Removal of Arsenite from Water by Ce-Al-Fe Trimetal Oxide Adsorbent: Kinetics, Isotherms, and Thermodynamics

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Ce-Al-Fe trimetal oxide adsorbent was prepared. The morphology characteristics of the new adsorbent were analysed by the transmission electron microscope (SEM) method. The SEM results implied its ability in the adsorption of As (III). To verify the analyses, bench-scale experiments were performed for the removal of As(III) from water. In the experiments of adsorption, As(III) adsorption capacity of the trimetal oxide adsorbent was presented significantly higher than activated aluminium oxide and activated carbon. As (III) adsorption kinetics resembled pseudo-second-order adsorption mode. When initial As (III) concentration was 3, 8, and 10 mg L⁻¹, the maximum adsorption capacity achieved was 1.48, 3.73, and 5.12 mg g⁻¹, respectively. In addition, the experimental adsorption data were described well by the Freundlich adsorption isotherm model at 20, 30, and 40 °C. The enthalpy change (ΔS), the standard free energy (ΔG), and entropy change (ΔH) indicated that the nature of As (III) adsorption was exothermic and spontaneous with increasing randomness on the interface of solid and liquid. And the adsorption mechanism can be interpreted as chemisorption with As (III) multilayer coverage formation on the adsorbent surface.

1. Introduction

Arsenic contamination of water, resulting from both natural processes and anthropogenic activities [1–3], has a great harm to human health and other living organisms due to the arsenic carcinogenicity and toxicity [4, 5]. In natural water, inorganic arsenic predominantly exists in two forms of As (III) and As (V) [6]. Compared with the latter, the former presented 25–60 times higher toxicity and is more mobile [7]. As (III) exists widely in sediment, surface water, and groundwater. Due to the existence of the reducing condition, the concentrated As (III) is released from sediment into water and this happened almost constantly [8–10]. Therefore, As (III) removal is becoming one of the hot topics in pollution incident emergency treatment and drinking water treatment researches.

Several technologies including adsorption [11], coagulation/precipitation [12], and ion exchange [13] have been used to remove As (III) from polluted surface water and water resources. When pH varied from weakly acidic to weakly alkaline in natural water, the hydrolyzed species of As (III) existed mainly in the form of nonionic H₂AsO₄⁻ [8, 14]. For the removal of As (III), coagulation/precipitation technology is generally not effective at natural pH [15] because of As (III) uncharged form. Adsorption is considered as one of the most promising methods for As (III) removal due to high removal efficiency without yielding by-products. The key component of adsorption processes is the adsorbents that are expected to have high adsorption capacities toward As [16]. Some investigations already reported that the composite oxides adsorbents based on iron [17], titanium [18], manganese and alumina oxide [19, 20], Fe-Ni binary oxide [21], and Fe-Cu binary oxide [22] are effective for As removal. However, these adsorbents have relatively low adsorption capacity for As, and iron oxide-based adsorbent has received great attention due to the binding affinity for inorganic As and relatively low production costs [23–25].

In recent years, hydrous cerium (Ce) oxide has been developed as a new adsorbent for arsenate [26], fluoride [27],
and phosphate removal [28] with high adsorption capacity [29, 30]. But the high cost of Ce limits its use. Therefore, a low cost adsorbent with high adsorption capacities of arsenic is desirable. Recently, many researchers successfully developed cerium-based bimetal oxide adsorbents, such as Ce-Ti [31, 32] and Fe-Ce [33]. The results indicated a remarkably higher adsorption capacity of As (V) than many reported adsorbents. However, the removal efficiency for As (III) is less than 58%.

In this work, a new Ce-Al-Fe trimetal oxide adsorbent, prepared by mixing iron, cerium, and aluminum oxides, was applied to remove As (III) from water to increase the adsorption capacity. Its adsorption capacity of As (III) was evaluated in comparison with commercial materials. The batch adsorption behaviors are including adsorption kinetics, isotherms, and thermodynamics.

2. Experiments

2.1. Adsorbent Preparation. At room temperature, AlCl₃·6H₂O, Ce(SO₄)₂·4H₂O (analytical grade, Binzhou Kun Bao Chemical Co., Ltd., China), and FeCl₃·6H₂O were dissolved with deionized water and the Al/Fe/Ce molar ratio of water is 2:1:0.2, 1:2:0.2, 2:1:0.5, 1:2:0.5, 2:1:1.5, and 1:2:1.5. At 200 rpm, the pH was adjusted to 10 by 6 M NaOH solution. After aging of 12 h, the precipitates were collected and washed using distilled water. Finally, the precipitates were dried at 70°C for 12 h.

