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Synthesis of CaO/Fe₃O₄ magnetic composite for the removal of Pb(II) and Co(II) from synthetic wastewater

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Kinetic study

In this study, pseudo-first-order and pseudo-second-order kinetic models were employed to predict the kinetic rate of Pb\(^{2+}\) and Co\(^{2+}\) adsorption. The linear form of the pseudo-first-order is shown in Eq. (S-1):\(^1\)

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

(S-1)

where \(k_1\) is the pseudo-first-order rate constant of the equation (min\(^{-1}\)), \(q_e\) and \(q_t\) are the amounts of lead and cobalt ions adsorbed on adsorbent at equilibrium and time \(t\), respectively (mg g\(^{-1}\)).\(^1\)\(^-\)4\(^\)

By plotting of \(\ln(q_e - q_t)\) versus \(t\), the adsorption rate constant, \(k_1\) and \(q_e\) for Pb\(^{2+}\) and Co\(^{2+}\) ions were calculated (Fig. S-3). The linear equation of the pseudo-second-order model is expressed in Eq. (S-2):

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

(S-2)

where \(k_2\) is the pseudo-second-order rate constant of the equation (g mg\(^{-1}\)min\(^{-1}\)), and \(q_e\) and \(k_2\) calculated by plot of \(t/q_t\) versus \(t\) (Fig. S-3).\(^1\)\(^\)2

For adjusting the laboratory data with kinetic models the correlation coefficient \((R^2)\) was used.
Fig. S-3. The adsorption kinetic curves related to: a) pseudo-first order and b) pseudo-second order model for the adsorption of Pb$^{2+}$ and Co$^{2+}$ at various contact time.

**Isotherm study**

The adsorption isotherm model describes the interaction between the amount of metal ions adsorbed on adsorbent and metal ion concentration at equilibrium. The experimental data from the study of Pb$^{2+}$ and Co$^{2+}$ adsorption by CaO/Fe$_3$O$_4$ are analyzed using Langmuir and Freundlich equations. The Langmuir isotherm assumes that the adsorbent surface is homogeneous, the number of active sites on the adsorbent is constant, and the adsorption process is reversible.

The Langmuir isotherm is expressed by:

$$q_e = \frac{1}{K_L q_m} + \frac{c_e}{q_m}$$

where $q_e$ / mg g$^{-1}$, $q_m$ / mg g$^{-1}$, $c_e$ / mg L$^{-1}$ and $k_L$ / L mg$^{-1}$ are metal uptake capacity at equilibrium state, maximum uptake capacity, concentration of adsorbate at equilibrium state and Langmuir constant, respectively.
Feasibility and shape of a Langmuir isotherm are calculated by following equation of equilibrium parameter:

\[ R_L = \frac{1}{1 + K_L c_e} \]  

(S-4)

where \( c_e \) is the initial metal ion concentration in the solution (mg L\(^{-1}\)) and \( K_L \) is Langmuir constant. The values of \( R_L \) indicate conditions and qualities of adsorption isotherm model.\(^{28}\) If \( R_L > 1, \) \( R_L = 1, \) \( 0 < R_L < 1 \) and \( R_L = 0 \), the adsorption process is unsuitable, linear, suitable and irreversible, respectively.\(^2\)

The Freundlich isotherm assumes that the adsorbent surface is heterogeneous and the active sites on the adsorbent have different energy.\(^1\) The linear form of the Freundlich can be depicted as below:

\[ \ln q_e = \ln k_f + \frac{1}{n} \ln c_e \]  

(S-5)

where \( k_f / \text{mg g}^{-1} \) and \( 1/n \) are Freundlich constants which are determined from Fig. S-4. The \( n \) represents an adsorption deviation from linearity. If \( n = 1 \), it

Fig. S-4. The adsorption isotherm curves related to a) Langmuir and b) Freundlich model for adsorption of Pb\(^{2+}\) and Co\(^{2+}\) on CaO/Fe\(_3\)O\(_4\) magnetic composite.
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shows that the adsorption process is linear, \( n < 1 \) indicating chemical adsorption process and \( n > 1 \) shows that the adsorption of metal ions on CaO/Fe\(_3\)O\(_4\) is a physical process at studied conditions.\(^1\) In Table S-I, the calculated parameters related to Langmuir and Freundlich equations are listed.

