Electronic Supplementary Information

Fabrication of dual-template molecularly imprinted mesoporous silica for simultaneous rapid and efficient detection bisphenol A and diethylstilbestrol in environmental water samples

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1. Equations

The pseudo-first-order rate equation is listed as follows:

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t
\]  

(1)

where \( Q_e \) and \( Q_t \) (mg/g) are the amount of BPA or DES adsorbed on DMIMS at equilibrium and time \( t \), respectively. \( k_1 \) (cm\(^{-1}\)) is the rate constant of pseudo-first-order model.

The pseudo-second-order rate equation is listed as follows:

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q^2_e} + \left(\frac{1}{Q_e}\right) t
\]  

(2)

where \( k_2 \) is the rate constant of pseudo-second-order model.

Scatchard analysis based on the equation as follows:

\[
\frac{Q}{C_e} = \frac{Q_{max}}{K_d} - \frac{Q}{K_d} 
\]  

(3)

where \( Q \) and \( Q_{max} \) are the experimental binding capacity (mg/g) of BPA and DES and the theoretical maximum binding capacity of the DMIMS or NIMS (mg/g), respectively, and \( C_e \) is the concentration of BPA or DES in equilibrium solution (mg/L), \( K_d \) is the dissociation constant (mg/ L). The values of \( K_d \) and \( Q_{max} \) can be calculated from the slope and intercept of the linear equation plotted in \( Q \) versus - \( Q/C_e \), respectively.

The non-linear form of Langmuir equation is as follows:

\[
Q_e = \frac{K_L Q_{max} C_e}{1 + K_L C_e}
\]  

(4)

The non-linear form of Freundlich equation is as follows:

\[
Q_e = K_F C_e^{1/n}
\]  

(5)

The non-linear form of Langmuir-Freundlich equation is as follows:
where \( K_L \) (L/mg) is the Langmuir constant, and \( Q_m \) (mg/g) is the maximum adsorption capacity for monolayer formation on the sorbents, \( C_e \) (mmol/L) is the free analytical concentration at equilibrium, and \( n \) and \( K_F \) are the Freundlich constants.

2. Supporting data

![High-resolution XPS spectra of (a) O1s and (b) Si2p of DMIMS](image1)

![TEM (a, b) images of DMIMS](image2)

![Scatchard plots of DMIMS (a) and NIMS (b)](image3)
Figure S4. Langmuir and Freundlich plots of DMIMS and NIMS for BPA and DES

Figure S5. Molecular structure of analogs used in this work

Figure S6 Calibration curve for the determination of BPA (a) and DES (b) by HPLC/UV

Figure S7 HPLC chromatograms of lake river (a) and river water (b): (1) water sample without spiked, (2) water sample spiked with 0.5 mg L\(^{-1}\) BPA and DES, 3) elution from DMIMS
Table S1 The Langmuir and Freundlich isotherm parameters obtained by the adsorption of BPA and DES onto DMIMS and NIMS

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$Q_e{_{(exp)}}$ (mg/g)</th>
<th>$Q_m$(mg/g)</th>
<th>$K_L$(L/mg)</th>
<th>$R^2$</th>
<th>$K_F$</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMIMS for BPA</td>
<td>66.8</td>
<td>66.9</td>
<td>0.52</td>
<td>0.999</td>
<td>69.4</td>
<td>0.35</td>
<td>0.995</td>
</tr>
<tr>
<td>NIMS for BPA</td>
<td>19.4</td>
<td>19.6</td>
<td>0.017</td>
<td>0.980</td>
<td>20.4</td>
<td>1.29</td>
<td>0.973</td>
</tr>
<tr>
<td>DMIMS for DES</td>
<td>43.9</td>
<td>44.1</td>
<td>0.26</td>
<td>0.997</td>
<td>45.4</td>
<td>0.36</td>
<td>0.992</td>
</tr>
<tr>
<td>NIMS for DES</td>
<td>12.3</td>
<td>12.4</td>
<td>0.014</td>
<td>0.964</td>
<td>12.0</td>
<td>1.68</td>
<td>0.959</td>
</tr>
</tbody>
</table>

Table S2 Comparison of the present method for determination of BPA and DES

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Target molecule</th>
<th>Binding capacity (mg/g)</th>
<th>Real samples</th>
<th>Recovery (%)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$@MIP</td>
<td>BPA</td>
<td>3.6</td>
<td>Tap water, lake water, drinking water</td>
<td>97.0-106.0</td>
<td>1</td>
</tr>
<tr>
<td>P-MIPs</td>
<td>BPA</td>
<td>6.2</td>
<td>Tap water, river water</td>
<td>100.4-102.4</td>
<td>2</td>
</tr>
<tr>
<td>T-MIPs</td>
<td>BPA</td>
<td>7.9</td>
<td>Seawater, yogurt</td>
<td>94.8-98.5</td>
<td>3</td>
</tr>
<tr>
<td>MWNTs@MMIPs</td>
<td>BPA</td>
<td>11.3</td>
<td>Tap water, rain water, lake water</td>
<td>87.3-95.4</td>
<td>4</td>
</tr>
<tr>
<td>MIMIO-ir</td>
<td>BPA</td>
<td>15.0</td>
<td>Tap water, lake water</td>
<td>99.5-105.2</td>
<td>5</td>
</tr>
<tr>
<td>MI-SBA-15</td>
<td>BPA</td>
<td>27.9</td>
<td>Tap water, river water, well water, wastewater</td>
<td>87-110.2</td>
<td>6</td>
</tr>
<tr>
<td>m-MINPs</td>
<td>DES</td>
<td>9.7</td>
<td>Milk</td>
<td>90.7-105.2</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$@APBA/MIP</td>
<td>DES</td>
<td>18.9</td>
<td>Lake water</td>
<td>97.1-103.2</td>
<td>8</td>
</tr>
<tr>
<td>MIP-QDs</td>
<td>DES</td>
<td>32.5</td>
<td>Seawater and river water</td>
<td>95.5-107.5</td>
<td>9</td>
</tr>
<tr>
<td>m-TiMIF</td>
<td>BPA/DES</td>
<td>15.8/13.2</td>
<td>Pork and chicken samples</td>
<td>81.6-102.4</td>
<td>10</td>
</tr>
<tr>
<td>DMIMS</td>
<td>BPA/DES</td>
<td>66.8/43.9</td>
<td>Tap water, river water, lake water</td>
<td>95.0-107.1</td>
<td>This work</td>
</tr>
</tbody>
</table>

References


