Supplementary information for

Water-compatible surface molecularly imprinted polymers with synergy of bi-functional monomers for enhanced selective adsorption of bisphenol A from aqueous solution

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**Synthesis of porous graphene oxides (PGO).** Graphene oxide was synthesized via Staudenmaier method. PGO was prepared by the method of Zhao’s group.\(^1\) Briefly, hard templates, silica nanospheres were synthesized by Stober method: ammonia solution (3 mL, 25%), distilled water (1 mL) and tetraethyl orthosilicate (2.3 mL) were mixed into 60 mL of ethanol. The mixed solution was reacted under vigorous stirring for 6 h at 25 °C. Then the solution was dialyzed for 48 h and then diluted to 75 mL with water. F108 (0.6 g), 1, 3, 5-trimethylbenzene (0.875 mL) and concentrated HCl (15 mL, 37%) were added into the diluted suspension and the reaction was continued for 48 h. Then ammonia solution was used to neutralize the suspension. Graphene oxide suspension (600 mL, 1.0 mg/mL) was mixed into the neutralized solution and the whole mixture was stirred for 12 h at room temperature. Then, the produced solid precipitate was collected by centrifugation at 4500 r.min\(^{-1}\) and dried at 50 °C. The dried precipitate was calcined at 400 °C for 1 h under argon atmosphere. The sample was then washed by HF solution (5 wt%) three times to remove the silica template and PGO was obtained.

**Adsorption capacity.** The adsorption capacity of adsorbent (mg/g) at equilibrium \(q_e\) was calculated according to the following equation:

\[
q_e = \frac{C_0 - C_e}{m}V
\]  
(1)
where $C_0$ and $C_e$ present the initial and equilibrium concentrations of BPA in the mixture solution (mg/L), respectively, $V$ is the volume of solution (L), and $m$ is the mass of adsorbent used (g).

**Characterization.** The morphologies of the parent PGO and functionalized PGO were characterized by transmission electron microscopy (TEM, JEOL-2100F). X-Ray energy dispersive spectroscopy (EDS) was used to obtain information about the chemical composition of the samples. Fourier-transform IR (FTIR) spectra were recorded on a Japan MODEL-8400s FTIR spectrometer using KBr pellet. Thermogravimetric (TG) analysis was carried out on a Netzsch TG 209 F3 instrument at a heating rate of 10°C/min under air atmosphere.

**Table S1** The detailed monomer doses of MIPs with different monomer ratio (molar ratio).

<table>
<thead>
<tr>
<th>AMPS:St</th>
<th>5:0</th>
<th>4:1</th>
<th>3:2</th>
<th>2.5:2.5</th>
<th>2:3</th>
<th>1:4</th>
<th>0:5</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPS (g)</td>
<td>0.8320</td>
<td>0.6656</td>
<td>0.4992</td>
<td>0.4160</td>
<td>0.3328</td>
<td>0.1664</td>
<td>-</td>
</tr>
<tr>
<td>St (μL)</td>
<td>-</td>
<td>92.0</td>
<td>184.0</td>
<td>230.0</td>
<td>276.0</td>
<td>368.0</td>
<td>460.0</td>
</tr>
</tbody>
</table>
**Fig. S1** Effect of contact time on the adsorption of MIPs with different molar ratio of AMPS to St (20 mg of each MIPs in 40 mL of 50 mg/L BPA solution at 293 K).

**Fig. S2** TG curves of (a) PGO, (b) silanized PGO, (c) AMPS/MIPs, (d) St/MIPs and (e) AMPS-St/MIPs.

**Adsorption kinetics studies of AMPS-St/MIPs**

Two conventional kinetics models (pseudo-first-order and pseudo-second-order) were applied to analyze the experimental data.

The pseudo-first-order model can be described as:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(2)

where \( k_1 \) is the rate constant of the pseudo-first-order model of adsorption (1/min), \( q_e \) and \( q_t \) (mg/g) are the adsorbed BPA amounts on AMPS-St/MIPs at equilibrium and at
various times t, respectively. The values of $q_e$ and $k_1$ can be determined from the intercept and slope of the linear plot of $\ln(q_e - q_t)$ versus $t$.

The pseudo-second-order model comprises all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion, which is described as:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(3)

where $q_e$ and $q_t$ are defined as in the above pseudo-first-order model and $k_2$ (mg/mg·min) is the rate constant of the pseudo-second-order model of adsorption, which can be obtained from the linear plot of $t/q_t$ versus $t$.

The kinetic parameters and correlation coefficients of BPA adsorption by AMPS-St/MIPs are fitted with the above two models under three different temperatures by nonlinear regression and summarized in Table S2.

