Supporting Information

Sulfide and ferrous iron preferentially target specific surface O-functional groups of graphene oxide: Implications for adsorption of contaminants

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Methods for Determining Aqueous Phase Concentrations of Organic Contaminants in GO Suspension

A fiber-enabled negligible depletion-solid-phase microextraction approach^{S1} was used to determine the equilibrium aqueous phase concentrations of naphthalene, 1,2,4,5tetrachlorobenzene and 2.4-dichlorophenol in the adsorption experiments to GO and reduced GOs. To initiate a fiber sorption experiment, experimental suspension was prepared in a 20-ml glass scintillation vial by adding a stock solution of an organic compound (in methanol) to the vial. The volume percentage of methanol was kept below 0.1% (v:v) to minimize the cosolvent effects. Then, a piece of fiber was added to the vial. The vial was capped and tumbled at 8 rpm in the dark until sorption equilibrium was reached. Next, the fiber was taken out, wiped with a wet tissue, and extracted with hexane (for 1,2,4,5-tetrachlorobenzene) or methanol (for naphthalene and 2.4-dichlorophenol) to analyze the mass of the organic compound on the fiber. The aqueous solution was diluted with methanol or extracted with hexane to analyze the concentration of the organic compound in the dissolved phase. The sorption data were fitted with the linear sorption isotherm: $C_{\text{fiber}} = K_{\text{fiber}} \cdot C_{\text{W}}$, where $C_{\text{fiber}} (\text{mg/L})$ and $C_{\text{W}} (\text{mg/L})$ are the equilibrium concentrations of an organic compound on the fiber and in the solution, respectively; K_{fiber} (L/L) is the fiberwater distribution coefficient.

To determine the equilibrium aqueous phase concentrations of naphthalene, 1,2,4,5tetrachlorobenzene and 2,4-dichlorophenol in the adsorption experiments to GO and reduced GOs, a piece of fiber was exposed in the suspension and allowed to equilibrate for 30 d (for naphthalene) or 7 d (for 1,2,4,5-tetrachlorobenzene and 2,4-dichlorophenol). The required equilibrium time was determined in previous research.^{S1} Afterward, the fiber was treated as described above to analyze the concentrations of the compounds on the fibers. The concentrations of freely dissolved compounds were calculated based on the concentrations on the fibers and the values of K_{fiber} . The adsorbed concentrations of the organic compounds on GOs were calculated based on a mass balance approach.

Table S1. Selected physicochemical properties of the organic compounds used in the adsorption experiments.

Adsorbate	$C_{\rm sat}$ (mg/L) a	log K _{OW} ^b	р <i>K</i> а ^с	α^{d} (cm ³)
Naphthalene	3.10E+01	3.30		1.75E-23
1,2,4,5-Tetrachlorobenzene	5.95E-01	4.60		1.82E-23
2,4-Dichlorophenol	4.50E+03	3.06	7.89	1.50E-23

^{*a*} Water solubility, data obtained from Schwarzenbach et al.^{S2} ^{*b*} *n*-octanol–water partition coefficient, data obtained from MacKay et al.^{S3}

^c Acid dissociation constant, data obtained from MacKay et al. ^{S3}

^d Polarizability, assessed using ACD Lab prediction software and available in the Chemspider database (http://www.chemspider.com/).

Adsorbate	Adsorbent ^b	$K_{\rm F}$ (mol ¹⁻ⁿ L ⁿ /kg) ^c	n ^c	R^2	$\mathrm{Log}K_{\mathrm{d}}(\mathrm{L/kg})$
Naphthalene	Pristine GO	39.8 ± 10.0	0.88 ± 0.06	0.991	4.77 - 5.05
	RGO–S(-II)	55.7 ± 4.0	0.85 ± 0.02	0.999	5.02 - 5.59
	RGO-Fe(II)	73.5 ± 6.0	0.73 ± 0.02	0.999	5.40 - 6.19
1,2,4,5-Tetrachlorobenzene	Pristine GO	11.0 ± 8.4	1.50 ± 0.12	0.984	4.41 - 4.68
	RGO-S(-II)	44.9 ± 7.2	0.96 ± 0.02	0.998	4.76 - 5.04
	RGO-Fe(II)	12.1 ± 4.1	0.72 ± 0.05	0.983	4.87 - 5.23
2,4-Dichlorophenol	Pristine GO	13.7 ± 1.4	1.84 ± 0.12	0.988	3.50 - 3.89
	RGO-S(-II)	12.3 ± 0.9	1.06 ± 0.06	0.988	3.99 - 4.54
	RGO-Fe(II)	17.5 ± 1.1	0.89 ± 0.04	0.992	4.29 - 4.71
Hg(II)	Pristine GO	111.4 ± 60.0	0.62 ± 0.13	0.883	3.87 - 4.35
	RGO-S(-II)	69.7 ± 24.1	0.70 ± 0.08	0.956	3.71 - 4.26
	RGO-Fe(II)	142.1 ± 30.6	0.75 ± 0.06	0.981	4.24 - 4.42
Pb(II)	Pristine GO	18.6 ± 6.8	0.83 ± 0.08	0.967	3.87 - 4.35
	RGO-S(-II)	5.5 ± 4.0	1.02 ± 0.15	0.929	3.71 - 4.26
	RGO-Fe(II)	54.2 ± 21.0	0.79 ± 0.09	0.949	4.24 - 4.43

