Supplementary Information

Cyclic Tetra [(Indolyl)-tetramethyl]-diethane-1,2-diamine (CTet) Impregnated Hydrous Zirconium Oxide as a Novel Hybrid Material for Enhanced Removal of Fluoride from Water.

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This file includes the Supplementary information of CTet-HZO Reaction mechanism. Figure S1 to Figure S8, Table S1, S2 and Scheme S1.
Step I:

\[
\text{Ethane-1,2-diamine} \quad \text{CH}_2\text{OH} \quad \text{Formaldehyde}
\]

\[
\text{H}_2\text{N} - \text{HN-C-OH} \quad \text{H}_2
\]

\[-\text{H}_2\text{O}
\]

\[
\text{H}_2\text{N} - \text{NH-CH}_2 \quad \text{H}_2\text{N} - \text{HN-CH}_2
\]

(a) 

(b)

Resonance Structure

Step II:

\[
1H-\text{Indole} \quad \text{CH}_2\text{-NH} \quad \text{NH}_2
\]

\[
\text{H} \quad \text{CH}_2\text{-NH} \quad \text{NH}_2
\]

\[
\text{H} \quad \text{CH}_2\text{-NH} \quad \text{NH}_2
\]

\[
\text{N}^1-(1H-\text{Indol-3-ylmethyl})-\text{ethane-1,2-diamine}
\]

Intermediate of Mannich Base
Step III:

\[ N^1-(1H-\text{Indol}-3-\text{ylmethyl})-\text{ethane}-1,2\text{-diamine} \]

\[ \text{Mannich Base} \]

\[ \xrightarrow{\text{Weak Acid}} \]

\[ \xrightarrow{-H^+} \]

\[ N^1-[(1H-\text{Indol}-2-\text{yl})-(1H-\text{indol}-3-\text{yl})-\text{methyl}]\text{-ethane}-1,2\text{-diamine} \]

\[ 2,3\text{-Dimer of mannich Base} \]
Step IV:

\[
\text{NH} \quad \text{NH}_2 \quad \text{NH} \quad \text{NH}_2
\]

\[
\text{HC} \quad \text{NH} \quad \text{NH} \quad \text{NH}_2
\]

\[
(\text{2,3-Dimer of Mannich Base})
\]

\[
\text{HCHO (Acetic Acid) Reflux for 2 hrs}
\]

\[
\text{NH}_2
\]

\[
(\text{CTet-HZO})
\]

Scheme S1: Reaction mechanism of CTet-HZO hybrid material.
Figure S1: Far IR spectra of CTet-HZO in Cl⁻ form (I-1) and fluoride sorbed
CTet-HZO (I-2).
Figure S2. EDX spectra of (a) hydrous zirconium oxide (b) CTet-HZO and (c) Fluoride sorbed CTet-HZO.
Figure S3. Differential thermal scanning (DSC) curve for CTet-HZO material.
Figure S4. Effect of pH on the removal of fluoride using HZO.
Figure S5. Effect of contact time on the % uptake of fluoride using CTet-HZO.
(Concentration 20 mgL⁻¹; pH 3.5; adsorbent dose 0.15g).
Figure S6. Effect of contact time for removal of fluoride using HZO.
Figure S7. Effect of adsorbent dose on the fluoride uptake using CTet-HZO. (Conc.; 20 mg/L, Temp.; 308 K, pH 3.5).
Figure S8. Kinetic plots. (a) Pseudo first order kinetic model (b) pseudo second order kinetic model.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>Total hardness as CaCO$_3$ (mgL$^{-1}$)</td>
<td>123-415</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>245-548</td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.84-3.62</td>
</tr>
<tr>
<td>Cl$^-$ (mg/L)</td>
<td>55-260</td>
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<tr>
<td>NO$_3^-$ (mg/L)</td>
<td>10-120</td>
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<tr>
<td>SO$_4^{2-}$ (mg/L)</td>
<td>&lt;180</td>
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<tr>
<td>Na$^+$ (mg/L)</td>
<td>28.9-37.4</td>
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<tr>
<td>K$^+$ (mg/L)</td>
<td>1.6-24.8</td>
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<td>Total iron as Fe (mg/L)</td>
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<tr>
<td>Turbidity</td>
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<tr>
<td>pH</td>
<td>6.5-8.2</td>
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<tr>
<td>Conductivity</td>
<td>510-2110</td>
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Table S2. Basic composition of fluoride containing groundwater (GW-3) and acidic effluent from metal finishing industry.

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<th>Species (mg L⁻¹)</th>
<th>Groundwater</th>
<th>Acidic effluent</th>
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<tr>
<td>F⁻</td>
<td>3.6</td>
<td>4.2</td>
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<tr>
<td>Cl⁻</td>
<td>80.1</td>
<td>72.1</td>
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<tr>
<td>SO₄²⁻</td>
<td>64.4</td>
<td>56.2</td>
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<tr>
<td>Alkalinity (as HCO₃⁻)</td>
<td>158.2</td>
<td>0</td>
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<tr>
<td>NO₃⁻</td>
<td>21.0</td>
<td>15.4</td>
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<tr>
<td>Total P</td>
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<td>&lt;0.06</td>
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<tr>
<td>Na⁺</td>
<td>210</td>
<td>108</td>
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<tr>
<td>K⁺</td>
<td>7.2</td>
<td>2.08</td>
</tr>
<tr>
<td>Total Hardness (as CaCO₃)</td>
<td>350</td>
<td>298</td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
<td>4.1</td>
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