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Effects of natural minerals on the adsorption of 17β-estradiol and bisphenol A on graphene oxide and reduced graphene oxide

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Preparation of GO and rGO

Graphite (2 g) was added to sulfuric acid (100 mL) that had been pre-cooled in an ice-bath (0–4 °C). After stirring for 15 min at 0–4 °C, $KMnO_4$ (12 g) was slowly added to the mixture. After stirring for a further 4 h at 45 °C, deionized (DI) water (100 mL) was added. The temperature was then raised to 90 °C and kept at this level for 24 h. To stop the oxidation reaction, the mixture was diluted with hot (80–90 °C) DI water (150 mL). After 15 min, H_2O_2 (20 mL) was added to the mixture, which was then agitated for a further 15 min. After centrifugation at 5000 rpm for 30 min, the supernatant was removed. The solid sample was washed sequentially with hydrochloric acid (5%, v/v) and DI water, and then freeze-dried. A suspension of GO was then obtained by exfoliation of the freeze-dried sample under ultrasonication for 12 h.

For rGO preparation, 1 g GO suspension was added in a 2-L round bottom flask with 1 L water. The dispersion was sonicated for 12 h. $N_2H_4 \cdot H_2O$ (15 mL) was then added and the solution was heated in a water bath at 100 °C under a water cooled condenser for 18 h. The reduced GO (a black solid) gradually precipitated out. The solid was filtrated, washed with water (10 × 100 mL), and freeze-dried.

Quantification of E2 and BPA

E2 and BPA concentrations were measured by means of a fluorescence quenching method with a fluorescence spectrophotometer (Cary Eclipse, Varian, Palo Alto, CA, USA) as described previously.[S1-S3] The excitation source was a 450 W xenon lamp with slits set to 5 nm for both excitation (Ex) and emission (Em). The fluorescence intensities of E2 and BPA were determined at 280 nm (Ex)/310 nm (Em). Calibration curves included six concentration levels in the range 0.02–2.4 mg L^{-1}, similar to the experimental conditions. The calibration curves were linear, with correlation coefficients (*R*) greater than 0.999. The fluorescence intensity of the 0.01 M NaCl background solution was measured and subtracted.

DLVO calculation

In this study, DLVO energy was estimated for Graphene-family nanomaterials (GFNs) interacting with a mineral surface using the sphere-plate configuration, and for GFNs interacting with GFNs and mineral interacting with mineral using the sphere-sphere configuration. The total DLVO interaction energy (Φ_{tot}) was calculated according to the following equation:[S4]

$$\Phi_{tot} = \Phi_{vdw} + \Phi_{edl} \qquad (2)$$

where Φ_{vdw} is the van der Waals interaction energy and Φ_{edl} is the electrical double-layer interaction energy.

(1) Sphere-sphere configuration

Φ_{vdw} can be written as:[S5,S6]

$$\Phi_{vdw} = -\frac{A_{131}}{6}\left[\frac{2r^2}{h^2+4rh} + \frac{2r^2}{h^2+4rh+4r^2} + \ln\left(\frac{h^2+4rh}{h^2+4rh+4r^2}\right)\right] \qquad (3)$$

where r is the radius of the GFN particles, h is the separation distance between two GFN particles, and A_{131} is the Hamaker constant for substance “1” in the presence of medium “3”.

Φ_{edl} can be written as:[S6,S7]

$$\Phi_{edl} = 32\pi r\varepsilon_r\varepsilon_0\left[\frac{k_BT}{ze}\right]^2\tanh\left[\frac{ze\psi_{p_1}}{4k_BT}\right]\tanh\left[\frac{ze\psi_{p_1}}{4k_BT}\right]\exp(-\kappa h) \qquad (5)$$

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2N_A I e^2}} \qquad (6)$$

where ε_r is the dielectric constant of the medium (78.4 for water), ε_0 is the vacuum permittivity (8.854×10^{-12} C^2 N^{-1} m^{-2}), k_B is the Boltzmann constant (1.381×10^{-23} C^2 J K^{-1}), T is the temperature (298.15 K), z is the valence of the electrolyte, e is the electron charge (1.602×10^{-19} C), ψ_{p1} is the surface potential of the GFN particles, κ is the reciprocal of the Debye length, N_A is Avogadro's constant (6.02×10^{23} mol^{-1}), and I is the solution ionic strength. The surface potential (ψ) of the GFNs could be calculated from their measured zeta potentials (ξ) as follows.[S8]

$$\psi = \xi\left(1 + \frac{d}{r}\right)\exp(\kappa d) \qquad (7)$$

where d is the distance between the surface of the charged particle and the slipping plane, usually taken as 5 Å.