TABLE S-I. Isotherm model parameters for the adsorption of Pb\(^{2+}\) and Co\(^{2+}\) using CaO/Fe\(_3\)O\(_4\) magnetic particles

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter</th>
<th>Pb(^{2+})</th>
<th>Co(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>( n )</td>
<td>1.0424</td>
<td>1.0424</td>
</tr>
<tr>
<td></td>
<td>( K_f ) / mg g(^{-1}) L(^{-1}) min(^{1/n})</td>
<td>0.523</td>
<td>0.510</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9999</td>
<td>0.9998</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( q_m ) / mg g(^{-1})</td>
<td>227.27</td>
<td>217.39</td>
</tr>
<tr>
<td></td>
<td>( K_L ) / L mg(^{-1})</td>
<td>0.00214</td>
<td>0.00219</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.979</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>( R_L )</td>
<td>0.002-0.085</td>
<td>0.002-0.083</td>
</tr>
</tbody>
</table>

The values of \( R_L \) in different initial concentrations of metal ions are shown in Fig. S-5. The values of \( R_L \) in initial ion concentration 5–50 mg/L of lead and cobalt ions were between 0 to 1. It indicates that CaO/Fe\(_3\)O\(_4\) adsorbent is a suitable adsorbent to adsorption Pb\(^{2+}\) and Co\(^{2+}\) from aqueous solution.

Fig. S-5. Plot of adsorption intensity (\( R_L \)) versus initial metal concentration (\( c_0\), mg/L) for the determination of \( R_L \) values.

**Thermodynamic study**

The values of the thermodynamic parameters of the adsorption, such as the Gibbs energy change, \( \Delta G \) / kJ mol\(^{-1}\), enthalpy change, \( \Delta H \) / kJ mol\(^{-1}\), and the entropy change, \( \Delta S \) / J mol\(^{-1}\) K\(^{-1}\), change were analyzed. These parameters were estimated by Eqs. (S-6)–(S-8):

\[
\Delta G = -RT \ln K_c
\]  
(S-6)
\[ \frac{\Delta S}{R} - \frac{\Delta H}{RT} = \ln K_c = -\frac{\Delta G}{RT} \]  
(S-7)

\[ \Delta G = \Delta H - T\Delta S \]  
(S-8)

where \( K_c \) is the equilibrium constant, \( T \) is the absolute temperature (K) and \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), respectively.\(^1\)\(^,\)\(^4\) The thermodynamic parameters for the adsorption of lead and cobalt ions are listed in Table S-II.

Also, \( \ln K_c \) versus \( T^{-1} \) for the determination of thermodynamic parameters is shown in Fig. S-6.

**TABLE S-II. Thermodynamic parameters for the adsorption of Pb\(^{2+}\) and Co\(^{2+}\) on CaO/Fe\(^{3+}\)O\(_4\) magnetic particles**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( \Delta G / ) kJ mol(^{-1})</th>
<th>( \Delta H / ) kJ mol(^{-1})</th>
<th>( \Delta S / ) kJ mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>84.58</td>
<td>-33.90</td>
<td>-33.90</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>60.08</td>
<td>-24.94</td>
<td>-24.94</td>
</tr>
</tbody>
</table>

Fig. S-6. Plot of \( \ln K_c \) vs. \( T^{-1} \) for the determination of thermodynamic parameters for the adsorption of Pb\(^{2+}\) and Co\(^{2+}\) onto CaO/Fe\(^{3+}\)O\(_4\) magnetic composite.

**REFERENCES**