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<td>Goh, Kok Hui; Lim, Teik-Thye; Dong, Zhili</td>
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Removal of arsenate from aqueous solution by nanocrystalline Mg/Al layered double hydroxide: sorption characteristics, prospects, and challenges

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Abstract

Removal of arsenate (As(V)) from aqueous solution using both nanocrystalline and coprecipitated Mg/Al layered double hydroxides (LDHs) was examined under different sorption/desorption conditions. The surface area, pore volume, and pore size of the nanocrystalline LDH were significantly higher than those of the coprecipitated LDH, thus resulting in a higher As(V) sorption maximum than the coprecipitated LDH. The calculated activation energy ($E_a$) value was 24.7 kJ/mol, suggesting the occurrence of anion exchange process for As(V) removal by the nanocrystalline LDH. The predominance of anion exchange process was further supported by the investigation of ionic strength effect, and XRD and FTIR analyses. The effect of aqueous matrix on As(V) sorption by the nanocrystalline LDH was found to increase in the order of nitrate < silica < sulfate < carbonate < phosphate. Regeneration study showed that a secondary sorption mechanism might occur concurrently for the As(V) sorption by nanocrystalline LDH besides the predominant anion exchange process. Prospects and challenges for practical application of the nanocrystalline LDH were also discussed in the latter part of this study.

Key words | arsenate, layered double hydroxide, nanocrystalline, sorption
INTRODUCTION

Arsenic (As) is ubiquitous in the environment and its existence threatens the health of plants, wildlife, and ultimately humans. Long-term exposure to As can cause skin lesions, hyperkeratosis, and various types of cancers. Sources of As contamination include both natural and anthropogenic. Countries like India, Bangladesh, and Vietnam have already been affected by high As levels in drinking water where well waters may contain several thousand ppb of As. The potential of groundwater and surface water contamination by As has therefore generated public concerns, demanding swift and proper treatment of As-contaminated waters.

Among the various treatment processes for As removal, sorption method is promising because it can be used in small scale treatment plants and household systems, is easy to operate, may provide largely sludge-free operation, and may have a regeneration capability. In the recent decades, various types of layered double hydroxides (LDHs) have been intensively investigated for their ability in removing As oxyanion and other toxic oxyanions (Goh et al. 2008), mainly due to their high anion exchange capacity, large surface area, good thermal stability, and ability to reconstruct the calcined LDH to its original layered structure through the “memory effect” (Cavani et al. 1991).

Majority of the LDHs examined for As sorption were synthesised by the commonly used coprecipitation method (Lazaridis et al. 2002; Gillman 2006; Goh et al. 2008) that produced large LDHs with aggregated crystallites. LDHs prepared by this conventional method offer a limited control over the morphology, particle size, surface area, and pore architecture (Géraud et al. 2005), and these parameters strongly influence their sorption performances.

On the other hand, nanocrystalline materials show numerous unique characteristics such as high specificity and large surface area, suggesting that they can potentially be used for water treatment applications. Nanocrystalline LDH has been successfully used in catalytic and fire-retardant applications (Zhang et al. 2004). However, almost no study has reported on the removal of environmentally significant oxyanions such as As(V) using nanocrystalline LDH. In addition, understanding the As(V) sorption characteristics by nanocrystalline LDH will allow the accurate prediction of the sorptive properties of this sorbent and lead to the optimisation of the sorption process. This study aimed to (1) evaluate the efficiency of nanocrystalline LDH for As(V) removal and compare its sorption characteristics with that of the LDH prepared by conventional coprecipitation method, (2) elucidate the As(V) reactions through sorption/desorption experiments and spectroscopic studies, and (3) identify the prospects and challenges facing the application of nanocrystalline LDH for oxyanions removal.
MATERIALS AND METHODS

Materials

All stock solutions were prepared using analytical grade chemicals and Milli-Q ultrapure water (18.2 MΩcm). The ultrapure water was decarbonated (DW) before use. The stock solution of As(V) was prepared from Na₃HAsO₄·7H₂O (Sigma, 99.4%). Mg(NO₃)₂·6H₂O (99%) was obtained from HiMedia Laboratories whereas Al(NO₃)₃·9H₂O (98%) was from Fluka Chemika. Anion solutions were prepared from NaNO₃ (Merck, 99.5%), Na₂SiO₃·9H₂O (Hayashi Pure Chemical), Na₂SO₄ (BDH, 99%), Na₂CO₃ (Merck, 99.5%), and NaH₂PO₄·2H₂O (Merck).