2.2. Adsorption Experiments for As (III). The experiment water was prepared by diluting stock solution containing 1000 mg·As L⁻¹, which was prepared by dissolving NaAsO₂ in deionized water. 2 g L⁻¹ adsorbent granule was added into the water of 100 mL. The mixture was shaken at 150 rpm and 25°C for a long time. Then, the samples were taken and filtered through a membrane of 0.45-µm, and the residual arsenite was determined on an Atomic Absorption Spectrophotometer (ABS-990, Beijing Purkinje General Instrument, China). In the investigation of adsorption kinetics, the initial arsenic concentrations were 3, 8, and 10 mg L⁻¹. When As (III) initial concentration varied from 1 to 50 mg·L⁻¹, the adsorption isotherms were studied. All experiments were conducted in three times, and all data were the average value.

The adsorption capacity was presented in

\[ q_e = \frac{(C_0 - C_e) \cdot V}{m}, \]

\[ q_t = \frac{(C_0 - C_t) \cdot V}{m}, \]  

where \( q_t \) (mg·g⁻¹) and \( q_e \) (mg·g⁻¹) are the adsorption capacity at time \( t \) (min) and at equilibrium and \( C_e \) (mg·L⁻¹) and \( C_0 \) (mg·L⁻¹) are equilibrium and initial As (III) concentration. At time \( t \), the concentrations of As (III) (mg·L⁻¹) are \( C_t \). And \( m \) (g) is the adsorbent granule weight, and \( V \) (L) is the water volume.

3. Results and Discussion

3.1. Morphology of Ce-Al-Fe Trimetal Oxide Adsorbent. The SEM image of Ce-Al-Fe trimetal oxide adsorbents is shown in Figure 1. Tiny uniformly distributed pores were present on the surface of Ce-Al-Fe trimetal oxide adsorbent. For adsorption, a large surface area was supported by this porous structure with great potential for the removal of As (III).

3.2. Comparison with Other Commercial Adsorbents. Figure 2 illustrates As (III) adsorption capacity onto the adsorbent with different Al/Fe/Ce molar ratio (2:1:0.2, 1:2:0.2, 2:1:0.5, 1:2:0.5, 2:1:1.5, and 1:2:1.5) and the capacities were compared with commercial adsorbents.

The adsorption capacities of As (III) on activated aluminium oxide (AA) and activated carbon (AC) were 3.75 and 1.84 mg·g⁻¹, respectively. And the responding As (III) removal percent was 37.5% and 18.4%. Regardless of the Al/Fe/Ce molar ratio, Ce-Al-Fe trimetal oxide adsorbents...
had higher adsorption capacity than that of AA and AC. Particularly, the adsorption capacity of As (III) on Ce-Al-Fe adsorbent with Al/Fe/Ce = 2:1:0.5 was up to 8.18 mg g\(^{-1}\). AA had a higher adsorption capacity than that of AC.

The adsorption capacity was improved as Ce/(Al + Fe) molar ratio increases from 0.2/3 to 0.5/3, while it decreased as Ce/(Al + Fe) molar ratio further increases to 1.5/3. The maximum adsorption capacity (8.18 mg g\(^{-1}\)) was achieved at Al/Fe/Ce molar ratio of 2:1:0.5.

### 3.3. Adsorption Kinetics

At initial As (III) concentration of 3, 8, and 10 mg L\(^{-1}\), As (III) adsorption kinetics on the adsorbent were shown in Figure 3.

The adsorption capacity presented the same trend of variability at different initial concentration. It can be found that Ce-Al-Fe trimetal oxide adsorbent had a high adsorption rate in the first 7 h and the adsorption equilibrium was reached at 24 h. When contact time increased from 24 h to 48 h, the adsorption capacity for As (III) showed no significant change. The equilibrium adsorption capacities of As (III) were 1.225, 3.273, and 4.097 mg g\(^{-1}\) when initial As (III) concentrations were 3, 8, and 10 mg L\(^{-1}\), respectively.

