Supplemental Material

Cotransport of Pesticide Acetamiprid and Silica Nanoparticles in Biochar-Amended Sand Porous Media

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**Calculation of DLVO Interaction Energies**

The surface element integration technique (Bhattacharjee and Elimelech, 1997) was used to calculate DLVO interaction energies between a 20 nm silica NP and a planar collector surface in Figure S6 of Supplementary Material. The Cartesian coordinate system was employed. The $xy$ plane of the coordinate system is oriented superposing the flat surface and the $z$ axis passes through the NP center and faces away from the NP. The NP surface was discretized into small area elements ($dS$). The total interaction energy ($U$) was calculated as the sum of the differential interaction energy ($E$) between each area element $dS$ and the corresponding surface element $dA$ (i.e., the projected area of $dS$ on the planar surface):

$$U(H) = \sum S E(h) n \cdot k dS$$

$$= \sum_{A} \left( E \left( H + R - \sqrt{R^2 - (x^2 + y^2)} \right) - E \left( H + R + \sqrt{R^2 - (x^2 + y^2)} \right) \right) dA$$  \hspace{1cm} (S1)$$

where $H$ is minimum separation distance between the NP and planar surface, $h$ is local separation distance between element $dS$ and $dA$, $n$ is unit outward normal to particle surface, $k$ is unit vector along the positive $z$-direction, $S$ is total surface area of the nanoparticle, $A$ is total projected area of the NP on the planar surface, $R$ is NP radius. The value of $E(h)$ is calculated by adding van der Waals (VDW) attraction, the double layer (DL) interaction, and the Born (BR) repulsion [i.e.,

$$E(h) = E_{VDW}(h) + E_{DL}(h) + E_{BR}(h)$$. The expressions derived by Hamaker (1937), Gregory (1975), and Oliveira (1997) were adopted to calculate $E_{VDW}$, $E_{DL}$, and $E_{BR}$ respectively, which were given in Table S2 of Supplementary Material. The values of Hamaker constant were taken as $6.3 \times 10^{-21} \text{ J}$ (Wang et al., 2012) and $8.8 \times 10^{-21} \text{ J}$
(Zhang et al., 2010) for the silica-water-quartz and silica-water-biochar systems, respectively. The minimum separation distance was taken as 0.158 nm in the BR expression (Hoek and Agarwal, 2006).

**Desorption of acetamiprid from biochar surfaces**

To testify whether acetamiprid can be irreversibly retained in biochar, 0.2 ml of acetamiprid solution with a concentration of 1000 ppm was thoroughly mixed with 2 g of biochar to allow the acetamiprid to sorb on biochar surfaces. Then 5 ml of acetonitrile was added to withdraw the adsorbed acetamiprid from biochar surfaces. We found that all adsorbed acetamiprid was desorbed from the biochar surfaces, indicating that irreversible sorption did not occur.

**Isotherm sorption of acetamiprid by silica NPs**

Sorption experiments were carrier out by agitating 50 mg of silica NPs with 100 ml of acetamiprid solution at 160 rpm in a rotary shaker. Five acetamiprid concentrations were considered: 4, 5, 10, 20, and 50 ppm. After 24 h of shaking, 1.5 ml of sample was taken from the shaker and the acetamiprid solution was separated from the adsorbent by centrifugation at 12500 rpm for 10 min. The supernatant was filtrated through 0.22 μm membrane and the concentration of the acetamiprid was determined by the HPLC.
References


Table S1. Zeta potentials of silica NPs, sand, and biochar, and diameter of the silica NPs in solutions at pH 7.