(2) Sphere-plate configuration

Φ_{vdw} can be written as:[S5]

$$\Phi_{vdw} = -\frac{A_{132}}{6}\left[\frac{r}{h} + \frac{r}{h + 2r} + \ln\left(\frac{h}{h + 2r}\right)\right] \qquad (8)$$

where A_{132} is the Hamaker constant for substance "1" interacting with substance "2" in medium "3". Here, "1", "2", and "3" denote GFN, mineral, and water, respectively.

Φ_{edl} can be written as:[S7,S9]

$$\Phi_{edl} = 64\pi r \varepsilon_r \varepsilon_0 \left[\frac{k_B T}{ze}\right]^2 \tanh\left[\frac{ze\psi_p}{4k_B T}\right] \tanh\left[\frac{ze\psi_c}{4k_B T}\right] \exp(-\kappa h) \qquad (10)$$

where ψ_c is the surface potential of the mineral.

(3) Determination of Hamaker constant

The value of A_{132} can be calculated from the interfacial tension parameters:[S10,S11]

$$A_{132} = 24\pi h_0^2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_W^{LW}})(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_W^{LW}}) \tag{15}$$

where γ^{LW} (mJ/m^2) is the Lifshitz–van der Waals interfacial tension value and h_0 is the minimum equilibrium distance (0.157 nm). For particles of the same type:

$$A_{131} = 24\pi h_0^2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_W^{LW}})^2 \tag{16}$$

The γ^{LW} values of GFNs and minerals can be calculated from the electron-accepting (γ^+) and electron-donating (γ^-) interfacial tension values, the surface interfacial tension parameters of the selected probe liquids (γ_i^L), and the contact angles (θ) of the NPs in three probe liquids (water, glycerol, and diiodomethane).[S10]

$$\gamma_i^L(1+\cos\theta) = 2\sqrt{\gamma_i^{LW}\gamma^{LW}} + 2\sqrt{\gamma_i^+\gamma^-} + 2\sqrt{\gamma_i^-\gamma^+} \tag{17}$$

where the subscript i denotes water (γ_W^L = 72.8, γ_W^{LW} = 21.8, and $\gamma_W^+ = \gamma_W^-$ = 25.5 mJ/m^2), glycerol (γ_g^L = 64.0, γ_g^{LW} = 34.0, γ_g^+ = 3.92, and γ_g^- = 57.4 mJ/m^2), or diiodomethane (γ_d^L = 50.8, γ_d^{LW} = 50.8, $\gamma_d^+ = \gamma_d^-$ = 0 mJ/m^2), respectively; θ is the contact angle of the material.[S11,S12]

The contact angles (θ) of the three probe liquids (water, glycerol, and diiodomethane) were acquired on a DSA25 Standard apparatus (Kruss, Germany) using thin films of GFNs and minerals on clean glass slides.[S13] The sessile drop technique was used for contact-angle measurements. The reported contact angles under all examined conditions are averages of 10 replicate measurements. The Hamaker constants, zeta potentials, and particle radii of the GFNs and minerals used in the DLVO calculations are shown in Table S4.

Table S1 Elemental compositions (%) of GO and rGO calculated from XPS spectra.

	C	O	N
GO	70.20	29.71	0.09
rGO	86.05	9.61	4.34

Table S2 Fitting results of E2 and BPA adsorption isotherms on GO and rGO alone and their mixtures with various minerals.

