Supporting Information

Mussel-Inspired Synthesis of Polydopamine-Functionalized Calcium Carbonate as Reusable Adsorbents for Heavy Metal Ions

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1. Reagents

Waste shells of ostracodan were collected from the local markets and were washed, sun dried. Dopamine was purchased from Sigma-Aldrich. All other reagents were of analytical grade. All solutions were prepared using ultrapure water (18.3 MΩ·cm) from the Millipore Milli-Q system.

2. Preparation of samples

Waste shells of ostracodan were calcined in the atmosphere at different temperatures to remove the organics. Using simple thermal calcination in air, the chitin and protein organic components in the shells can be removed to form pure CaCO₃. Then pure CaCO₃ powers were dipped into the 5 mM dopamine buffer solution (Tris-HCl, pH=8.5). After deposition for 6 h, CaCO₃ powers modified with dopamine (PDA-CaCO₃) were rinsed by deionized water and freeze drying.

3. Materials characterization

Scanning electron microscopy (SEM) images were acquired on a Scanning Electron Microscope (S-4800 Hitachi, Japan) with a 8~10 mm working distance and 10 kV accelerating voltage. Specific surface of the samples were measured on Specific Surface Tester (ASAP 2020, Micromeritics Instrument, America). Infrared transmission spectra of the samples were performed on Fourier Transform Infrared Spectrometer (Nicolet 6700, Thermo Fisher Scientific, America). X-ray photoelectron spectroscopy (XPS) of the samples were measured using a X-ray Photoelectron Spectroscopy (Al K-Alpha, Thermo Fisher Scientific, America). Sample chamber pressure was 5×10⁻⁹ torr. X-ray power was 72 W and the diameter was 50 μm. Zeta potential of was measured using Zeta Potential Analyzer (Zetasizer Nano, Malvern, UK). The concentration of metal ions was determined by Graphite Furnace Atomic Absorption Spectrometer (Thermo M, Thermo Fisher Scientific, America).

4. Adsorption equilibrium experiments

Batch adsorption experiments were carried out at room temperature to investigate the adsorption behaviors of Pb(II) and Cd(II). Typically, 10 mg PDA-CaCO₃ or pure
CaCO₃ was placed into 100 mL aqueous solutions containing one of the pollutants with different concentrations in a flask and was shaken in a thermostatic reciprocating shaker for 24 h to reach adsorption equilibrium. After adsorption, the free-standing PDA-CaCO₃ or pure CaCO₃ was directly removed from the solution by centrifugal separation (1000 r/min, 5 min). The concentrations of the heavy metals ions remaining in the solution were measured by atomic absorption spectroscopy. The amount of the heavy metal ions at equilibrium qₑ (mg/g) on the adsorbent samples were calculated according the following equation:

\[ qₑ = \frac{(C₀ - Cₑ)V}{W} \]  

Where \( C₀ \) and \( Cₑ \) represent the initial and equilibrium concentrations (mg g⁻¹), respectively, where \( V \) is the volume of the solutions (mL), and \( W \) is the amount of the adsorbents (mg).

The adsorption capacities of the two adsorbents progressively increased with increasing concentrations of metals ions, and finally reached the saturation states (Figure 6). These adsorption data were fitted into the Langmuir isotherm models (2) with the equations given as following:

\[ qₑ = \frac{qₘₐₓ K_L Cₑ}{1 + K_L Cₑ} \]  

Where \( qₑ \) is the amount (mg g⁻¹) of metal ions adsorbed at equilibrium, \( Cₑ \) is the equilibrium concentration (mg L⁻¹) of metal ions, \( K_L \) and \( qₘₐₓ \) (maximum adsorption capacity) are the Langmuir constants of adsorption.

In order to study the influence of pH on the removal efficiency, HCl solution was used to adjust and control the pH of the initial heavy metals solution. HCl solution (100 mL, 1 mM) was used as desorption agent for Pd(II) and Cd(II) to regenerate the adsorbents of PDA-CaCO₃ or pure CaCO₃ after shaken for 2 h.

5. Adsorption kinetic experiments

The adsorption kinetic experiments were identical to those of isotherm experiments. The aqueous samples were taken to preset time intervals and the
concentrations of heavy metal ions were similarly measured. The amount of adsorption at time \( t \), \( q_t \) (mg/g), was calculated by:

\[
q_t = (C_0 - C_t)V/W
\]  

(3)

Where \( C_0 \) and \( C_t \) (mg/L) are the liquid phase concentrations of heavy metal ions at initial and any time \( t \), respectively, where \( V \) is the volume of the solutions (mL), and \( W \) is the amount of the adsorbents (mg).

The pseudofirst order (3) and pseudosecond order (4) kinetic models were employed to fit the experimental data according to the equations as following:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(4)

\[
t/q_t = 1/k_2 q_e^2 + t/q_e
\]  

(5)

Where \( q_e \) and \( q_t \) are the capacities (mg g\(^{-1}\)) of metal ions adsorbed at equilibrium and time \( t \) (min), \( k_1 \) is the rate constant of pseudofirst order model (min\(^{-1}\)), and \( k_2 \) is the rate constant of the pseudosecond order model of adsorption (g mg\(^{-1}\) min\(^{-1}\)).
Fig. S1 Nitrogen gas adsorption and desorption isotherms of pure CaCO$_3$(a) and PDA-CaCO$_3$(b).
Fig. S2 IR of pure CaCO$_3$ and PDA- CaCO$_3$.
Fig. S3 XPS spectra of pure CaCO$_3$ and PDA-CaCO$_3$. 
Fig. S4 Zeta-potentials of pure CaCO$_3$ and DPA-CaCO$_3$ under different pH values.
Fig. S5 XPS spectra of Pb 4f(a) and Cd 3d(b) after their adsorption on PDA-CaCO$_3$. 
Fig. S6 TEM images of PDA-$\text{CaCO}_3$ after adsorption-desorption for the first time (a) and for the tenth time (b).
7. Table S1

Table S1 Comparison of the maximum adsorption capacities of various adsorbents for the heavy metal ions of Pb(II) and Cd(II).

<table>
<thead>
<tr>
<th>Absorbents</th>
<th>Metal Ions</th>
<th>( r^2 )</th>
<th>( q_e ) (mg g(^{-1}))</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( r^2 )</th>
<th>( q_e ) (mg g(^{-1}))</th>
<th>( k_1 ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDA-CaCO(_3)</td>
<td>Pb(II)</td>
<td>0.9577</td>
<td>265.43</td>
<td>0.058</td>
<td>0.9960</td>
<td>282.65</td>
<td>0.41×10(^{-3})</td>
</tr>
<tr>
<td>PDA-CaCO(_3)</td>
<td>Cd(II)</td>
<td>0.9468</td>
<td>122.46</td>
<td>0.032</td>
<td>0.9955</td>
<td>136.52</td>
<td>0.34×10(^{-3})</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>Pb(II)</td>
<td>0.9573</td>
<td>56.67</td>
<td>0.021</td>
<td>0.9973</td>
<td>65.68</td>
<td>0.18×10(^{-3})</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>Cd(II)</td>
<td>0.9431</td>
<td>26.45</td>
<td>0.012</td>
<td>0.9967</td>
<td>30.26</td>
<td>0.12×10(^{-3})</td>
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</tbody>
</table>