Metal-organic framework MIL-100(Fe) for artificial kidney application

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EXPERIMENTAL SECTION

Chemicals and Reagents

All chemicals and reagents used were at least of analytical grade. Ultrapure water (Wahaha, Tianjin, China) was used throughout all experiments. Iron powder, trimesic acid (1,3,5-BTC), hydrofluoric acid (40.0%), and creatinine were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Nitric acid (65%-68%) was purchased from Tianjin Chemical Reagent No.5 Plant (Tianjin, China). Ethanol, N,N-dimethylformamide (DMF), methanol and acetonitrile were purchased from Concord Fine Chemical Research Institute (Tianjin, China). Phosphate buffer solutions (PBS, pH 4-10) were prepared with H$_3$PO$_4$, NaH$_2$PO$_4$, Na$_2$HPO$_4$, and NaOH (Guangfu Fine Chemical Research Institute, Tianjin, China).

Instrumentation

X-ray diffraction (XRD) patterns was obtained from a D/max-2500 diffractometer (Rigaku, Japan) using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). The thermal gravimetric analysis (TGA) was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 800 °C at a ramp rate of 10 °C min$^{-1}$. The scanning electron microscopy (SEM) images were collected on a Shimadzu SS-550 scanning electron microscope at 15.0 kV. An ASAP 2010 micropore physisorption analyzer (Micromeritics, Norcross, GA) was used to measure the Brunauer-Emmett-Teller (BET) surface area of MIL-100(Fe) using nitrogen adsorption at 77 K in the range 0.02 ≤ $P/P_0$ ≤ 0.20. Zeta potentials of the MIL-100(Fe) and creatinine were measured on a zeta potential analyzer (Brookhaven Instruments Co., Holtsville, NY, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD (Kratos Analytical Ltd. Britain).
The measurements of creatinine were performed on a chromatographic system consisting of a Waters 510 HPLC pump and a Waters 486 tunable absorbance detector at the wavelength of 235 nm on a C18 column (4.6 mm × 250 mm, Baseline, Tianjin, China).

Synthesis and Purification of MIL-100(Fe)

MIL-100(Fe) was synthesized according to Horcajada et al.\textsuperscript{1} Typically, 687.5 mg of 1,3,5-BTC, 277.5 mg of iron powder, 200 μL of hydrofluoric acid and 190 μL of nitric acid were mixed with 25 mL of ultrapure water in a 30-mL Teflon-lined bomb. The bomb was then sealed, placed in an oven and heated at 150 °C for 12 h. The light orange solid product was then obtained by centrifugation and washing with ultrapure water. To remove the unreacted substances from the as-synthesized MIL-100(Fe), the solid was refluxed with DMF and subsequently ethanol until no colored impurities in the solution were detected. The purified MIL-100(Fe) was dried in vacuum overnight to form activated MIL-100(Fe). The obtained MIL-100(Fe) was characterized by XRD, TGA, SEM, and N\textsubscript{2} adsorption (Figure S1).

Adsorption Kinetics of Creatinine on MIL-100(Fe)

To study the adsorption kinetics of creatinine on MIL-100(Fe), 15 mg of MIL-100(Fe) was dispersed with 25 mL of a fixed initial concentration of creatinine solution (50-200 mg L\textsuperscript{-1}) in a 25-mL test tube. The same procedure was followed for a 25 mL of creatinine solution without MIL-100(Fe) as control. The mixtures were maintained at 37 °C for various pre-determined periods (10 min to 6 h). After adsorption for a pre-determined time, the mixture was filtered with 0.22 μm filter, and the filtrate was determined by HPLC. The amounts of the adsorbed creatinine were calculated based on the difference between the initial and equilibrium concentrations of...
creatinine. The adsorption capacity \((q_t)\) at time \(t\) (mg g\(^{-1}\)) was then calculated for the kinetics study.

**Adsorption Isotherm and Thermodynamics of Creatinine on MIL-100(Fe)**

To study the adsorption isotherm of creatinine on MIL-100(Fe), 15 mg of MIL-100(Fe) was mixed with 25 mL of the creatinine solution in a 25-mL test tube. The adsorption proceeded at a certain temperature (30 to 60 °C) for 2 h. The mixture was filtered with a 0.22-μm filter, and the filtrate was determined by HPLC. The adsorbed creatinine amounts were calculated and expressed as \(q_e\) (mg g\(^{-1}\)) according to equation (1).

\[
q_e = \frac{(C_0 - C_e) \times V}{W}
\]

where \(C_0\) and \(C_e\) (mg L\(^{-1}\)) are the initial and equilibrium concentrations of the creatinine, respectively, \(V\) (L) is the volume of the creatinine solution, and \(W\) (g) is the mass of MIL-100(Fe) used.

**Desorption of Creatinine from MIL-100(Fe)**

Creatinine-preadsorbed MIL-100(Fe) was first prepared for desorption experiments as follows: 15 mg of MIL-100(Fe) was mixed with 25 mL of 100 mg L\(^{-1}\) creatinine solution for 2 h at 37 °C, the mixture was centrifuged at 10000 rpm for 5 min, and the supernatant was removed to collect creatinine-preadsorbed MIL-100(Fe) for subsequent desorption experiments.