Adsorbate	Adsorbent	Linear[a]		Langmuir[b]			Freundlich[c]		
		K_d	R^2	Q_m	b	R^2	K_f	1/n	R^2
E2	GO	122	0.979	714	0.222	0.051	111	0.788	0.986
	Mon/GO=10	80.6	0.993	1429	0.059	0.185	80.0	0.955	0.995
	Kao/GO=10	68.8	0.861	152	0.892	0.801	70.3	0.630	0.970
	Goe/GO=10	46.4	0.940	147	0.527	0.730	49.0	0.685	0.977
	Mon/GO=50	277	0.977	556	0.667	0.704	245	0.834	0.991
	Kao/GO=50	44.1	0.733	101	1.03	0.933	49.2	0.576	0.987
	Goe/GO=50	12.0	0.836	17.6	0.299	0.592	8.68	1.43	0.913
E2	rGO	397	0.539	189	26.5	0.994	237	0.312	0.939
	Mon/rGO=10	331	0.253	182	18.3	0.990	215	0.342	0.914
	Kao/rGO=10	326	0.170	179	18.7	0.980	201	0.296	0.970
	Goe/rGO=10	273	0.848	169	17.7	0.998	196	0.450	0.877
	Mon/rGO=50	470	0.195	238	8.40	0.979	309	0.520	0.882
	Kao/rGO=50	226	0.157	156	32.0	0.993	163	0.216	1.00
	Goe/rGO=50	234	0.809	156	32.0	0.983	164	0.207	0.975
BPA	GO	97.9	0.989	667	0.172	0.474	96.5	0.893	0.992
	Mon/GO=10	53.7	0.995	1429	0.004	0.091	53.7	0.954	0.992
	Kao/GO=10	36.3	0.964	154	0.349	0.185	38.6	0.742	0.980
	Goe/GO=10	23.7	0.977	167	0.181	0.699	25.0	0.849	0.992
	Mon/GO=50	96.1	0.906	2000	0.063	0.454	98.9	0.899	0.967
BPA	rGO	29.8	0.206	65.8	1.48	0.992	36.0	0.559	0.884
	Mon/rGO=10	27.1	0.480	64.9	1.11	0.989	32.5	0.563	0.964
	Kao/rGO=10	24.7	0.561	64.1	0.929	0.976	29.4	0.609	0.970
	Goe/rGO=10	18.1	0.495	48.1	0.985	0.980	22.1	0.595	0.961
	Mon/rGO=50	7.86	0.359	20.9	1.06	0.985	10.2	0.514	0.978

[a] Linear equation: $Q_e=K_d \cdot C_e$ (1)

[b] Langmuir equation: $Q_e = \frac{Q_m \cdot b \cdot C_e}{1 + b \cdot C_e}$ (2)

[c] Freundlich equation: $Q_e=K_f \cdot C_e^{1/n}$ (3)

where Q_e (mg/g) is the amount adsorbed after equilibrium, C_e (mg/L) is the aqueous equilibrium concentration of E2 or BPA, K_d (L/g) is the distribution coefficient, Q_m (mg/g) is the maximal adsorption capacity, b (L/mg) is the Langmuir constant, K_f ((mg/g)/(mg/L)$^{1/n}$) is the Freundlich distribution coefficient, and 1/n is the Freundlich empirical constant describing the degree of nonlinearity.

Table S3 The (001) peak positions and interlayer distances of different montmorillonite samples.

Sample	2θ (°)	Interlayer space (Å)
Dry Mon	6.65	13.3
Wet Mon	−	−
Wet Mon-E2	4.83	18.3
Wet Mon-BPA	5.13	17.2
Wet Mon-GO	4.68	18.9
Wet Mon-rGO	−	−

Table S4 Contact angles, Hamaker constants, zeta potentials, and particle radii used in the DLVO calculations.

	Zeta potential (mV)	Particle radius (nm)	Contact angle (°)			Hamaker constant ($\times 10^{-21}$ J)		
			Water	Glycerol	Diiodomethane	A_{131}	A_{132} (GO)	A_{132} (rGO)
GO	-36.7	262	2.0	23.0	25.6	8.26	–	–
rGO	-25.8	437	39.3	36.9	35.5	6.01	–	–
Mon	-31.9	673	17.6	24.7	15.4	10.1	9.13	7.78
Kao	-45.1	420	16.8	25.0	17.7	9.75	8.98	7.65
Goe	23.0	356	2.0	24.9	16.3	9.96	9.07	7.74

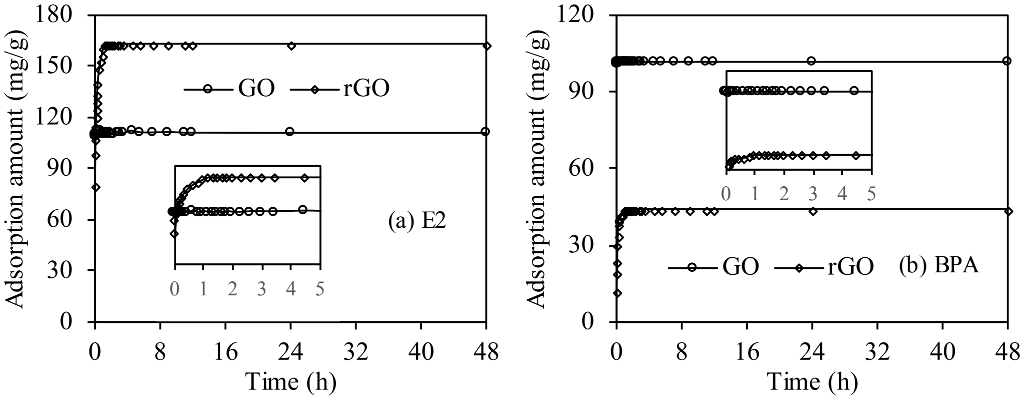

Fig. S1 Adsorption kinetics of E2 and BPA (ionic strength 0.01 M NaCl, GFN concentration = 10 mg/L, pH 6.5 ± 0.1).