<table>
<thead>
<tr>
<th>Table S2 Kinetic parameters for the adsorption of BPA by AMPS-St/MIPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
</tr>
<tr>
<td>--------------</td>
</tr>
<tr>
<td>293K</td>
</tr>
<tr>
<td>298K</td>
</tr>
<tr>
<td>303K</td>
</tr>
</tbody>
</table>

Adsorption isotherm and thermodynamic studies of AMPS-St/MIPs

Two commonly used models, the Langmuir and Freundlich models were adopted to describe the adsorption isotherms of BPA on AMPS-St/MIPs.
The Langmuir model, which assumes the adsorption takes place on a homogeneous surface with monolayer coverage and uniform energies, is expressed as:\textsuperscript{2-4}

\[
\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L}
\]  \hspace{1cm} (4)

where \(q_e\) represents the amount of adsorbed BPA on AMPS-St/MIPs (mg/g), \(C_e\) is the equilibrium concentration of BPA in solution (mg/L), \(q_m\) is the maximum adsorption capacity of the adsorbent (mg/g), and \(K_L\) is the Langmuir constant (L/mg), which is related to the affinity of the binding sites. The values of \(q_m\) and \(K_L\) are determined from the slope and intercept of the linear plot of \(C_e/q_e\) against \(C_e\).

Freundlich model is an empirical model based on multilayer adsorption on a heterogeneous surface. The equation of Freundlich model is given as follows:\textsuperscript{5, 6}

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]  \hspace{1cm} (5)

where \(q_e\) and \(C_e\) are defined the same as in the Langmuir model, and \(K_F\) and \(n\) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. If \(n > 1\), suggesting favorable adsorption, then adsorption capacity increases. \(K_F\) and \(n\) can be calculated by a linear plot of \(\ln q_e\) versus \(\ln C_e\). The corresponding parameters calculated according to the Langmuir and Freundlich models are listed in Table S3.

**Table S3** Isotherm parameters for the adsorption of BPA by AMPS-St/MIPs.

<table>
<thead>
<tr>
<th>temperature</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_m) (mg/g)</td>
<td>(K_L) (L/mg)</td>
</tr>
<tr>
<td>-------------</td>
<td>------------</td>
<td>-------------</td>
</tr>
</tbody>
</table>
The $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ are calculated from the following equations:

$$\Delta G^\circ = - RT \ln K^\circ$$  \hspace{1cm} (6)

$$\ln K^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$  \hspace{1cm} (7)

$$K_d = \frac{C_0 - C_e V}{C_e} \frac{V}{m}$$  \hspace{1cm} (8)

where $R$ is the universal gas constant (8.314 J/K•mol), $T$ is the absolute temperature (K), $K_d$ is the distribution adsorption coefficient (g/L), $C_0$ is the initial concentration (mmol/L), $C_e$ is the equilibration concentration of BPA in solution (mmol/L), $V$ is the volume of the solution (L), and $m$ is the mass of the adsorbent (g). The adsorption equilibrium constant, $K^\circ$, can be calculated by plotting $\ln K_d$ versus $C_e$ and extrapolating $C_e$ to zero. The value of the intercept is $\ln K^\circ$. The thermodynamic parameters calculated from equations (6)-(8) at three different temperatures are listed in Table S5.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Thermodynamic constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>84.06 0.05369 0.9893 10.8740 1.4847 0.9952</td>
</tr>
<tr>
<td>298</td>
<td>73.64 0.05021 0.9849 9.4046 1.5472 0.99672</td>
</tr>
<tr>
<td>303</td>
<td>67.33 0.03798 0.9738 7.5155 1.6782 0.9995</td>
</tr>
</tbody>
</table>

Table S4 Thermodynamic parameters of BPA adsorption on AMPS-St/MIPs.
<table>
<thead>
<tr>
<th>lnK°</th>
<th>3.092</th>
<th>2.835</th>
<th>2.767</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG° (kJ/mol)</td>
<td>-7.39</td>
<td>-7.02</td>
<td>-6.97</td>
</tr>
<tr>
<td>ΔH° (kJ/mol)</td>
<td></td>
<td>-24.06</td>
<td></td>
</tr>
<tr>
<td>ΔS° (J/mol*K)</td>
<td></td>
<td></td>
<td>-56.68</td>
</tr>
</tbody>
</table>

**Fig. S3** (a) Effect of the solution pH (20 mg, BPA concentration: 50 mg/L, volume: 40 mL, adsorption time: 1.5 h, temperature: 293 K); (b) Effect of ionic strength (20 mg, BPA concentration: 50 mg/L, volume: 40 mL, adsorption time: 1.5 h, temperature: 293 K, pH 6.0) on the BPA adsorption by AMPS-St/MIPs.

**REFERENCES**


