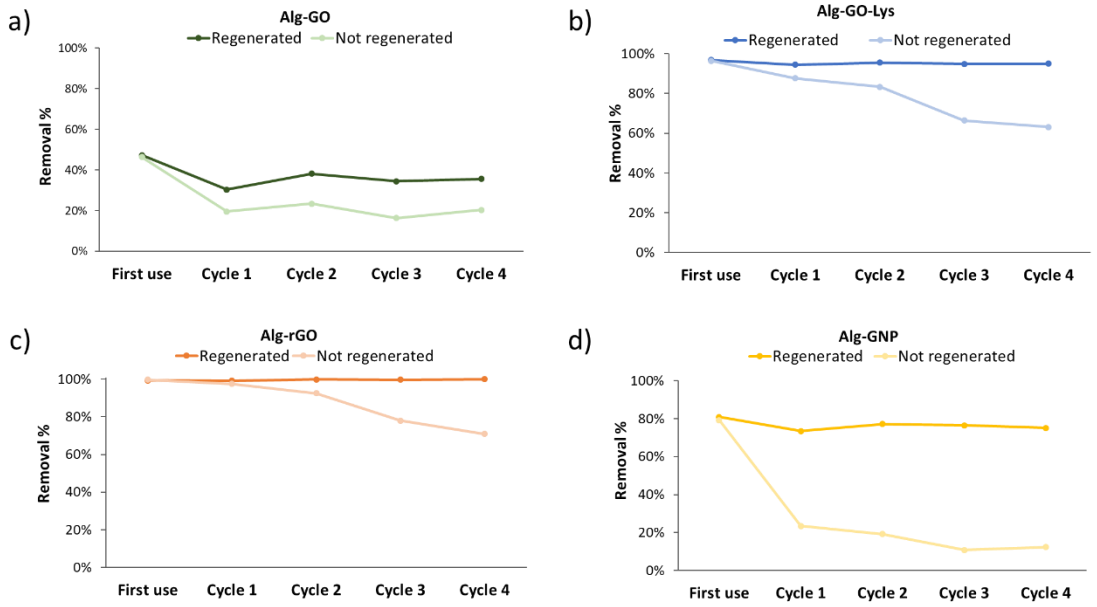

Fig. S5. Comparison between regenerated and not regenerated beads of (a) Alg-GO, (b) Alg-GO-Lys, (c) Alg-rGO and Alg-GNP.

References

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2. Khaliha, S.; Marforio, T. D.; Kovtun, A.; Mantovani, S.; Bianchi, A.; Luisa Navacchia, M.; Zambianchi, M.; Bocchi, L.; Boulanger, N.; Iakunkov, A.; Calvaresi, M.; Talyzin, A. V.; Palermo, V.; Melucci, M., Defective graphene nanosheets for drinking water purification: Adsorption mechanism, performance, and recovery. *FlatChem* **2021,** *29*.