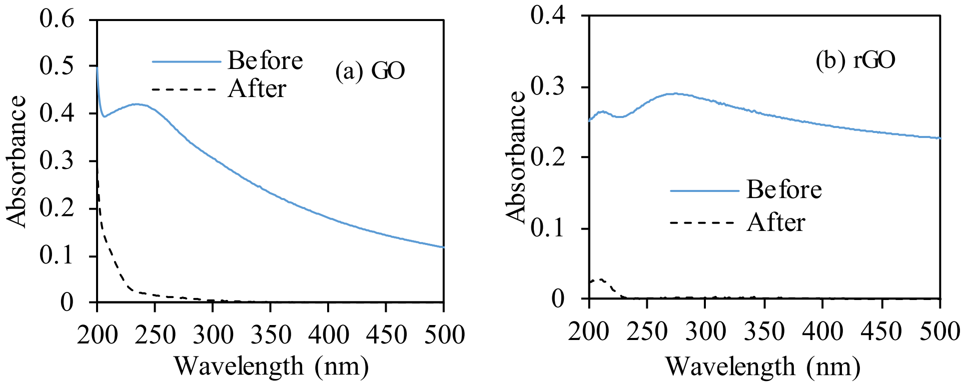

Fig. S2 The absorbance of GO or rGO solution before and after centrifugation and filtration (ionic strength 0.01 M NaCl, GFN concentration = 10 mg/L, pH 6.5 ± 0.1).