LDH preparation and characterisation

Coprecipitated Mg/Al LDH was prepared by adding a mixture of salt solution into NaOH solution followed by aging, separation, washing, and drying. The nanocrystalline Mg/Al LDH was prepared by fast coprecipitation followed by the hydrothermal treatment method. A solution containing 16mmol Mg(NO₃)₂·6H₂O and 8mmol Al(NO₃)₃·9H₂O was rapidly added into NaOH solution within 5s under vigorous stirring and nitrogen purging. The LDH precipitate was then separated with centrifugation, washed several times with DW, and subsequently dispersed in 40 mL of DW. This aqueous suspension was then added into a Teflon-lined stainless steel autoclave (Parr Instrument), hydrothermally treated under autogenous pressure at 80°C for 16 h, and finally freeze-dried.

The QuantaChrome Autosorb-1 Analyzer was used to determine the BET surface area and porosity characteristics of the LDH samples. X-ray diffraction patterns for the LDHs were obtained using Bruker AXS (D8 Advance) X-ray diffractometer (XRD). Fourier transform infrared spectroscopy (FTIR) spectra of the LDHs were recorded with a Perkin Elmer 2000 FTIR spectrometer. The transmission electron micrograph (TEM) images of the LDHs were obtained by JEOL JSM-2010F.

Batch sorption experiments

The As(V) solutions used for the sorption experiments were prepared by dilution from the stock solutions with DW. NaNO₃ was used as the background electrolyte. Unless otherwise stated, all the experiments were carried out in batch mode at 25°C and at pH 9.5.

Sorption isotherms and kinetics

The equilibrium isotherms were determined by reacting LDH with As(V) concentrations in the range of 0.013–0.667 mM. The LDH and As(V) solution were reacted in the centrifuge tubes and agitated for 24 h to enable complete equilibrium. The suspension in each tube was then
centrifuged, filtered, and the concentrations of As(V) were determined by ICP-OES (Perkin Elmer Optima 2000). The kinetic experiment was performed by adding LDH into 0.2mM As(V) solution in a covered container. The suspension was stirred for 6 h, and at selected time intervals, 4 mL samples were extracted, filtered, and the As(V) concentrations were determined. Selected LDH solids remaining at the end of the experiment were characterised by XRD and FTIR.

Effect of aqueous matrix

To investigate the effect of aqueous matrix on the sorption of As(V) by nanocrystalline LDH, anions such as nitrate, silica, sulfate, carbonate, and phosphate (with concentrations ranging from 0.4–40 mM) were added into a solution containing 0.4mM As(V). The suspensions were agitated for 24 h, separated, and the concentrations of As(V) were determined.

pH and ionic strength effects on As(V) sorption

As(V) sorption was investigated as a function of ionic strength (0.005 M and 0.5 M NaNO₃) and pH values ranging from 5 to 11. The LDH dose was 0.4g/L while the concentration of As(V) was 0.4 mM. LDH samples were hydrated in 0.005 M and 0.5 M NaNO₃ solutions for a few days prior to the pH adjustment using either HNO₃ or NaOH. The LDH suspensions were equilibrated for a few hours after pH adjustment. An appropriate amount of As(V) stock solution was subsequently added to attain an initial concentration of 0.4 mM. The suspensions were reacted for 4 h with intermittent pH monitoring. The equilibrium pH was measured and the suspensions were separated and the As(V) concentrations were analysed.

