Supplementary Materials: Adsorption characteristics of phenolic compounds on graphene oxide and reduced graphene oxide: a batch experiment combined theory calculation

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1. Supplementary Information: Text

Text S1. Preparation of GO dispersion

In brief, concentrated H_2SO_4 (46 mL) was added to a mixture of graphite flakes (1 g) and $NaNO_3$ (1 g) in a 250 mL beaker. The mixture was stirred for 0.5 h in an ice bath at 5 °C. $KMnO_4$ (6 g) was added slowly in small portions to keep the reaction temperature below 5 °C, being followed by stirring for 2 h. Then the mixture was heated up to 35 °C and stirred for 2 h. After that, 46 mL of deionized water was gradually added into the solution. The reaction temperature was raised to 98 °C. After it was maintained at 98 °C for 15 min, the heat was removed. Additional water (100 mL) and 30% H2O2 (20 mL) were added. The mixture was centrifuged and washed with deionized water sequentially. The obtained product was dispersed in water, exfoliated through ultrasonication for 1 h, and used as a stock of GO suspension in water.

Text S2. The calculation of kinetic parameters

The pseudo-first-order model can be expressed as eq. (2),

$$\ln (qe - qt) = \ln qe – k1t \quad (2)$$

the pseudo-second-order model as described by eq. (2),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where k1 and k2 is the rate constant of the pseudo-first and second-order model of adsorption (1 h-1 and g mmol-1 h-1), qe and qt are the maximum adsorption capacity at the equilibrium state and the adsorption capacity at time t.

Text S3. Langmuir Adsorption Models

The Langmuir model was utilized to fit the adsorption isotherms. The following expression describes the Langmuir equation:

$$\frac{c_e}{q_e} = \frac{1}{q_m} c_e + \frac{1}{q_m K_L} \quad (1)$$

where qe (mmol g-1) and ce (mmol L-1) were the equilibrium adsorption capacity and equilibrium concentration of an adsorbate in solution, respectively, KL was the Langmuir constant (L mmol-1), which was related to the affinity of the binding sites, and qm represents the maximum adsorption capacity of the adsorbent (mmol g-1). The values of qm and KL were calculated from the slope and intercept of the linear plot of ce / qe against ce

Text S4. The calculation of thermodynamic parameters

The standard free energy change (ΔG0), enthalpy change (ΔH0), entropy change (ΔS0) were determined. The standard free energy change (ΔG0) can be calculated from the following equation:

$$\Delta G^0 = -RT \ln K^0 \quad (1)$$

Where R is the universal gas constant (8.314 J mol-1 K-1), T is the temperature in Kelvin. The adsorption equilibrium constant K0 can be calculated by plotting ln qe/ce versus ce and extrapolating ce to zero. The value of the intercept is the value of the lnK0

According to eq. (2), lnK0 was plotted versus 1/T, and the standard enthalpy change (ΔH0) and entropy change (ΔS0) were obtained from the slope and intercept of the line.

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (2)$$

2. Supplementary Information: Tables

Table S1. Kinetic parameters for the adsorption of five phenolics (40 mg L-1) on GO and RGO fitted with the pseudo-second-order model .

Adsorbent	Adsorbate	$q_{e,exp}$ (mmol/g)	Pseudo-First-Order			Pseudo-Second-Order		
			k_1 (1 h^{-1})	$q_{e,cal}$ (mmol g^{-1})	R^2	k_2 (g $mmol^{-1}$ h^{-1})	$q_{e,cal}$ (mmol g^{-1})	R^2
GO	PE	0.271	0.185	0.134	0.802	318.8	0.274	0.9998
	ME	0.356	0.158	0.159	0.727	209.9	0.337	0.9995
	IPE	0.454	0.112	0.138	0.615	210.3	0.459	0.9998
	BPA	0.4	0.126	0.143	0.779	219.0	0.409	0.9998
	PPE	0.7	0.114	0.089	0.432	418.3	0.704	0.9999
RGO	PE	0.483	4.756	0.216	0.742	70.7	0.497	0.9981
	ME	0.841	13.917	0.282	0.932	249.9	0.833	0.9999
	IPE	1.117	20.066	0.638	0.962	297.4	1.123	0.9999
	BPA	1.56	12.635	0.113	0.943	159.6	1.571	0.9995
	PPE	2.054	11.153	0.015	0.751	1037.9	2.055	0.9999

Table S2. Chemical structures and some properties of the tested phenolics.

