Sulfate-Rich Metal-Organic Framework for High Efficiency and Selective Removal of Barium from Nuclear Wastewater

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12. Elemental analysis of Zr-BDC-NH$_2$-SO$_4$ after Ba$^{2+}$ adsorption.
1. Structures of MOFs.

Figure S1. Structures of Zr-BDC-NH$_2$-SO$_4$ (a) and MOF-808-SO$_4$ (b). Color code: C, black gray; O, red; H, white; S, yellow; N, ultramarine blue; Zr, cyan.

2. Elemental analysis of Zr-BDC-NH$_2$-SO$_4$.

Table S1. Elemental analysis of Zr-BDC-NH$_2$-SO$_4$.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21.16</td>
<td>2.31</td>
<td>2.78</td>
<td>5.98</td>
</tr>
</tbody>
</table>

3. TGA plots of Zr-BDC-NH$_2$-SO$_4$.

Figure S2. TGA spectra of Zr-BDC-NH$_2$-SO$_4$. 

Adsorption kinetics data fitting was carried out using the two models follows:

Pseudo-first-order model: \( \ln(q_e - q_t) = \ln q_e - k_1 t \)  \hspace{1cm} (S1)

Pseudo-second-order model: \( \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \)  \hspace{1cm} (S2)

where \( q_e \) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \( q_t \) (mg g\(^{-1}\)) is the adsorption capacity at time \( t \) (min), \( k_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first-order model and \( k_2 \) (g min\(^{-1}\) mg\(^{-1}\)) is the rate constant of the pseudo-second-order model.

![Figure S3](image)

**Figure S3.** Pseudo-first-order model (a) and pseudo-second-order model (b) linearized plots of the adsorption of barium on Zr-BDC-NH\(_2\)-SO\(_4\).

**Table S2.** Kinetic parameters of the adsorption of barium on Zr-BDC-NH\(_2\)-SO\(_4\).

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first-order model</th>
<th>pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>2.609</td>
<td>7.282</td>
</tr>
<tr>
<td>( k_1 ) (min(^{-1}))</td>
<td>0.014</td>
<td>0.021</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.959</td>
<td>0.999</td>
</tr>
</tbody>
</table>

5. Adsorption isotherm data fitting.

Adsorption isotherms data fitting was carried out using the two models follows:

The Langmuir equation: \( \frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \)  \hspace{1cm} (S3)
The Freundlich equation: 
\[ \ln q_e = \ln k_F + \frac{1}{n} \ln c_e \]  

(S4)

where \( c_e \) (mg L\(^{-1}\)) is the equilibrium concentration, \( q_e \) (mg g\(^{-1}\)) is the amount adsorbed on the adsorbent at equilibrium, \( q_m \) (mg g\(^{-1}\)) is the adsorption capacity for Langmuir isotherms, \( k_L \) is the Langmuir constant, \( k_F \) is the Freundlich constant and \( n \) is an empirical parameter.

**Figure S4.** Langmuir isotherm model (a) and Freundlich isotherms model (b) linearized plots of the adsorption of barium on Zr-BDC-NH\(_2\)-SO\(_4\).

**Table S3.** Adsorption isotherm parameters of the adsorption of barium on Zr-BDC-NH\(_2\)-SO\(_4\).

<table>
<thead>
<tr>
<th></th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m ) (mg g(^{-1}))</td>
<td>181.8</td>
<td>k(_F) (mg g(^{-1}))</td>
</tr>
<tr>
<td>( k_L ) (L mg(^{-1}))</td>
<td>0.08122</td>
<td>n</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99875</td>
<td>( R^2 )</td>
</tr>
</tbody>
</table>

![Barium removal efficiency](image)

**Figure S5.** Removal efficiency for barium of Zr-BDC-NH$_2$-SO$_4$ and Na$_2$SO$_4$, initial concentration= 10 mg L$^{-1}$.

7. SEM image of Zr-BDC-NH$_2$-SO$_4$ after Ba$^{2+}$ adsorption.

![SEM image](image)

**Figure S6.** SEM image of Zr-BDC-NH$_2$-SO$_4$ after Ba$^{2+}$ adsorption.
8. $\text{N}_2$ adsorption-desorption isotherms of Zr-BDC-NH$_2$-SO$_4$ before and after gamma irradiated.

![Graph showing adsorption-desorption isotherms](image)

**Figure S7.** $\text{N}_2$ adsorption-desorption isotherms of Zr-BDC-NH$_2$-SO$_4$ before and after gamma irradiated.

9. XRD pattern of Zr-BDC-NH$_2$-SO$_4$ after soaking in HCl solution.

![XRD pattern graph](image)

**Figure S8.** XRD pattern of Zr-BDC-NH$_2$-SO$_4$ after soaking in HCl solution (pH=1).
10. Zeta potential of Zr-BDC-NH$_2$-SO$_4$ before and after soaked in barium solution.

**Table S4.** Zeta potential of samples at natural pH.

<table>
<thead>
<tr>
<th></th>
<th>Before adsorption</th>
<th>After adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential</td>
<td>18.3 mV</td>
<td>21.3 mV</td>
</tr>
</tbody>
</table>

11. Element molar ratio in Ba$^{2+}$ loading samples at various temperatures.

**Table S5.** Element molar ratio in samples after saturated adsorption.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Zr/Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>4.8</td>
</tr>
<tr>
<td>318</td>
<td>4.3</td>
</tr>
<tr>
<td>333</td>
<td>3.2</td>
</tr>
</tbody>
</table>

12. Elemental analysis of Zr-BDC-NH$_2$-SO$_4$ after Ba$^{2+}$ adsorption.

**Table S6.** Elemental analysis of Zr-BDC-NH$_2$-SO$_4$ after Ba$^{2+}$ adsorption.

<table>
<thead>
<tr>
<th>C</th>
<th>N</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.18</td>
<td>1.86</td>
<td>2.27</td>
<td>4.82</td>
</tr>
</tbody>
</table>