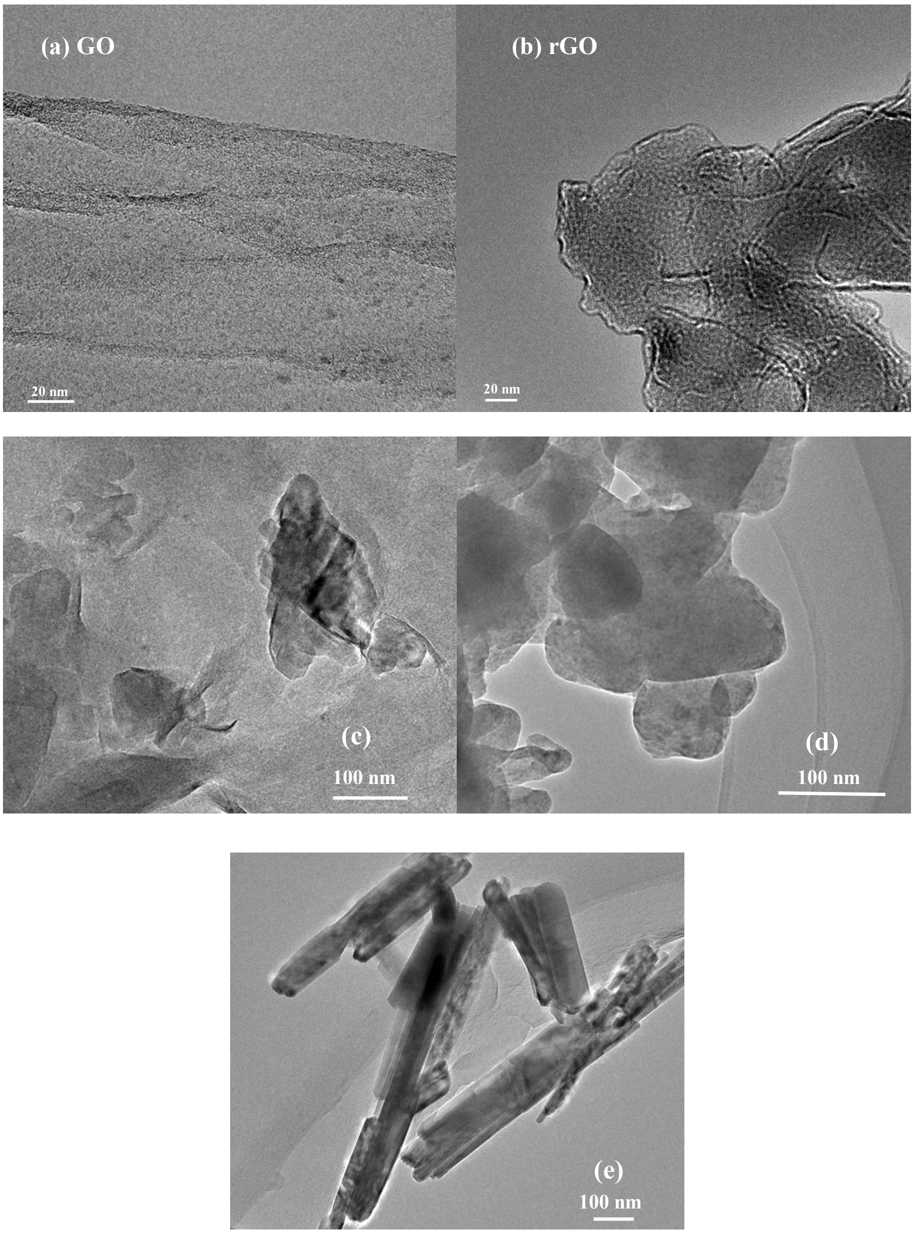

Fig. S3 TEM images of GO (a), rGO (b), montmorillonite (c), kaolin (d), and goethite (e).

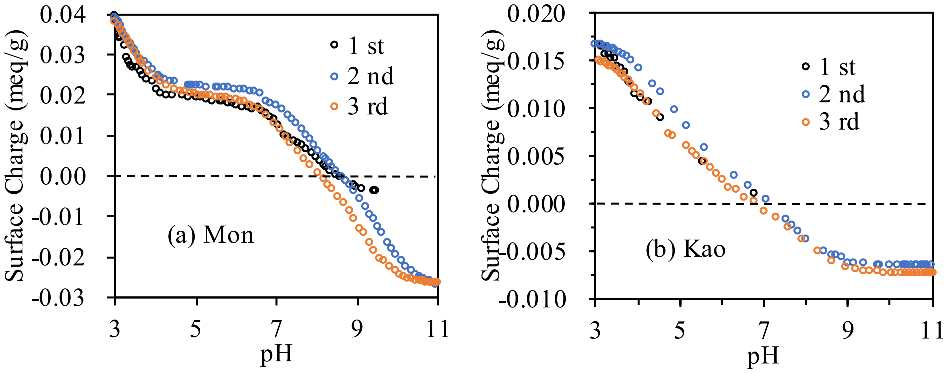

Fig. S4 Surface charges of montmorillonite and kaolin.

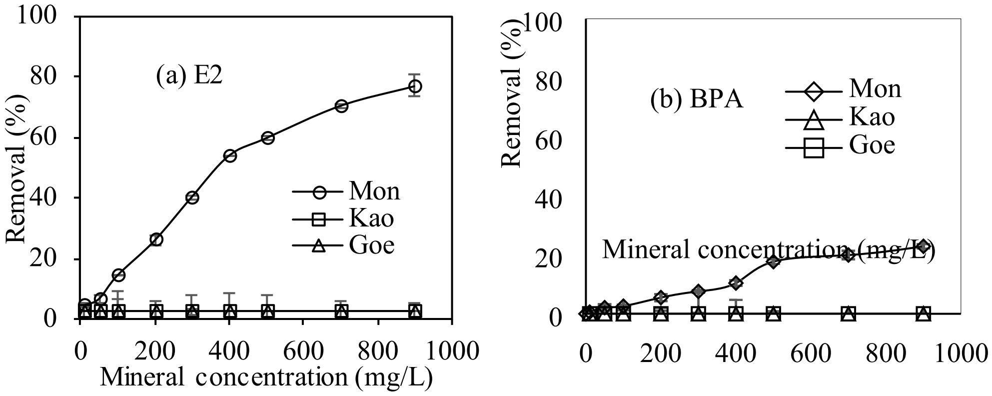

Fig. S5 Removal of E2 and BPA by minerals.

