Electronic supporting information

Phosphorus adsorption by a modified polyampholyte-diatomaceous earth material containing imidazole and carboxylic acid moieties: batch and dynamic studies.†

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**ESI 1.** Final pH vs initial pH of the polyampholyte – DE mixture.

**ESI 2.** FTIR assignments for the FT-IR spectra depicted in Figure 2

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{\text{CH}} )</td>
<td>1275,1370</td>
<td>1275,1370</td>
<td>1275,1343, 1400</td>
<td>1275,1343, 1400</td>
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<tr>
<td>C-O-C</td>
<td>1077</td>
<td>1077</td>
<td>1077</td>
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<tr>
<td>( \nu_{\text{C=C}} ) and ( \nu_{\text{C=N}} )</td>
<td>628, 721, 838, 921</td>
<td>628, 721, 838, 921</td>
<td>628, 721, 838, 921</td>
<td>628, 721, 838, 921</td>
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<tr>
<td>( \nu_{\text{Si-O-Si}} ) (asymmetric stretching in plane)</td>
<td>1450,1560,1638</td>
<td>1450,1560,1638</td>
<td>1450,1560,1638</td>
<td>1450,1560,1638</td>
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<tr>
<td>( \nu_{\text{Si-OH}} )</td>
<td>791</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Si-O</td>
<td>615</td>
<td></td>
<td></td>
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<tr>
<td>Al-O stretching</td>
<td>1715</td>
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<td></td>
</tr>
<tr>
<td>( \nu_{\text{C=O}} )</td>
<td>1560</td>
<td>1715</td>
<td>1715</td>
<td>1715</td>
<td></td>
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<tr>
<td>( \nu_{\text{-CO2-}} )</td>
<td>1560</td>
<td>1715</td>
<td>1715</td>
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<td></td>
</tr>
</tbody>
</table>

**A:** DE, **B:** polyampholyte, **C:** polyampholyte - DE mixture, **D:** polyampholyte - DE mixture after exposure to a P solution at pH 5 and **E:** polyampholyte - DE mixture after exposure to a P solution at pH 7
**ESI 3.** FT-Raman spectra of A: DE, B: polyampholyte, C: polyampholyte – DE mixture.

**ESI 4.** Raman assignments for the Raman spectra depicted in Figure 3

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{\text{CH}} )</td>
<td>2957 - 2887</td>
<td>2957 - 2887</td>
<td>2957 - 2887</td>
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<tr>
<td>C-O-C</td>
<td>1027</td>
<td>1027</td>
<td></td>
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<tr>
<td>( \nu_{\text{C=C}} ) and ( \nu_{\text{C=N}} )</td>
<td>1109 - 1080</td>
<td>1109 - 1080</td>
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<td>Amorphous Si-O bonds</td>
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<td>406</td>
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<tr>
<td>( \nu_{\text{C=O}} )</td>
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<td>1604</td>
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<tr>
<td>( \nu_{\text{C=C}} )</td>
<td>1003-851-753-631</td>
<td>1003-851-753-631</td>
<td>1003-851-753-631</td>
</tr>
<tr>
<td>( \nu_{\text{C=C}} )</td>
<td>1109</td>
<td>1109</td>
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<tr>
<td>Hetero ring</td>
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<td></td>
</tr>
<tr>
<td>( \text{CH}_2 )</td>
<td>1428-1456</td>
<td>1428-1456</td>
<td></td>
</tr>
</tbody>
</table>

**A:** DE  **B:** Polyampholyte  **C:** Polyampholyte – DE. \( \nu \), stretching
ESI 5 FT-IR spectra of A: polyampholyte - DE mixture exposed at 25 °C, B: polyampholyte - DE mixture exposed at 37 °C and C: polyampholyte - DE mixture exposed at 40 °C.

ESI 6. Adsorption capacity vs pH
Isotherm adsorption models

Langmuir and Freundlich models have been widely applied to the adjustment of biosorption equilibrium data. The former assumes that a sorbate interacts homogeneously, at homogeneous sorption sites, until a monolayer is formed in the sorbent surface. On the other hand, Freundlich model have proved to describe better the adjustment of sorbents with heterogeneous adsorption sites and dissimilar interactions.\textsuperscript{31} Langmuir and Freundlich adsorption isotherms can be expressed using equations (1) and (2) respectively.\textsuperscript{32}

\[ q_{eq} = \frac{q_m \cdot K_a \cdot C_{eq}}{1 + K_a \cdot C_{eq}} \]  

(1)

\[ q_{eq} = k \cdot C_{eq}^n \]  

(2)

where \( K_a \) is the adsorption equilibrium constant (L/mg), \( q_m \) is the maximum adsorption capacity (mg/g) and \( k \) and \( n \) are arbitrary parameters. The dimension of \( k \) depends on the value of \( n \).

The non-linear Sips isotherm equation predicts a monolayer sorption capacity characteristic of the Langmuir isotherm at high sorbate concentrations.\textsuperscript{33} On the other hand, at low sorbate concentrations it exhibits a departure from Henry’s law such as Freundlich isotherm. It can be represented as:

\[ q_{eq} = \frac{q_m (a_s C_C^n)}{a_s C_C^n + s} \]  

If the value of \( n_s \) is equal to 1 then this expression turns to be a Langmuir equation, where \( a_s \) is the adsorption equilibrium constant. Alternatively, as either \( C \) or \( a_s \) approaches 0, this isotherm reduces to the Freundlich isotherm.

The Redlich-Peterson isotherm (R-P) incorporates features of both the Langmuir and Freundlich equations: at low concentrations the R-P isotherm approximates to Henry’s law and at high concentrations its behaviour approaches that of the Freundlich isotherm.\textsuperscript{33}

\[ q_c = \frac{K_r C}{1 + a_R C_C^n} \]

When the value of \( n_R \) is equal to 1, the above equation is reduced to the Langmuir Model with their heterogeneity parameters (\( n_s \) and \( n_R \)) close to a value of 1, while it reduced to a Freundlich isotherm in case the value of \( a_R C_C^n \) is much bigger than 1. The ratio of \( K_R/a_R \) indicates the adsorption capacity.

Dynamic adsorption model
Thomas model

The Thomas model is another one frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming the second-order reversible reaction kinetics and the Langmuir isotherm. Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small. The Thomas model is given by Equation 3

\[
\frac{C_t}{C_0} = \frac{1}{e^{\frac{k_{Th}q_0m}{Q} - (C_tQ^0)}}
\]

where \(k_{Th}\) is the Thomas rate constant, \(m\) is the mass of adsorbent in the column, \(Q\) is the flow rate, \(q_0\) is the adsorption capacity of the column.