To further understand the rate-controlling step and adsorption behavior of Ce-Al-Fe adsorbent for As (III), the adsorption kinetic data were fitted by the pseudo-second-order and pseudo-first-order models, which are usually expressed as [34]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},
\]

\[
\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{2}
\]

where \(q_e\) (mg g\(^{-1}\)) and \(q_t\) (mg g\(^{-1}\)) are As (III) adsorption capacity at equilibrium and time \(t\) (h), \(k_1\) (h\(^{-1}\)), and \(k_2\) (g mg\(^{-1}\) h\(^{-1}\)) are the rate constants. The adsorption rate \(v_0 = \frac{d q_t}{d t}\) can be considered to be the rate as \(t\) approaches 0.

For the adsorption process, the rate limiting step was studied by the intraparticle diffusion model, which is expressed in [35]

\[
q_t = k_w t^{1/2} + C, \tag{3}
\]

where \(C\) is the intercept and \(k_w\) (mg g\(^{-1}\) h\(^{1/2}\)) is the rate constant.

The fitted curves of the three models and the fitting parameters are shown in Figure 4 and Table 1, respectively.

### Table 1: The kinetic parameters for the pseudo-first-order, pseudo-second-order, and intraparticle diffusion model at different initial As (III) concentrations and 25°C.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>3 mg L(^{-1})</th>
<th>8 mg L(^{-1})</th>
<th>10 mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(q_{e,exp}) (mg g(^{-1}))</td>
<td>1.225</td>
<td>3.273</td>
<td>4.097</td>
<td></td>
</tr>
<tr>
<td>(k_1) (h(^{-1}))</td>
<td>0.048</td>
<td>0.038</td>
<td>0.031</td>
<td></td>
</tr>
<tr>
<td>(q_{e,cal}) (mg g(^{-1}))</td>
<td>0.905</td>
<td>1.300</td>
<td>1.440</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.929</td>
<td>0.767</td>
<td>0.810</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_2) (g mg(^{-1}) h(^{-1}))</td>
<td>0.503</td>
<td>0.150</td>
<td>0.171</td>
<td></td>
</tr>
<tr>
<td>(q_{e,cal}) (mg g(^{-1}))</td>
<td>1.269</td>
<td>3.393</td>
<td>4.214</td>
<td></td>
</tr>
<tr>
<td>(v_0) (mg g(^{-1}) h(^{-1}))</td>
<td>0.810</td>
<td>1.732</td>
<td>3.042</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_w) (mg g(^{-1}) h(^{1/2}))</td>
<td>0.526</td>
<td>1.332</td>
<td>2.088</td>
<td></td>
</tr>
<tr>
<td>(C_1)</td>
<td>0.085</td>
<td>0.198</td>
<td>0.358</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>(K_w) (mg g(^{-1}) h(^{1/2}))</td>
<td>0.330</td>
<td>0.811</td>
<td>0.829</td>
<td></td>
</tr>
<tr>
<td>(C_2)</td>
<td>0.228</td>
<td>0.580</td>
<td>1.391</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.885</td>
<td>0.948</td>
<td>0.969</td>
<td></td>
</tr>
<tr>
<td>(K_w) (mg g(^{-1}) h(^{1/2}))</td>
<td>0.036</td>
<td>0.109</td>
<td>0.112</td>
<td></td>
</tr>
<tr>
<td>(C_3)</td>
<td>0.992</td>
<td>2.346</td>
<td>3.356</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.882</td>
<td>0.936</td>
<td>0.881</td>
<td></td>
</tr>
</tbody>
</table>
The high correlation coefficient ($R^2$) and the good agreement between the theoretical adsorption capacity ($q_{e,cal}$) and the experimental adsorption capacity ($q_{e,exp}$) indicated that As (III) adsorption on Ce-Al-Fe trimetal oxide adsorbent was fitted well by the pseudo-second-order model. This suggested that the adsorption process might be chemisorption [36–38]. The adsorption rate ($v_0$) increased with initial increasing As (III) concentration due to increasing driving force.

As shown in Figure 4(c), the intraparticle diffusion kinetic curves presented three linear stages, indicating that the intraparticle diffusion may be one of the rate-controlling steps. The fitted values of $C$ values were not zero, giving an indication of the boundary layer thickness. At different As (III) concentration, the diffusion rate constant presents order of $k_1 > k_2 > k_3$. This result suggested that As (III) was adsorbed quickly onto the exterior surface of Ce-Al-Fe trimetal oxide adsorbent at first. Afterwards, the adsorption on the external surface reached equilibrium and As (III) entered into the adsorbent pores slowly. Then, on the interior surface, As (III) adsorption reached equilibrium.