Regeneration study

Several regenerating solutions were tested for As(V) desorption from the nanocrystalline LDH. The exhausted nanocrystalline LDH was immersed in the regenerating solution and reacted for several hours. The amount of As(V) desorbed was determined through analysis of As(V) released into the solution whereas the amount of As(V) sorbed by the regenerated nanocrystalline LDH was determined through analysis of As(V) removed from the solution. For the best-performing regeneration method, four cycles of As(V) sorption-desorption were performed.

RESULTS AND DISCUSSION

Characteristics of coprecipitated and nanocrystalline LDHs

The pore size of nanocrystalline LDH fell in the meso size range, showing its mesoporous behavior (Table 1). Indeed N₂ adsorption-desorption isotherm of nanocrystalline LDH was of type IV, confirming that the material was typical of mesoporous materials. The surface area, pore
volume, and pore size of the nanocrystalline LDH was significantly higher than the coprecipitated LDH, probably due to the effective dispersion of agglomerated LDH aggregates into individual LDH crystallites during the hydrothermal treatment of nanocrystalline LDH.

According to Inorganic Crystal Structure Database (ICSD), the major phase of coprecipitated and nanocrystalline LDHs was hydrotalcite-like compound (ICSD 81963), which matched well with the expected pattern (Figure 1(a)). Though nanocrystalline LDH exhibited a poorer crystallinity compared to coprecipitated LDH, it however showed smaller crystallite size and higher interlayer spacing as indicated by the smaller c value (Table 1). Figure 1(b) shows characteristic FTIR spectra of layered materials for both LDHs. A broad band at 3,479–3,599 cm\(^{-1}\) for both LDHs indicated the OH stretching vibration of hydrogen-bonded groups in the brucite-like sheets and water in the interlayer space, a peak at \(-1,637\) cm\(^{-1}\) showed the water bending vibrations of the interlayer water, whereas a slightly strong peak at \(-1,384\) cm\(^{-1}\) revealed the intercalation of NO\(_3^-\) in the interlayer space for both LDHs. Platelet structure with a uniform size (40–100 nm) of the nanocrystalline LDH was clearly seen in the TEM image (figure not shown). High resolution TEM (HRTEM) image of the nanocrystalline LDH showed that it consisted of nanocrystalline grains of 5 to 6 nm diameters.

**Sorption isotherms and kinetics**

Two commonly used isothermal models, i.e. Freundlich and Langmuir models, were used to fit the experimental data. Langmuir isotherm was more appropriate to describe the sorption of As(V) on both coprecipitated and nanocrystalline LDHs based on the coefficient of determination \(R^2\) and Chi-square statistical test \(\chi^2\) (Table 2). The Langmuir sorption maximum for As(V) on the nanocrystalline LDH was 114 cmol/kg (equivalent to 85 mg/g), about 5 times higher than that of the coprecipitated LDH. Both the values of constant \(K_L\) (Langmuir) and \(n\) (Freundlich) for the nanocrystalline LDH were greater than the values of the coprecipitated LDH, reflecting its superior affinity for As(V). The higher As(V) sorption capacity of the nanocrystalline LDH could be attributable to its higher surface area, better porosity characteristics, and nanocrystalline property.

Four different kinetic models were used to fit the experimental time-dependent sorption data, namely pseudo-first order and pseudo-second order models, modified multiplex model, and Elovich model. The modified multiplex model was used since the sorption of As(V) on the nanocrystalline LDH might be a two-step process whereas the Elovich model has been successfully used for fitting experiment data of ion exchange process (Cheung et al. 2000). The modified multiplex model (Lv et al. 2007) is based on a combination of the pseudo-first order and pseudo-second order models:

