Supporting Information

Effect of humic acid on the sulfamethazine adsorption by functionalized multi-walled carbon nanotubes in aqueous solution: mechanisms study

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There are 9 figures and 3 tables.

There are 14 pages totally.
Fig. S1. Adsorption kinetics of HA onto P-MWCNT (□), C-MWCNT (○), and H-MWCNT (Δ).
Fig. S2 The effect of membrane pore size on measurement of solubility of SMZ. $C_{s0.22}$ and $C_{s0.45}$ are the solubility of SMZ filtered by 0.22 μm and 0.45μm, respectively.
**Fig. S3.** Ultraviolet-visible absorbance spectra of HA with concentrations from 10 to 60 mg L$^{-1}$ at 190–900 nm. The solid line represents the HA concentration before adsorption and the dotted line shows the HA concentration at adsorption equilibrium.
Fig. S4. HA concentration-absorbance calibration curve.
Fig. S5. μ-FTIR spectra of P-MWCNT (a), C-MWCNT (b), and H-MWCNT (c).
Fig. S6. Zeta potential of P-MWCNT (□), C-MWCNT (○), and H-MWCNT (Δ) as a function of pH.
Fig. S7. Effect of HA on SMZ adsorption. (a) Concentration of HA as affected by Ca\(^{2+}\) (0–100 mM). The initial concentrations of HA were 10 and 30 mg/L. \(C_{HA}\) is the concentration of HA at which HA precipitation was caused by Ca\(^{2+}\) and separated using a 0.45 μm hydrophilic membrane filter. (b) Recovery percentage of SMZ. The HA was precipitated by Ca\(^{2+}\) and was separated immediately using a 0.45 μm hydrophilic membrane filter.
**Fig. S8.** Relative solubility based on a background solution (value = 1) of SMZ in the presence of HA.
Fig. S9. The species distribution for SMZ at different solution pH.
Table S1 Basic MWCNTs structural properties.

<table>
<thead>
<tr>
<th>Name</th>
<th>Outer diameter (nm)</th>
<th>Inner diameter (nm)</th>
<th>Carbon content (%)</th>
<th>Oxygen content (%)</th>
<th>Surface area (m²·g⁻¹)</th>
<th>Mesopore volume (cm³·g⁻¹)</th>
<th>Micropore volume (cm³·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-MWCNTs</td>
<td>10-20</td>
<td>5-10</td>
<td>99</td>
<td>0.85</td>
<td>167</td>
<td>0.619</td>
<td>0.016</td>
</tr>
<tr>
<td>C-MWCNTs</td>
<td>10-20</td>
<td>5-10</td>
<td>97</td>
<td>2.16</td>
<td>178</td>
<td>0.629</td>
<td>0.015</td>
</tr>
<tr>
<td>H-MWCNTs</td>
<td>10-20</td>
<td>5-10</td>
<td>92</td>
<td>7.07</td>
<td>185</td>
<td>0.756</td>
<td>0.024</td>
</tr>
</tbody>
</table>

a The data are herein presented in Table S1 were firstly published in Chen et al., 2009.

b The diameters were determined by transmission electron microscope (TEM);

c The carbon and oxygen contents were determined by X-ray photoelectron spectroscopy (XPS);

d The surface area and pore volume were determined by nitrogen gas adsorption and desorption at 77K with ASAP2000 (Micromeritics Instrument Corporation).
Table S2 Elemental compositions and $^{13}$C NMR estimates of carbon distributions for HA.

<table>
<thead>
<tr>
<th>sample</th>
<th>Elemental composition (%)$^a$</th>
<th>Ash(%)$^a$</th>
<th>(O+N)/C$^b$</th>
<th>Integration of NMR results (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>AHA</td>
<td>57.07</td>
<td>3.25</td>
<td>36.85</td>
<td>1.47</td>
</tr>
</tbody>
</table>

$^a$ Mass-based percentages. The C, H and N were determined by CHN Elemental Analyzer (EA 1112, Thermo Finnigan, Italia), the ash were determined using combustion the processed ash at 750 °C for 4 hour, and the oxygen content were calculated by mass difference [ Oxygen content = 100 % -(C content +H content +N content)].

$^b$ Molar-based ratios.

$^c$ Aliphaticity was calculated as aliphatic C (0-109 ppm)/aromatic C (109-163 ppm) ratio$^2$. The major structural carbons were measured using a 300M Hz NMR spectrometer (Bruker AV300, Switzerland).
Table S3 Structural and physicochemical properties of sulfamethazine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS number</th>
<th>Chemical structure</th>
<th>Molecular weight (g·mol⁻¹)</th>
<th>Water solubility (g·L⁻¹)</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfamethazine</td>
<td>57-68-1</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>278.33</td>
<td>Fig. 5(a)</td>
<td>2.28</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.42</td>
</tr>
</tbody>
</table>

a from chemBlink Database of Chemicals from Around the World
http://www.chemblink.com/products/57-68-1.htm
b The water solubility of SMZ were determined at temperature 298 K.
c Reference from 3-5.
Literature cited