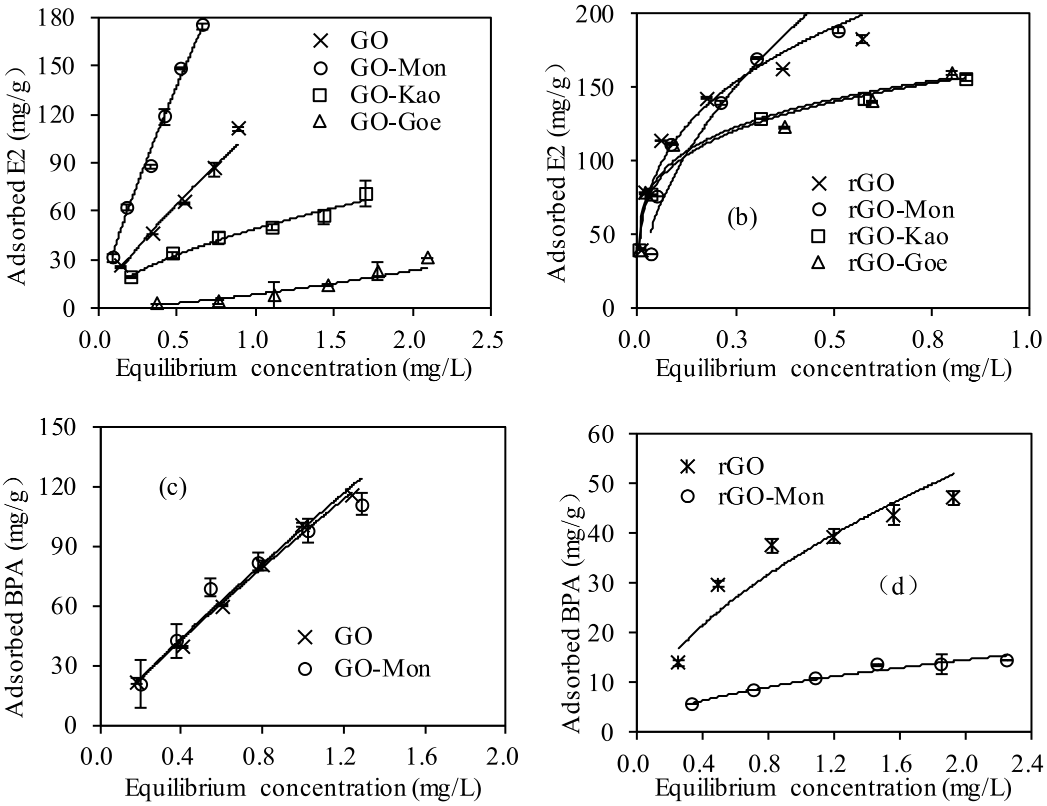

Fig. S6 Adsorption isotherms of E2 (a, b) and BPA (c, d) on GO and rGO in the absence and presence of minerals (ionic strength 0.01 M NaCl, GFN concentration = 10 mg/L, mineral/GFN = 50, pH 6.5 ± 0.1).

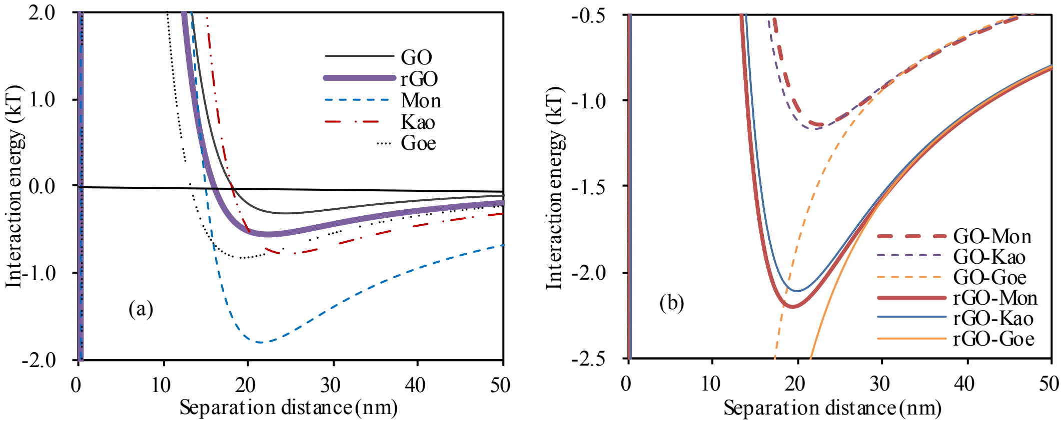

Fig. S7 The depth of secondary minimum between identical (a) and different (b) GFNs and mineral particles calculated by DLVO theory.

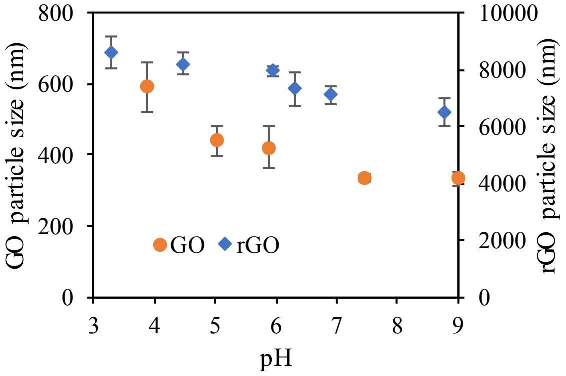

Fig. S8 Particle sizes of GO and rGO at various pH.