\[
\frac{dq_t}{dt} = k_{m1}(q_e - q_t) + k_{m2}(q_e - q_t)^2
\] (1)
where $q_t$ (cmol/kg) and $q_e$ (cmol/kg) is the amount of As(V) sorbed at time $t$ and at equilibrium, respectively, and $k_{m1}$ (min\(^{-1}\)) and $k_{m2}$ (g/mg/min) are the rate constants. Elovich equation is given as:

$$q_t = \beta \ln (\alpha \beta) + \beta \ln t$$  \hspace{1cm} (2)

where $\alpha$ and $\beta$ are the Elovich constants. The Elovich constant $\alpha$ is related to the sorption rate while $\beta$ is related to the surface coverage. Elovich model provided the best overall fit for the As(V) sorption kinetics on both LDHs on the basis of the statistical parameters ($R^2 > 0.99$, $x^2 > 0.95$, and $\Delta q < 5$). The As(V) sorption on both LDHs expeditiously increased in the first few minutes after which it approached equilibrium (Figure 2(a)). Figure 2(b) displays the As(V) sorption on the nanocrystalline LDH obtained at different isothermal conditions and the Arrhenius plot. The gradient of this plot is $-(E_a/R)$ and $E_a$ can be calculated according to Arrhenius expression. The $E_a$ value is usually less than 30 kJ/mol for anion exchange-controlled processes (Ho et al. 2000). The calculated $E_a$ value in this study was 24.7 kJ/mol, indicating the occurrence of anion exchange process for As(V) removal by the nanocrystalline LDH.

**Effect of aqueous matrix**

Figure 3 demonstrates the effect of aqueous matrix on the sorption of As(V) by nanocrystalline LDH. These results showed that nitrate almost has no effect on the sorption of As(V) on nanocrystalline LDH up to a concentration of 40 mM. Silica and sulfate have a modest effect, causing about 62 and 72% reductions in As(V) sorption, respectively, when their concentration was 40 mM. Carbonate and phosphate caused the greatest percentage decrease in As(V) sorption among the anions. The higher interfering effect of carbonate and phosphate could be due to their relatively higher ionic potentials. Furthermore, phosphate competed with As(V) for the same sorption sites on the LDH as a result of their structure and chemical similarities.

**Effects of pH and ionic strength**

The effects of pH and ionic strength on As(V) sorption are shown in Figure 4. At the ionic strength of 0.005 M, As(V) sorption decreased gradually with increasing pH at pH about 5.1–9.5. However, the sorption decreased drastically at pH > 9.5. The decline of As(V) sorption with increasing pH was owing to the decreasing Coulombic attraction resulting from the decreasing positive charge of nanocrystalline LDH. As(V) sorption appeared to be sensitive to the changes in ionic strength in the investigated pH range (pH 5–11). The percentage of As(V) sorption decreased by 18–48% with increasing ionic strength from 0.005 M to 0.5 M at pH 5–11. Ionic strength effect on sorption is often used as indirect evidence for whether an outer-sphere or
inner-sphere complex forms (Hayes *et al.* 1988). Based on this method, the formation of inner-sphere complexes is not greatly affected by ionic strength whereas the existence of outer-sphere complexes is indicated by the changes in sorption with changing ionic strength owing to the competitive sorption with counter anions. Therefore, our findings suggested that As(V) predominantly formed outer-sphere complexes on the nanocrystalline LDH at pH 5–11, as a result of the predominant anion exchange process (an electrostatic Coulombic interaction). In addition, the increment of the interlayer spacing of As (V)-loaded nanocrystalline LDH (as shown by the increased c value in Table 1) indicated the exchange of larger As(V) (molecular diameter = ~0.5 nm) for interlayer nitrate (molecular diameter = ~0.4 nm). FTIR spectra also provided evidence for the anion exchange process by depicting the weakened band of interlayer nitrate (1,384 cm⁻¹) and the appearance of a new band at 830 cm⁻¹ (corresponding to As-O stretching vibration) after As(V) removal.