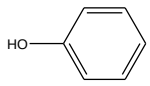
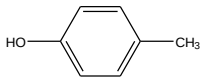
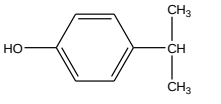
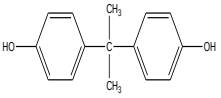
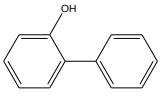
Phenolics	Structure	S_W (g/L)	logK_{OW}	pK_a
phenol (PE)		67	1.46	9.95
4-methylphenol (ME)		20	1.9	10.19
4-isopropylphenol (IPE)		NA	2.9	10.3
bisphenol A (BPA)		0.12–0.3	3.3	9.5
2-phenylphenol (PPE)		0.7	3.1	9.9

Table S3. Parameters for adsorption of phenols on GO and RGO obtained by data fitting with the Langmuir model at 298K.

Phenols	Adsorbents	q_m(mmol g^{-1})	K_L(L mmol^{-1})	R^2
phenol (PE)	GO	1.086	1.158	0.907
	RGO	1.393	1.239	0.959
4-methylphenol (ME)	GO	1.116	1.791	0.889
	RGO	2.017	1.945	0.969
4-isopropylphenol (IPE)	GO	1.576	1.776	0.988
	RGO	2.237	3.842	0.981
bisphenol A (BPA)	GO	0.947	4.776	0.991
	RGO	2.507	27.673	0.996
2-phenylphenol (PPE)	GO	2.268	2.635	0.853
	RGO	2.788	40.978	0.994

Table S4. Parameters for adsorption of phenolics on GO and RGO obtained by data fitting with the Freundlich model at three different temperatures.

Phenolics	T(K)	GO				RGO			
		Q_F	1/n	K_m	R^2	Q_F	1/n	K_m	R^2
PE	298	0.645	0.745	0.555	0.997	0.882	0.758	0.847	0.992
	313	0.524	0.689	0.391	0.996	0.754	0.769	0.693	0.985
	333	0.443	0.662	0.292	0.988	0.624	0.77	0.542	0.989
ME	298	0.939	0.751	0.92	0.986	1.695	0.703	2.118	0.993
	313	0.781	0.721	0.71	0.974	1.374	0.678	1.598	0.985
	333	0.656	0.717	0.555	0.977	1.108	0.708	1.156	0.995
IPE	298	1.264	0.723	1.382	0.995	2.393	0.599	4.292	0.981
	313	1.099	0.759	1.132	0.997	2.103	0.613	3.362	0.995
	333	0.972	0.783	0.964	0.998	1.979	0.698	2.658	0.986
BPA	298	1.124	0.566	1.229	0.992	3.675	0.321	57.667	0.973
	313	1.039	0.603	1.065	0.991	3.287	0.345	31.475	0.94
	333	0.948	0.623	0.918	0.996	3.281	0.4	19.499	0.902
PPE	298	2.194	0.667	3.248	0.99	3.819	0.272	137.89	0.968
	313	2.159	0.752	2.783	0.994	3.68	0.32	58.651	0.976
	333	2.001	0.799	2.382	0.995	3.66	0.34	45.425	0.973

2. Supplementary Information: Figures

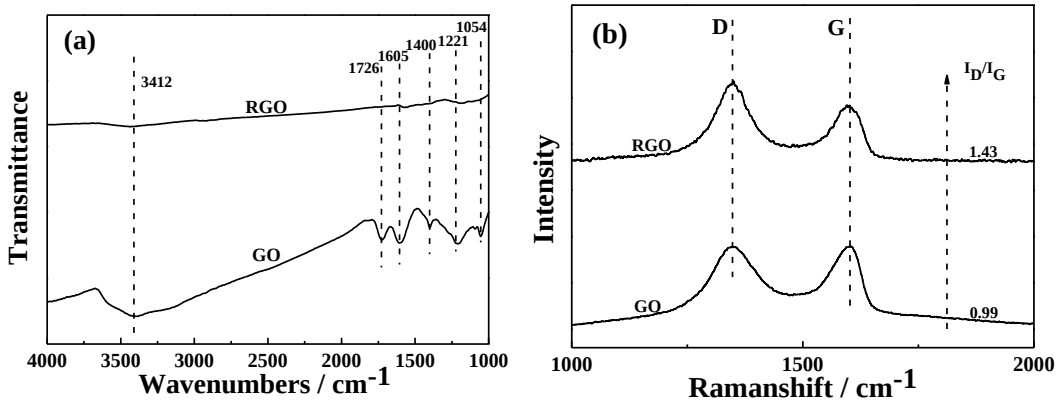


Figure S1. FT-IR (a) and Raman (b) spectra of GO and RGO samples.