Table S2. Freundlich model fits to adsorption data of naphthalene, 1,2,4,5-tetrachlorobenzene, 2,4-dichlorophenol, Hg(II) and Pb(II) to pristine and reduced GO^a.

^a The adsorption data were shown in Fig. 1 and 2.
^b RGO–S(-II)/Fe(II) represents GO reduced by 0.5 mM S(-II) or Fe(II) in experimental suspension containing 10 mg/L GO.
^c Values after ± sign indicate standard error range estimated by Freundlich model.



Fig. S1. Gas chromatogram of 10 mg/L (A) 1,2,4,5-tetrachlorobenzene, and high performance liquid chromatography spectra of 10 mg/L, (B) naphthalene and (C) 2,4-dichlorophenol.



Fig. S2. Mass spectra and proposed structures of model compounds (A) 1,4-dihydro-1,4-epoxynaphthalene, (B) 1,4-naphthoquinone, (C) naphthoic acid and (D) phenol.



Fig. S3. High performance liquid chromatography-mass spectra of the reaction products of reaction B, C and D in Figure 5 (A, C, E) and the corresponding standard samples (B, D, F).



Fig. S4. C1s X-ray photoelectron spectroscopy (XPS) spectra of (A) pristine GO and (B-F) RGO-S(-II). Value in parenthesis is dose of S(-II) (mM-S(-II)/(10 mg/L of GO)).



Fig. S5. C1s X-ray photoelectron spectroscopy (XPS) spectra of pristine (A) GO and (B-F) RGO-Fe(II). Value in parenthesis is dose of Fe(II) (mM-Fe(II)/(10 mg/L of GO)).



Fig. S6. Raman spectra of (A) RGO-S(-II) and (B) RGO-Fe(II). Value in parenthesis is dose of S(-II) or Fe(II) (mM/(10 mg/L of GO)).



Fig. S7. TEM images of GO (A) and reduced GOs by S(-II). Doses of S(-II) (per 10 mg/L GO) are: 0.05 mM (B), 0.1 mM (C), 0.5 mM (D), 1 mM (E), and 3 mM (F).



Fig. S8. TEM images of GO (A) and reduced GOs by Fe(II). Doses of Fe(II) (per 10 mg/L GO) are: 0.05 mM (B), 0.1 mM (C), 0.5 mM (D), 1 mM (E), and 3 mM (F).



Fig. S9. Distribution coefficients (K_d) of naphthalene, 1,2,4,5-tetrachlorobenzene and 2,4dichlorophenol between aqueous phase and GO reduced by different doses of (A) S(-II) and (B) Fe(II). Data points represent the average of duplicate samples.



Fig. S10. Correlations of the adsorption affinity, quantified as distribution coefficient K_d , of naphthalene, 1,2,4,5-tetrachlorobenzene and 2,4-dichlorophenol with the (A) Relative hydrophobicity and (B) I_G/I_D of graphene nanomaterials.



Fig. S11. Fourier transform infrared (FTIR) spectra of (A) RGO-S(-II) and (B) RGO-Fe(II). Value in parenthesis is dose of S(-II) or Fe(II) (mM/(10 mg/L of GO)).



Fig. S12. Zeta potential of pristine GO, RGO-S(-II) and RGO-Fe(II). Dose of S(-II) or Fe(II) was 0.5 mM/10 mg/L of GO. The error bars represent standard deviations of triplicate samples.



Fig. S13. Mass spectra and proposed structures of the reduction products of 1,4-dihydro-1,4epoxynaphthalene by (A) sulfide and (B) ferrous iron; the reduction product of naphthoic acid by (C) sulfide; the reduction product of 1,4-naphthoquinone by (D) ferrous iron; the reduction product of phenol by (E) ferrous iron.

References

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