### Reusability of LDH

The As(V) desorption behaviours were examined using various types of regenerating solutions, namely 0.05 M and 0.1M NaOH, 1M NaNO₃, 1M Mg(NO₃)₂, a mixture of 1M NaNO₃ and 0.1NaOH, and 0.1M Na₂CO₃. Among these solutions, highest As(V) desorption rate, i.e. ~76%, was attained by desorbing As(V)-loaded nanocrystalline LDH in Na₂CO₃. This was probably due to the higher ionic potential of carbonate ion and the orientation of carbonate with its planes parallel to the principal layers that is more preferred in LDH formation. The results for cyclic regeneration of nanocrystalline LDH with 0.1 M Na₂CO₃ followed by calcination are illustrated in Figure 5. Both desorption and regeneration rates declined gradually with the number of cycles. Dissolution of Mg was relatively high in the initial cycles but progressively decreased to <0.15% in the fourth cycle. Dissolution of Al maintained at <0.1% in each cycle. These findings demonstrated that nanocrystalline LDH has sufficient chemical stability over several sorption-desorption repetitions. However, it is also interesting to note that about 24% of As(V) was not displaceable by Na₂CO₃, suggesting the possible occurrence of a secondary mechanism that might involve irreversible and specific adsorption of As(V) on the surface of nanocrystalline LDH.

### Prospects and challenges for LDH application

Nanocrystalline LDH produced in this study has exhibited excellent affinity for As(V). It can be potentially used for removing trace As(V) and other harmful oxyanions from the surface water and groundwater. However, a few challenges remain to be overcome to make this LDH suitable for commercial scale applications. One important consideration is the mineral stability of the
LDH. Conditioning the LDH in deionised water prior to usage can help to improve its stability (Yang et al. 2006). Powdered LDH sorbents are not suitable to be used in practical water treatment applications. They give rise to problems like high pressure drops, high diffusion resistance, difficult particle separation, and they are usually not amenable to scale-up. Therefore, it may be desirable to fabricate LDH into microspheric or palletised form to mitigate the foregoing problems.

The recent microspherical LDH formed through spray drying may be a good approach to overcome the disadvantages of powdered LDH (Wang et al. 2008). The spray drying involves atomising a solution into an aerosol and subsequently allowing for self-assembly into the spherical form, and it has also been successfully used in the pharmaceutical and food processing industries. Another possible alternative is to disperse the nanocrystalline LDH within a macroporous polymeric host material to form a mixed matrix LDH granule (Figure 6). One such hybrid sorbent, produced by dispersing hydrated ferric oxide (HFO) nanoparticles inside a polymeric anion exchanger, exhibited high affinity for phosphate removal (Blaney et al. 2007). While the LDH granules retain their intrinsic sorption/desorption properties, the polymeric support offers adequate mechanical strength, durability, and favourable hydraulic properties. The microspherical LDHs produced by these methods may be feasible for large scale production and suitable for use in fluidised-bed or fixed-bed columns. For the regenerated LDH, a significant decrease in its sorption capacity within four cycles has been observed. Moreover, the calcination stage between the sorption-desorption cycles may make the process less attractive. Further study is thus necessary to fine-tune the regeneration method. The spent LDH media can be added as filler in concrete products but the leaching properties of the solidified concrete matrix should be carefully assessed.

CONCLUSIONS

Nanocrystalline Mg/Al LDH showed significantly higher As(V) sorption capacity than conventional coprecipitated Mg/Al LDH, probably due to its higher surface area, better porosity characteristics, unique morphology, and nanocrystalline property. Elovich model was appropriate for describing As(V) sorption kinetics on the LDHs. The calculated $E_a$ value obtained in this study, sensitivity of As(V) sorption to the changes in ionic strength, enhanced interlayer spacing, and weakened FTIR band of interlayer nitrate indicated the predominance of anion exchange process for As(V) removal by the nanocrystalline LDH. Na$_2$CO$_3$ was found effective in desorbing As(V) among the regenerating solutions; however, ~24% non-displaceable As(V) suggested the occurrence of a secondary mechanism. A few challenges remain to be overcome to make the nanocrystalline LDH suitable for commercial scale applications. LDH micro-sphere produced by spray drying and mixed matrix LDH granule produced by dispersing nanocrystalline LDHs within a polymeric host material may be suitable for use in fluidised-bed
or fixed-bed systems.