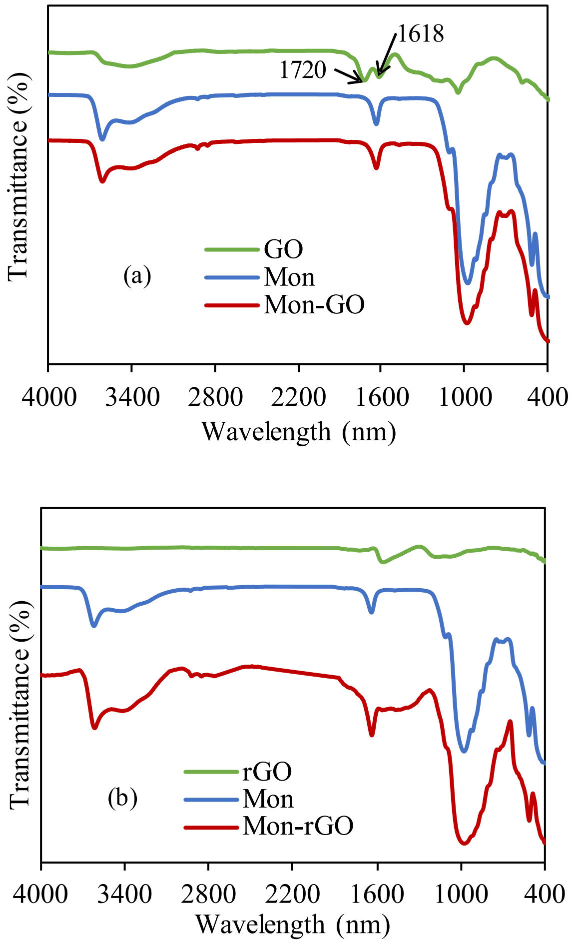

Fig. S9 FTIR spectra of GO, rGO, and montmorillonite alone and their mixtures.

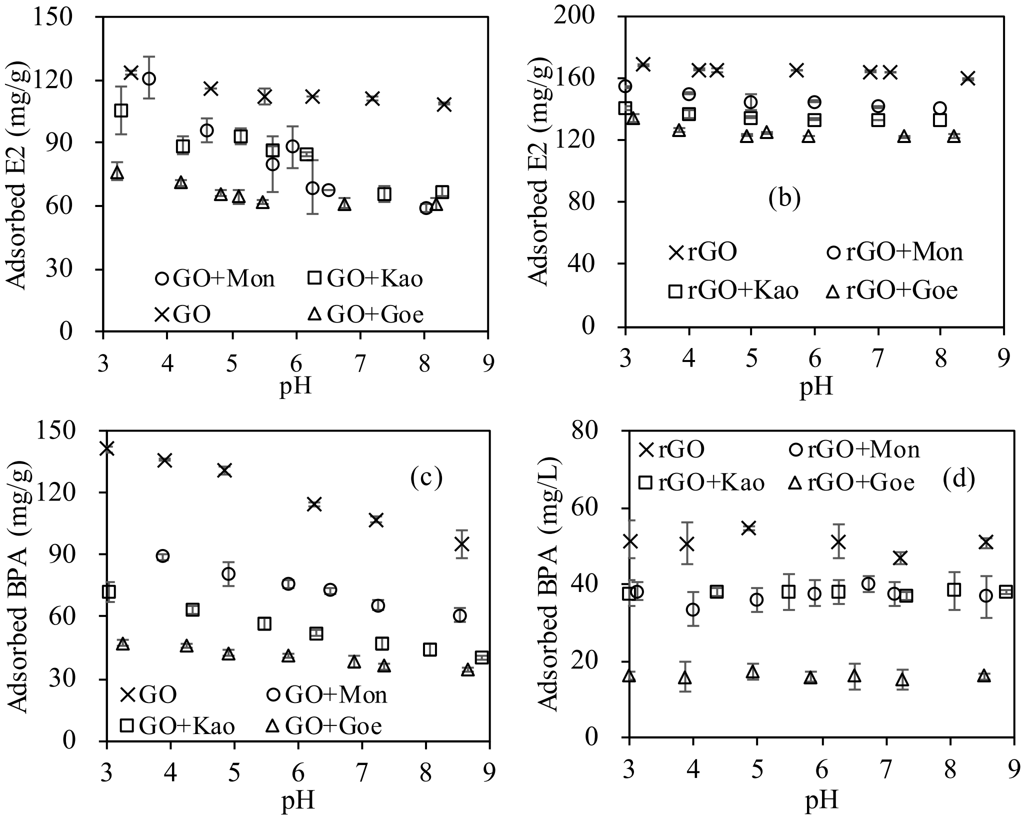

Fig. S10 Effect of pH on the adsorption of E2 and BPA on GFNs in the absence and presence of minerals.