3.4. Adsorption Isotherm. At 20, 30, and 40°C, As (III) adsorption isotherm was investigated with As (III) concentration of 1, 10, 30, 40, and 50 mg·L$^{-1}$. Figure 5 presented curves of the adsorption capacity ($q_e$, mg·g$^{-1}$) versus As (III) equilibrium concentration ($C_e$, mg·L$^{-1}$). The adsorption capacity increased as temperature and As (III) concentrations increase.
Table 2: The parameters of Langmuir and Freundlich models at different temperatures.

<table>
<thead>
<tr>
<th>Adsorption isotherm models</th>
<th>Parameters</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_{\text{max}} ) (mg g(^{-1}))</td>
<td>44.385</td>
<td>41.580</td>
<td>32.787</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>( b ) (L mg(^{-1}))</td>
<td>0.051</td>
<td>0.060</td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.840</td>
<td>0.856</td>
<td>0.840</td>
</tr>
<tr>
<td></td>
<td>( K_F ) (mg(^{1-1/n}) L(^{1/n}) g(^{-1}))</td>
<td>2.005</td>
<td>2.186</td>
<td>2.427</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.121</td>
<td>1.115</td>
<td>1.128</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.999</td>
<td>0.996</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table 3: The thermodynamic parameters for the adsorption of As (III) on the adsorbent.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
<th>Thermodynamic parameters</th>
<th>( \Delta H ) (kJ mol(^{-1}))</th>
<th>( \Delta S ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>(-1.695 \pm 0.24)</td>
<td>( \Delta G )</td>
<td>7.278 \pm 0.45</td>
<td>30.580 \pm 2.03</td>
</tr>
<tr>
<td>303.15</td>
<td>(-1.970 \pm 0.32)</td>
<td>( \Delta H )</td>
<td>11.15</td>
<td>1.128</td>
</tr>
<tr>
<td>313.15</td>
<td>(-2.308 \pm 0.19)</td>
<td>( \Delta S )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5: Adsorption isotherm of As (III) on Ce-Al-Fe trimetal oxide adsorbent at different temperature (pH = 7.0, initial concentration of As (III) = 1, 10, 30, 40, and 50 mg L\(^{-1}\), and adsorbent dosage = 0.2 g L\(^{-1}\)).

3.5. Adsorption Thermodynamics. To evaluate the nature of the adsorption, three thermodynamic parameters including entropy change (\( \Delta S \), kJ mol\(^{-1}\)), enthalpy change (\( \Delta H \), kJ mol\(^{-1}\)), and standard free energy (\( \Delta G \), kJ mol\(^{-1}\)), which present the inherent energetic changes, were expressed in [41, 42]

\[
\Delta G = RT \ln K_F = \Delta H - \Delta S, 
\]

where \( K_F \) (mg\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)) was the Freundlich adsorption equilibrium constant and \( R \) (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) (K) are the gas constant and the absolute temperature in Kevin. \( \Delta H \) and \( \Delta S \) can be determined from the intercept and slope of the linear plot of \( \ln K_F \) versus \( 1/T \). Table 3 listed the thermodynamic parameters.

\[
\ln K_F = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},
\]

\( \Delta G \) decreased as temperature increases, which indicated that adsorption process of As (III) is more favorable at higher temperatures [43]. \( \Delta G \) values were negative, which suggested the thermodynamic favorability and spontaneity of As (III) adsorption. The positive \( \Delta H \) values confirmed
an endothermic nature of As (III) adsorption on Ce-Al-Fe trimetal oxide adsorbent. In addition, the positive $\Delta S$ values indicated As (III) adsorption process at the solid/solution interface presented an increasing randomness [44].

4. Conclusions

Ce-Al-Fe adsorbent with tiny uniformly distributed pores has been developed for As (III) removal.

At initial As (III) concentration of 3, 8, and 10 mg L$^{-1}$, the maximum adsorption capacities of As (III) were 1.48, 3.73, and 5.12 mg g$^{-1}$, respectively. Kinetics of fitting by the pseudo-second-order model with $R^2$ higher than 0.998 suggested that the chemisorption was rate-determining process. The adsorption data of Ce-Al-Fe adsorbent can be expressed well by the Freundlich isotherm with $R^2$ greater than 0.996. The negative $\Delta G$, positive $\Delta S$, and positive $\Delta H$ suggested that As (III) adsorption nature was exothermic, spontaneous, and increasing randomness on the interface of water and adsorbent.

The adsorption mechanism can be interpreted as chemisorption with multilayer adsorption of As (III) on the adsorbent surface.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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