To determine the time needed for the desorption of creatinine from MIL-100(Fe), the above creatinine-preadsorbed MIL-100(Fe) was mixed with 1 mL of desorption solvent (methanol, ethanol, or acetonitrile), and the mixture was then desorbed under ultrasonication (80 W) for a pre-determined time (2.5 to 60 min). The mixture was then centrifuged at 10000 rpm for 5 min,
and the concentration of creatinine in the supernatant was determined by HPLC. The amounts of desorbed creatinine at a fixed time were calculated to study the desorption kinetics.

To evaluate the effect of the solvent volume on the desorption of creatinine from MIL-100(Fe), the above creatinine-preadsorbed MIL-100(Fe) was mixed with 1 mL of desorption solvent, and the mixture was desorbed under ultrasonication for 5 min. The mixture was then centrifuged at 10000 rpm for 5 min, and the supernatant was collected. The collected supernatants were analyze by HPLC, and the relationship between the desorbed amount of creatinine and the volume of desorption solvent was obtained.

**Regeneration of MIL-100(Fe)**

The used MIL-100(Fe) was washed with 1 mL of methanol under ultrasonication for 5 min. The mixture was then centrifuged at 10000 rpm for 5 min and the supernatant was removed. The above procedure was repeated three times. The collected MIL-100(Fe) was dried at 120 °C for reuse.

**Adsorption of Creatinine from Blood Mimicking Solution**

To study the potential of MIL-100(Fe) for the adsorption of creatinine from blood mimicking solution, 15 mg of MIL-100(Fe) was mixed with 25 mL of the creatinine Tyrode buffer solution (a solution mimicking the mineral composition and pH of blood)\(^2\) in a 25-mL test tube. The adsorption was proceeded at 37 °C for 2 h. The mixture was filtered with a 0.22-μm filter, and the creatinine in the filtrate was determined by HPLC. The adsorbed creatinine amounts were then calculated.

**NMR Experiments**
Twenty milligram of creatinine is dissolved with 0.55 mL of D$_2$O in a NMR tube. The NMR tube was then introduced for $^1$H- and $^{13}$C-NMR experiments. A NMR tube with 20 mg of creatinine, 2 mg of FeCl$_3$, and 0.55 mL of D$_2$O was used for the study of the interaction between creatinine and Fe$^{3+}$. 
Table S1: Pseudo-second-order rate constant ($k_2$, g mg$^{-1}$ min$^{-1}$), equilibrium adsorption capacity ($q_e$, mg g$^{-1}$), and correlation coefficient ($R^2$) for the adsorption of creatinine on MIL-100(Fe) at various initial creatinine concentrations

<table>
<thead>
<tr>
<th>Concentration (mg L$^{-1}$)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>11.11 ± 0.05</td>
<td>$1.7 \times 10^{-2} \pm 1.6 \times 10^{-3}$</td>
<td>0.999</td>
</tr>
<tr>
<td>100</td>
<td>21.23 ± 0.14</td>
<td>$4.4 \times 10^{-3} \pm 2.1 \times 10^{-4}$</td>
<td>0.999</td>
</tr>
<tr>
<td>200</td>
<td>30.49 ± 0.26</td>
<td>$2.7 \times 10^{-3} \pm 0.8 \times 10^{-4}$</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table S2: Comparison of the maximum adsorption capacities of various sorbents for creatinine

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Maximum adsorption capacity (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotubes</td>
<td>25</td>
<td>S3</td>
</tr>
<tr>
<td>Zeolite</td>
<td>37.5</td>
<td>S4</td>
</tr>
<tr>
<td>Mordenite zeolite</td>
<td>44</td>
<td>S5</td>
</tr>
<tr>
<td>Mordenite zeolite</td>
<td>22.6</td>
<td>S6</td>
</tr>
<tr>
<td>MIP</td>
<td>32</td>
<td>S7</td>
</tr>
<tr>
<td>MIP</td>
<td>12</td>
<td>S8</td>
</tr>
<tr>
<td>MIP</td>
<td>6.5</td>
<td>S9</td>
</tr>
<tr>
<td>Poly(ether sulfone)/Activated Carbon</td>
<td>87</td>
<td>S2</td>
</tr>
<tr>
<td>MIL-100(Fe)</td>
<td>190.5</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table S3: Comparison of pore size, window size, and adsorption capacities of various MOFs for creatinine (100 mg L$^{-1}$)

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Pore size (Å)</th>
<th>Window size (Å)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>11.4</td>
<td>3.4</td>
<td>2.9</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>17</td>
<td>13</td>
<td>4.9</td>
</tr>
<tr>
<td>MIL-101(Cr)</td>
<td>29 and 34</td>
<td>12 and 16</td>
<td>9.1</td>
</tr>
<tr>
<td>MIL-100(Fe)</td>
<td>25 and 29</td>
<td>5.6 and 8.6</td>
<td>21.2</td>
</tr>
</tbody>
</table>

References


(S9) H. A. Tsai, M. J. Syu, *Biomaterials* 2005, **26**, 2759.

**Fig. S1** (a) XRD patterns of the synthesized MIL-100(Fe) and the simulated one; (b) TGA curve of the synthesized MIL-100(Fe); (c) SEM image of the synthesized MIL-100(Fe); (d) N$_2$ adsorption-desorption isotherms of MIL-100(Fe).

**Fig. S2** Van’t Hoff plot for the adsorption of creatinine on MIL-100(Fe).
Fig. S3 Effect of the number of regeneration with 1 mL the solvent for 5 min ultrasonication on the desorption of creatinine from MIL-100(Fe).