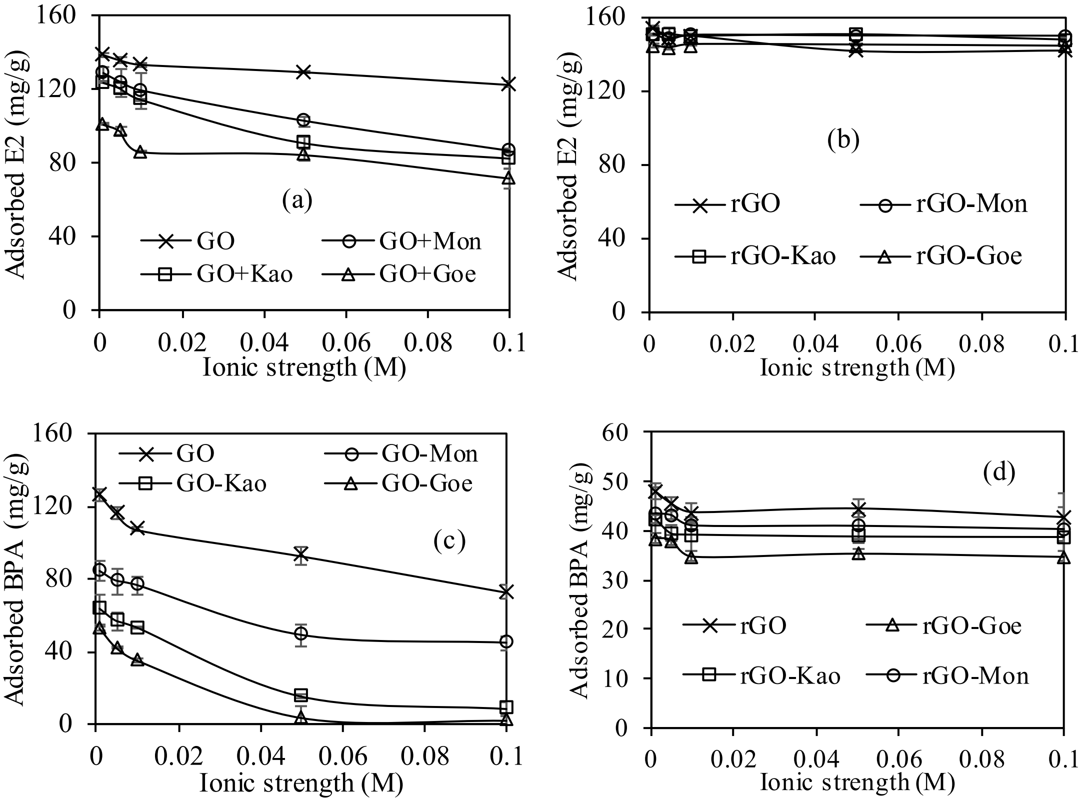

Fig. S11 Effect of ionic strength (NaCl) on the adsorption of E2 and BPA on GFNs in the absence and presence of minerals.

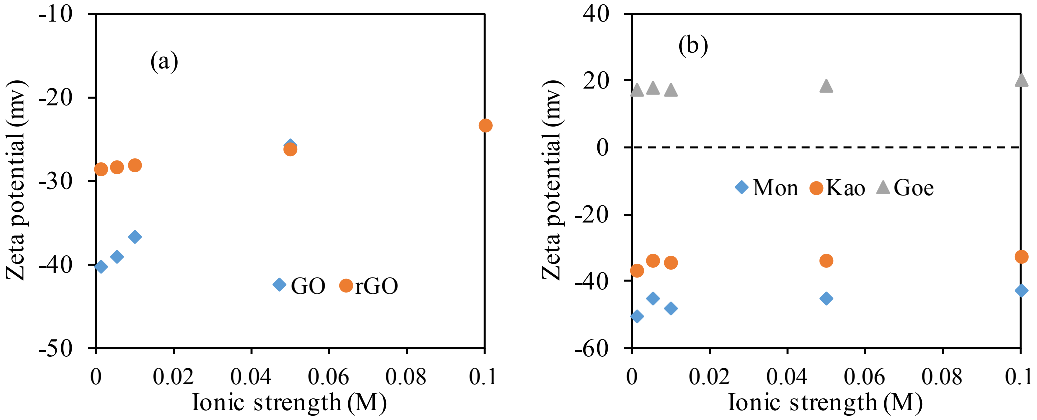

Fig. S12 Zeta potentials of GFNs and minerals at different ionic strengths.

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