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REFERENCES


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Table.1  Surface area, porosity characteristics, and lattice parameters of the LDHs

Table.2  Freundlich and Langmuir isotherm parameters for As(V) sorption by the LDHs
<table>
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<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>a' (Å)</th>
<th>c' (Å)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coprecipitated LDH</td>
<td>22</td>
<td>0.01</td>
<td>1.4</td>
<td>3.04</td>
<td>22.91</td>
<td>12.1</td>
</tr>
<tr>
<td>Nanocrystalline LDH</td>
<td>127</td>
<td>0.31</td>
<td>8.0</td>
<td>3.04</td>
<td>23.53</td>
<td>5.9</td>
</tr>
<tr>
<td>Nanocrystalline LDH (As(V)-loaded)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>3.04</td>
<td>23.90</td>
<td>9.1</td>
</tr>
</tbody>
</table>

*a = 2 × d(110).
*c = 3 × d(003).
n/a denotes "data not available".
| Sample                | Freundlich | | | | Langmuir | | | |
|-----------------------|------------|--------|---|---|----------------|--------|
|                       | $K_f$      | $n$    | $R^2$ | $x^2$ | $K_L$ (L/cmol) | $q_m$ (cmol/kg) | $R^2$ | $x^2$ |
| Coprecipitated LDH    | 155        | 1.73   | 0.935 | 4.23  | 157            | 21     | 0.985 | 1.45  |
| Nanocrystalline LDH   | 390        | 3.57   | 0.881 | 80.7  | 4,400          | 114    | 0.949 | 11.0  |

Table 2
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Fig.1  (a) XRD patterns of the LDHs, and (b) FTIR spectra of the LDHs.

Fig.2  (a) Time-dependent sorption of As(V) on the LDHs (the inset is the magnified sorption result in the first 15 min) and (b) time-dependent sorption of As(V) on nanocrystalline LDH at different temperatures (the inset is Arrhenius plot); the curve is Elovich model.

Fig.3  Effect of aqueous matrix on the sorption of As(V) by nanocrystalline LDH (time =24h, pH = 9.5, dose = 0.4g/L, As(V) concentration = 0.4 mM).

Fig.4  Ionic strength effect on As(V) sorption by nanocrystalline LDH.

Fig.5  Reusability of nanocrystalline LDH with number of cycles.

Fig.6  Schematic representation of a mixed matrix LDH granule.
Fig. 1
Fig. 2

(a) Coprecipitated LDH  Nanocrystalline LDH

\[ q_t \text{ (cmol/kg)} \]

\[ \text{Time (min)} \]

\[ \text{pH} = 9.5; \text{Dose} = 1 \text{ g/L; As(V) = 0.2 mM; Background = 0.01 M NaNO}_3 \]

(b)  

\[ q_t \text{ (cmol/kg)} \]

\[ \text{Time (min)} \]

\[ \text{pH} = 9.5; \text{Dose} = 0.4 \text{ g/L; As(V) = 0.2 mM; Background = 0.01 M NaNO}_3 \]

\[ R^2 = 0.989 \]

\[ \ln k \text{ vs. } 1/T(\text{K}^{-1}) \]

\[ T = 5^\circ\text{C, 25^\circ\text{C, 45^\circC, 65^\circC}} \]
Fig. 3
Time = 4 h; Dose = 0.4 g/L; As(V) = 0.4 mM

Sorption (%) vs pH

ionic strength = 0.005 M
ionic strength = 0.5 M

Fig. 4
Fig. 5
Fig. 6

Polymeric host material

Nanocrystalline LDH

Mixed matrix LDH granule