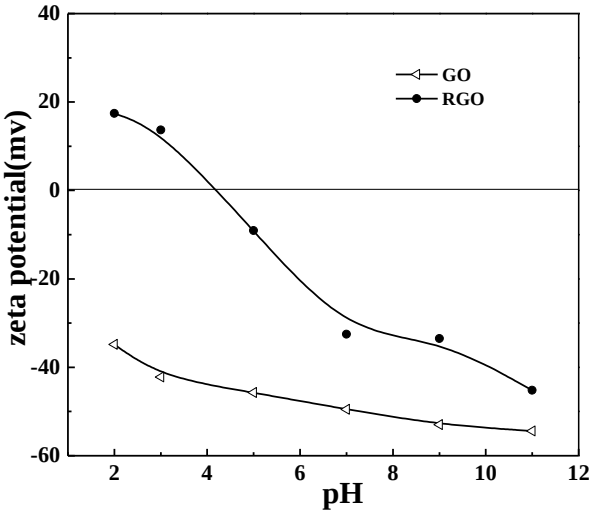


Figure S2. zeta potential of GO and RGO samples as a function of pH.

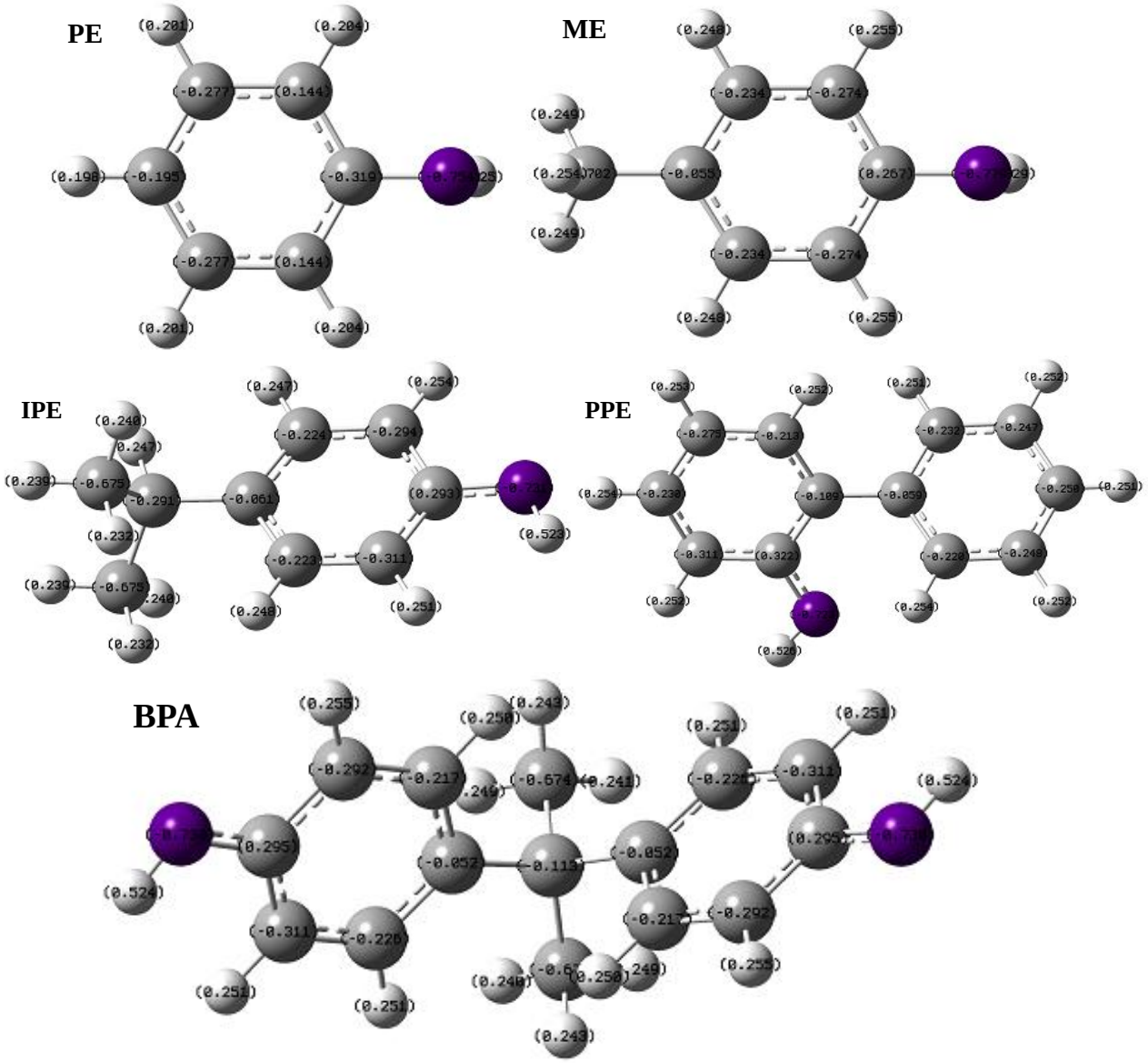


Figure S3. Electrons distribution schematics of PE, ME, IPE, BPA and PPE.