UiO-66-(SH)$_2$ as stable, selective and regenerable adsorbent for the removal of mercury from water under environmentally relevant conditions

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TNAV, 06.12.2016

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         dr. Karen Leus
Mercury contamination in a global perspective

Horvat et al., UNEP Minamata Convention, 2011
Research Rationale

Metal-containing waste + Adsorbent = Adsorbent + Metal

Wastewater treatment

Recovered water

Water reuse

Waste

Mercury removal: Adsorption-based technology
Research Rationale

Metal-containing waste + Adsorbent → Wastewater treatment

Recovery of water → Water reuse

Regeneration of adsorbent
Metal organic frameworks (MOFs)

Advantage of MOFs

- High specific surface areas (1000-7000 m$^2$ g$^{-1}$)
- Tunable structural framework: inorganic and organic part
- Versatile applications: gas capture/separations, catalysis, luminescence, biotechnology

Hendrickx et al., Inorg. Chem, 2015, 10701-10710
Synthesis of “isoreticular” MOFs using different metal ions or organic linkers

The “limits” are only in your imagination!

M. Eddaoudi et al., Science, 2002, 469-472
Why develop functionalized MOFs?

MOF synthesis using series of pre-functionalized linkers

Possibility to be chemically tailored to adapt the target application

Deng et al., Science, 2010, 946-850
Research Aim

Evaluate the performance of UiO-66-(SH)$_2$ for mercury removal

- Examine adsorption capacity
- Determine the effects of environmental parameters on adsorption:
  - Contact time
  - pH
  - Interfering ions
  - Performance in wastewater
- Verify regenerability and recyclability
Synthesis and characterization

Solvothermal synthesis

ZrOCl₂ · 8H₂O + DMA, formic acid

Characterizations:
- N₂ sorption
- XRD
- ICP-OES
- HAADF-STEM & EDX

Yee et al., J. Am. Chem. Soc., 2013, 7795-7798
Adsorption Experiments

Maximum adsorption capacity

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{max}$ (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>28.7</td>
</tr>
<tr>
<td>UiO-66-(SH)$_2$</td>
<td>236.4</td>
</tr>
</tbody>
</table>

L/S ratio = 250 mg L$^{-1}$; pH 3-5; 30 rpm; contact time = 24 h

Functionalization improved the adsorption capacity significantly (~8.2 times)

Adsorption isotherm of Hg(II) on UiO-66-(SH)$_2$ fitted on the Langmuir isotherm
Adsorption experiments

Adsorption mechanism

Proposed binding interaction:

- \( SH + Hg^{2+} + 2NO_3^- \rightarrow S^- Hg^+ + HNO_3 \)
- \( SH + HgOH^+ + NO_3^- \rightarrow S^- HgOH + HNO_3 \)

HAADF-STEM image of UiO-66-(SH)$_2$ after adsorption of Hg(II) coupled with EDX maps showing adsorbed Hg (green) on the thiol moieties (red)
Adsorption Kinetics

Intra-particle diffusion model

- Functionalized adsorbent → Fast uptake rates due to increased affinity for Hg(II)

- Equilibrium Hg(II) concentration after 24 hours → Reduced to EU limit for surface water discharges (0.07 µg L⁻¹)

- Diffusion of Hg(II) species → Not diffusion-limited

- Gradual adsorption of Hg(II) species → Rate-limiting step

Initial Hg concentration = 10 µg L⁻¹; L/S ratio = 250 mg L⁻¹; neutral pH; 30 rpm; contact time = 24 hours
Adsorption Experiments

Influence of pH on Hg(II) removal

pH independent at relevant environmental concentration

initial Hg concentration = 10 µg L\(^{-1}\); L/S ratio = 250 mg L\(^{-1}\); neutral pH; 30 rpm; contact time = 24 hours

Influence of potentially interfering ions and adsorption performance in wastewater

No reduction in removal efficiencies
Desorption and regeneration studies

Regeneration cycles

Desorption condition:
1 M HCl + 0.66 M thiourea (pH 0.2), 70 °C, 4 hours

initial Hg concentration = 1 g L\(^{-1}\); L/S ratio = 250 mg L\(^{-1}\)

Excellent regeneration performance

→ Good desorption over successive cycles
→ Excellent chemical stability
Summary and Conclusion

UiO-66-(SH)$_2$

✓ Good adsorbent for the recovery of Hg
✓ Good maximum adsorption capacity
✓ Fast metal uptake
✓ Excellent removal at wide pH range, in the presence of potentially-interfering ions and in Hg-spiked wastewater
✓ Remarkable regenerability and recyclability

Further perspectives:
Column studies
UiO-66-(SH)$_2$ as stable, selective and regenerable adsorbent for the removal of mercury from water under environmentally relevant conditions

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