

Supplementary Materials

Green Graphene–Chitosan Sorbent Materials for Mercury Water Remediation

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BET analysis of GO–CH aerogel

The result for the specific surface area (S_{BET}) of the GO–CH aerogel was very low ($9.06 \text{ m}^2 \text{ g}^{-1}$, with a pore volume of $0.016 \text{ cm}^3 \text{ g}^{-1}$). This is not uncommon, as the S_{BET} of graphene-based aerogels is normally substantially lower than the expected value for the single-sheet graphene ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$) [1]. The determination of S_{BET} for GO-based aerogels is generally quite challenging and is normally largely underestimated. The possible overlapping of graphene sheets, high degree of oxidation and the presence of water molecules at the surface may difficult the access of N_2 molecules, thus triggering such low S_{BET} values.[2] In a previous study of GO aerogels, we observed H3-type hysteresis loop, which can be assigned to the presence of plate-like particle aggregates and slit-shaped pores. The plateau was not reached even in saturation conditions, which can be a result of unrestricted multilayer adsorption in large mesopores and macropores, which can ultimately hinder an accurate estimation of the real pore volume [3].

Table S1. Sorption reaction kinetic models.

Kinetic model	Equation	References
Pseudo-first-order (Lagergren)	$q_t = q_e(1 - e^{-k_1 t})$	[4]
Adsorption capacity Pseudo-second-order (Ho)	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	[5]
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$	[6]

q_t is the amount of metal sorbed per gram of sorbent at time t ($\mu\text{mol g}^{-1}$), q_e amount of metal adsorbed per gram of sorbent at equilibrium ($\mu\text{mol g}^{-1}$), k_1 rate constant of pseudo-first order (h^{-1}), k_2 rate constant of pseudo-second order ($\text{g } \mu\text{mol}^{-1} \text{ h}^{-1}$), α initial sorption rate ($\mu\text{mol g}^{-1} \text{ h}^{-1}$), β desorption constant ($\text{g } \mu\text{mol}^{-1}$).

In addition to the reaction models, two widely known diffusion-based models, Boyd’s film-diffusion [7] and Webber’s pore-diffusion [8], were used in order to analyse the sorption mechanism and the rate-controlling step involved in the sorption process.

Boyd’s film-diffusion model presumes that the main resistance to diffusion is in the boundary layer surrounding the adsorbent particle[9,10] and it is expressed as:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp.(-n^2 Bt) \quad (4)$$

where F is the fractional attainment of equilibrium, at different times, t , and Bt is a function of F :

$$F = \frac{q_t}{q_e} \quad (5)$$

Bt can be calculated as:

$$\text{For } F \text{ values} > 0.85, \quad Bt = -0.4977 - \ln(1 - F) \quad (6)$$

$$\text{For } F \text{ values} < 0.85, \quad Bt = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F}{3}} \right)^2 \quad (7)$$

If the plot Bt vs t (Boyd's plot) excludes the origin, one can conclude that film diffusion or chemical reaction is the rate-controlling step. If the plot is linear and passes through the origin the intra-particle diffusion controls the rate of mass transfer.

Weber's intraparticle-diffusion model is defined by the following equation [9,10]:

$$q_t = k_i t^{1/2} \quad (8)$$

Where k_i is the intraparticle-diffusion parameter ($\text{mg g}^{-1} \text{h}^{-1/2}$). If intraparticle-diffusion is the rate-limiting step, then a plot of q_t vs t will give a straight line with a slope that equals k_i and an intercept equal to zero. If not, some other mechanism along with intraparticle diffusion must also be involved. The analysis of the experimental data using film-diffusion and the intraparticle-diffusion models, as well as the prediction of the diffusion coefficients, was performed following the piecewise linear regression methodology (PLR) proposed by Malash et al. [9] using a Microsoft® Excel™ worksheet developed by these authors.

Table S2. Elemental analysis of natural waters before and after Hg removal studies by GO-CH.

Water source	Tap		River $\sigma = 33.1 \mu\text{S/m}$		Sea Sal. = 34.7	
	Initial	GO-CH	Initial	GO-CH	Initial	GO-CH
pH	7.13	7.45	4.30	4.32	7.80	7.69
<i>Major elements (mg L⁻¹)</i>						
Ca	33	33	1.3	1.3	411	399
Na	8.5	8.3	5.5	4.9	>1000	>1000
K	1.9	1.9	0.5	0.5	>500	>500
Mg	2.0	2.0	0.5	0.5	>2000	>2000
<i>Minor elements (μ L⁻¹)</i>						
B	10	7.5	4.3	4.3	5346	5340
Al	34	<5	54	54	178	86
Cr	0.7	<0.5	<0.5	<0.5	16.8	16.8
Fe	54	<10	12	<5	351	351
Co	<0.1	<0.1	<0.1	<0.2	<40	<40
Ni	<1	<1	<1	<1	<20	<20
Cu	2.7	<1	<1	<1	<20	<20
Zn	76	31	7.8	5	1120	1000
As	<2	<2	<2	<2	<100	<100
Se	<2	<2	<2	<2	185	185
Sr	21	21	7	7	9338	9338

Cd	<0.1	<0.1	0.21	<0.1	<40	<40
Sb	<0.1	<0.1	<0.1	<0.1	<2	<2
Ba	6.1	5.3	2.3	2.0	160	158
Pb	<0.1	<0.1	2.2	<0.2	<80	<80

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