<table>
<thead>
<tr>
<th>IS (mM)</th>
<th>electrolyte</th>
<th>zeta potential (mV)</th>
<th>diameter of silica NPs (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>silica NPs</td>
<td>sand</td>
</tr>
<tr>
<td>0.1</td>
<td>DI water</td>
<td>-42.3</td>
<td>-45.2</td>
</tr>
<tr>
<td>10</td>
<td>NaCl</td>
<td>-37.3</td>
<td>-32.8</td>
</tr>
<tr>
<td>200</td>
<td>NaCl</td>
<td>-23.6</td>
<td>-15.7</td>
</tr>
<tr>
<td>1</td>
<td>CaCl$_2$</td>
<td>-21.1</td>
<td>-32.6</td>
</tr>
<tr>
<td>10</td>
<td>CaCl$_2$</td>
<td>-6.4</td>
<td>-10.5</td>
</tr>
</tbody>
</table>
Table S2. Expressions for calculating $E_{\text{VDW}}$, $E_{\text{DL}}$, and $E_{\text{BR}}$ differential interaction energies. $A_H$ is the Hamaker constant, $h$ is the separation distance between a surface element on a silica NP surface and the collector surface, $\varepsilon_0$ is the dielectric permittivity in vacuum ($8.85 \times 10^{-12}$ F/m), $\varepsilon$ is the relative dielectric permittivity of solvent (78.5), $\kappa$ is the inverse Debye screening length, $\nu$ is the charge number, $e$ is the electronic charge ($1.6 \times 10^{-19}$ C), $\psi_1$ and $\psi_2$ are the surface potentials of silica NP and collector, respectively, and $H_0$ is minimum separation distance between the silica NP and collector (0.158 nm).

<table>
<thead>
<tr>
<th>type of interaction</th>
<th>expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDW</td>
<td>$E_{\text{VDW}}(h) = -\frac{A_H}{12\pi h^2}$</td>
</tr>
<tr>
<td>DL</td>
<td>$E_{\text{DL}}(h) = 32\varepsilon\varepsilon_0\kappa \tanh\left(\frac{ve\psi_1}{4kT}\right) \tanh\left(\frac{ve\psi_2}{4kT}\right) \left(\frac{kT}{ve}\right)^2 \exp\left(-\kappa h\right)$</td>
</tr>
<tr>
<td>BR</td>
<td>$E_{\text{BR}}(h) = -\frac{A_H H_0^6}{48\pi h^8}$</td>
</tr>
</tbody>
</table>
Figure S1. Chemical structure of acetamiprid ((E)-N-[(6-chloro-3-pyridyl) methyl]-N’-cyano-N-methyl-acetamidine).
Figure S2. Measured and fitted BTCs for the acetamiprid from (a) pure or (b) biochar-amended sand columns in 10 mM or 200 mM NaCl solution at pH 6.4. The modeled parameter values were given in Table 1.
Figure S3. SEM images of fresh (a) sand and (b) biochar.
Figure S4. SEM images to illustrate the attachment of silica NPs on (a) sand and (b) biochar surfaces in 10 mM CaCl$_2$. 
Figure S5. SEM-EDX analysis result for (a) pristine biochar and (b) biochar that have interacted with silica NPs in 10 mM CaCl₂.
Figure S6. Interaction of a spherical NP with a planar surface. $H$ is minimum separation distance between the NP and the collector surfaces, $dS$ is differential area element on the NP surface, $dA$ is the projected area of $dS$ on the collector surface, $h$ is local distance between $dS$ and $dA$, $n$ is unit outward normal to the NP surface, $k$ is unit vector normal along the positive $z$-direction.
Figure S7. Re-plotted BTCs of Figures 3 and 4 on a semi-log scale for the silica NPs from (1) pure and (2) biochar-amended sand columns in (a) NaCl and (b) CaCl\textsubscript{2} solutions with different ISs.
Figure S8. Re-plotted BTCs of Figures 3 and 4 for the silica NPs from (1) pure and (2) biochar-amended sand columns in (a) NaCl and (b) CaCl$_2$ solutions with different ISs to highlight the transport of silica NPs in phase 2.
Figure S9. Sorption of acetamiprid on biochar surfaces.
Figure S10. Measured and fitted BTCs for the acetamiprid from biochar-amended sand columns in 10 mM NaCl at pH 6.4 (a) with or (b) without pretreatment of the columns with acetamiprid solutions.
Figure S11. Attached silica NPs in biochar-amended sand in (a) NaCl and (b) CaCl2 at different ISs with (black) and without (white) acetamiprid copresent.