Extracting organic molecules out of water using the metal-organic framework

Cr^{III}(OH)\{O_2C-C_6H_4-CO_2\}

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Synthesis and activation of MIL-47

MIL-53(Cr) was synthesized based on the procedure described in C. Serre et al., J. Am. Chem. Soc., 2002, 124, 13519. 0.7 g of HF was added to a mixture of 0.66 g of Cr(NO₃)₃·9H₂O and 0.67 g of H₂BDC dissolved in 8.33 g of distilled water. The solution is loaded into a teflon lined steel autoclave and heated at 493 K for 96 h. After cooling, the reaction mixture is filtered and washed three times with water to obtain MIL-53(Cr)as. MIL-53(Cr) is obtained by calcining MIL-53(Cr)as during 72 hrs at 603 K to remove uncoordinated terephthalic acid molecules out of the pores.
Batch experiments

Liquid phase batch adsorption experiments were carried out at 298 K in 10 ml glass vials filled with 0.1 g of adsorbent and a water solution containing either phenol or \( p \)-cresol following a literature procedure (L. Alaerts, C. Kirschock, M. Maes, M. van der Veen, V. Finsy, A. Depla, J. Martens, G. Baron, P. Jacobs, J. Denayer, D. De Vos, *Angew. Chem. Int. Ed.*, 2007, 46, 4372; L. Alaerts, M. Maes, M. van der Veen, P. Jacobs, D. De Vos, *Phys. Chem. Chem. Phys.*, 2009, 11, 2903). For each adsorbed compound, the percentual uptake is calculated from GC data using formula 1:

\[
q(\%) = \left(1 - \frac{\text{relative peak area} \%_S}{\text{relative peak area} \%_R}\right) \times 100 \quad (1)
\]

in which \( S \) stands for the sample containing the adsorbent material, and \( R \) for a reference sample without adsorbent. The uptake (wt\%) is calculated according to formula 2:

\[
\text{uptake (wt\%)} = \left(\frac{q(\%) \times m_{\text{component}}}{100 \times m_{\text{adsorbent}}}\right) 
\]

in which \( m \) stands for mass (g); \( m_{\text{component}} \) is the mass of adsorbate initially offered. Uptakes (volume \%) were directly calculated from the wt\% uptake using the density of MIL-53(Cr) – 0.4 g/cm\(^3\) – and the density of activated carbon – 0.32 g/cm\(^3\). These data are consistent with what is found in the Sigma Aldrich data (http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=fr&N4=688738|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC) and the data provided by ASI Instruments (http://www.asiinstr.com/technical/Material_Bulk_Density_Chart_A.htm).

Repeated GC injections and data analysis showed a relative uncertainty of 2.5 \% on the relative peak areas. To calculate uncertainties on the volume\% uptake, the uncertainty on the percentual uptake is first calculated. The percentual uptake is the calculated via the quotient of two relative peak areas; hence the rules for error propagation as shown in formula 3 are used:
with \( u \) being the relative uncertainty. Both \( u(A) \) and \( u(B) \) were determined to be 2.5%. Based on the relative uncertainty in percentual uptakes, the error bars for the volume\% uptake in Figure 1 can be calculated.
Continuous experiments

Breakthrough chromatographic experiments were performed following a literature procedure (L. Alaerts, C. Kirschock, M. Maes, M. van der Veen, V. Finsy, A. Depla, J. Martens, G. Baron, P. Jacobs, J. Denayer, D. De Vos, *Angew. Chem. Int. Ed.*, **2007**, **46**, 4372). Columns were hand made by loading approximately 0.6 g of MIL-53(Cr) into a stainless steel column ($L = 5$ cm, $D = 0.45$ cm) under nitrogen atmosphere. The average breakthrough volume is the eluted volume at which the sigmoidal curve is halfway. Regeneration of the column is performed by flushing with typically 200 ml of pure water at the same temperature and pressure as during adsorption.
N$_2$-physisorption

Nitrogen physisorption measurements were carried out with a Coulter Omnisorp CX and analyzed with Coulter SA-Reports software for the determination of BET and Langmuir surfaces and t-plots from which pore volume and external surface were calculated. Samples were pretreated overnight under vacuum at 423 K.

![N$_2$-physisorption on activated MIL-53(Cr)](image)

**Figure S.1.** N$_2$-physisorption on activated MIL-53(Cr).

The S$_{BET}$ for MIL-53(Cr) based on Figure S.1 is 942 m$^2$ g$^{-1}$ and the pore volume is 0.50 cm$^3$ g$^{-1}$. 
Figure S.2. N₂-physisorption on activated carbon.

The $S_{\text{BET}}$ for activated carbon based on Figure S.2 is 1440 m² g⁻¹. The pore volume is 1.55 cm³ g⁻¹ and the pore distribution is obtained from the Norit Company.

<table>
<thead>
<tr>
<th>Type</th>
<th>Volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pore volume</td>
<td>1.55</td>
</tr>
<tr>
<td>Micro ($\phi &lt; 2$ nm)</td>
<td>0.45</td>
</tr>
<tr>
<td>Meso ($\phi 2 - 50$ nm)</td>
<td>0.75</td>
</tr>
<tr>
<td>Macro ($\phi &gt; 50$ nm)</td>
<td>0.35</td>
</tr>
</tbody>
</table>
XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a S-Probe monochromatized XPS spectrometer from Surface Science Instruments (VG) with an Al Kα X-ray (1486.6 eV) monochromatic source. The take off angle was 45° with the voltage and power of the source of 10 kV and 200 W respectively. A base pressure of 2 10⁻⁹ mbar was obtained in the measuring chamber and the pass energy spectra was 56 eV. The analysis surface was 250 x 1000 µm² with a flood gun (neutralizer) setting of 4.5 eV. The accumulation time was about 10 h for each spectrum.

Using the work of A.P. Terzyk (Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2001, 177, 23) the C1s and O1s region were analysed:

- 1) C 284.2 eV 18.8% Graphitic carbon
- 2) C-O 285.6 eV 19.7% Phenolic, alcoholic, etheric
- 3) C=O 286.8 eV 20.9% Carbonyl or quinone
- 4) COO 288.3 eV 15.3% Carboxyl or ester
- 5) C=O/C=C 289.7 eV 17.4% Carbonate, ocluded CO, p-electrons in aromatic ring
- 6) p–p transition 291.6 eV 7.9% The transition due to conjugation

Figure S.3. C1s region. The table shows the peak position and the relative contributions of each component to the C1s region.
Figure S.4. O1s region. The table shows the peak positions and the relative contributions of each component to the O1s region.

1) C=O 532.4  23.5%  Oxygen doubly bonded to carbon
2) C-O- 534.5  44.8%  Oxygen singly bonded to carbon in aromatic rings, in phenols and ethers
3) C=O 537.5  31.7%  Ocluded CO or CO2