Supporting Information

Metal-organic frameworks@graphene hybrid aerogel for solid-phase extraction of non-steroidal anti-inflammatory drugs and selective enrichment of proteins

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Fig. S1. SEM image of MIL-101.

Fig. S2. XRD patterns of MIL-101 and MIL-101 treated by hydrazine vapor at 95 °C for 24 h.

Fig. S3. SEM images of hybrid aerogels after (A) replicate extractions and (B) dramatic ultrasonic for 10 min in a mixture solution of EtOH and water.
Fig. S4. Photographs of (A) newly prepared hybrid aerogel packed SPE cartridges and (B) SPE cartridges after 20 replicate extractions.

Table S1
Analytical figures of merit through MIL-101@graphene hybrid aerogel based SPE-HPLC-UV method.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>pKa</th>
<th>Regression equation(^a)</th>
<th>R(^2)</th>
<th>Linear range (ng mL(^{-1}))</th>
<th>LOD (ng mL(^{-1}))</th>
<th>RSD (%)</th>
<th>Run-to-run (n=6)</th>
<th>Day-to-day (n=3)</th>
<th>Cartridge-to-cartridge (n=4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naproxen</td>
<td>4.39</td>
<td>y = 0.21478x + 0.05264</td>
<td>0.9996</td>
<td>0.2 – 50</td>
<td>0.01</td>
<td></td>
<td>6.1</td>
<td>4.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Felbinac</td>
<td>4.30</td>
<td>y = 0.03735x + 0.00176</td>
<td>1.000</td>
<td>0.2 – 50</td>
<td>0.08</td>
<td></td>
<td>4.4</td>
<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Carprofen</td>
<td>4.42</td>
<td>y = 0.08628x - 0.00782</td>
<td>0.9997</td>
<td>0.2 – 50</td>
<td>0.03</td>
<td></td>
<td>5.6</td>
<td>5.3</td>
<td>9.1</td>
</tr>
<tr>
<td>Flurbiprofen</td>
<td>4.42</td>
<td>y = 0.03066x + 0.02130</td>
<td>0.9984</td>
<td>0.2 – 50</td>
<td>0.04</td>
<td></td>
<td>8.5</td>
<td>9.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>4.38</td>
<td>y = 0.03806x + 0.02115</td>
<td>0.9973</td>
<td>0.2 – 50</td>
<td>0.10</td>
<td></td>
<td>3.7</td>
<td>3.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\)y=peak area in mAU min and x= concentration in ng mL\(^{-1}\).
Table S2
Comparison of different methods for the determination of non-steroidal anti-inflammatory drugs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Detection</th>
<th>Sample volume (mL)</th>
<th>LOD (ng mL⁻¹)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow fiber liquid-phase microextraction</td>
<td>UPLC-MS/MS</td>
<td>5</td>
<td>0.5-1.25</td>
<td>[38]</td>
</tr>
<tr>
<td>C18 sorbent based microextraction</td>
<td>HPLC-PDA</td>
<td>0.1</td>
<td>0.03</td>
<td>[39]</td>
</tr>
<tr>
<td>Electromembrane extraction</td>
<td>HPLC-DAD</td>
<td>10</td>
<td>0.08-3.36</td>
<td>[40]</td>
</tr>
<tr>
<td>Magnetic matrix solid phase dispersion</td>
<td>HPLC-UV</td>
<td>1000</td>
<td>1-2</td>
<td>[41]</td>
</tr>
<tr>
<td>Immobilized carboxylated carbon nanotubes based SPE</td>
<td>CE-MS</td>
<td>5</td>
<td>1.6-2.6</td>
<td>[42]</td>
</tr>
<tr>
<td>MIL-101@graphene hybrid aerogel based SPE</td>
<td>HPLC-UV</td>
<td>100</td>
<td>0.01-0.10</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table S3
Recoveries of environmental water samples spiked with five NSAIDs (n=3).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration added (ng mL⁻¹)</th>
<th>Tap water samples</th>
<th>River water samples</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Recovery (%)</td>
<td>RSD (%)</td>
<td>Recovery (%)</td>
</tr>
<tr>
<td>Naproxen</td>
<td>0.5</td>
<td>97.6</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>105.0</td>
<td>5.7</td>
</tr>
<tr>
<td>Felbinac</td>
<td>0.5</td>
<td>105.5</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>106.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Carprofen</td>
<td>0.5</td>
<td>106.5</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>99.1</td>
<td>3.7</td>
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<td>Flurbiprofen</td>
<td>0.5</td>
<td>82.6</td>
<td>2.6</td>
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<tr>
<td></td>
<td>2.0</td>
<td>93.8</td>
<td>5.5</td>
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<tr>
<td>Ibuprofen</td>
<td>0.5</td>
<td>96.2</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>92.0</td>
<td>3.4</td>
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</tbody>
</table>