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<td>Author(s)</td>
<td>Lim, Teik-Thye; Goh, Kok Hui; Goei, Ronn; Dong, Zhili</td>
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<td><a href="http://hdl.handle.net/10220/9405">http://hdl.handle.net/10220/9405</a></td>
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Mechanistic and thermodynamic studies of oxyanion sorption by various synthetic Mg/Al layered double hydroxides

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ABSTRACT

In this study, Mg/Al layered double hydroxides (LDHs) were investigated for their potential in scavenging several harmful oxyanions from aqueous solution. LDHs could effectively remove oxyanions and the selectivity of LDHs was governed by both the valencies and the ionic radii of the oxyanions. LDHs prepared by the fast coprecipitation with hydrothermal treatment (FCHT) method and sol-gel with solvothermal treatment method (SGST) had higher oxyanion (i.e. arsenate) removal efficiency than those prepared by the conventional routes, owing to their lower carbonate content, higher surface area, larger pore volume, larger pore size, and nanocrystalline characteristic. The sorption of arsenate by FCHT-LDH was found primarily due to anion exchange mechanism and might involve a secondary sorption mechanism. The negative $\Delta G^\circ$ for arsenate sorption confirmed the spontaneity of the removal process. The positive values of $\Delta H^\circ$ and $\Delta S^\circ$ provided further evidence of the anion exchange process in the removal mechanism.

\textit{Key words}: anion exchange, arsenate, layered double hydroxide, oxyanion, sorption
INTRODUCTION

Several harmful inorganic oxyanions like arsenate, borate, chromate, etc. have been encountered in the natural environment, drainage water, and wastewater (Qiu et al. 2000; Mohan & Pittman Jr 2006; Zhang et al. 2007). The source of water containing oxyanions is extensive and can be attributed to both natural and anthropogenic inputs. The occurrence of these oxyanions has raised potential health and regulatory concerns as a result of their toxic and carcinogenic properties. For instance, tens of thousands of people already suffer from symptoms such as skin lesion, hyperkeratosis, liver cancer, etc. due to their exposure to arsenic-contaminated water (Berg et al. 2001). These oxyanions have high solubilities and are usually mobile at most hydrogeological environments. Since oxyanion contamination is a health risk for many countries, therefore there is an urgent need for an effective and economical technique for removal of the oxyanions from water.

Sorbent technologies, which are often appropriate for small systems, can have high oxyanion removal efficiencies and relatively small footprints. Layered double hydroxides (LDHs) have been recently investigated and developed for effective oxyanions removal (Alvarez-Ayuso & Nugteren 2005; Liu et al. 2006; Goh et al. 2008) owing to their interesting properties such as large surface area, high anion exchange capacity (AEC), good thermal stability, and ability to rehydrate a calcined LDH precursor by the structural “memory effect” (Cavani et al. 1991; Li & Duan 2005). LDHs are lamellar mixed hydroxides containing positively charged main layers and the charge is compensated by the anions in the interlayer region. Unlike other oxyanion sorbents, LDH not only can provide binding sites for oxyanions on their external surfaces, but also exchange sites in their interlayer region, and this particular property can potentially enhance the oxyanion sorption capacity.

Though LDH has been explored as a potential sorbent for removing various oxyanions (Goh et al. 2008), the sorption study on emerging deleterious oxyanions such as borate, molybdate, perchlorate, and vanadate remains scarce. Recently, the alternative LDH synthetic routes, i.e. fast coprecipitation with hydrothermal treatment method (FCHT)
and sol-gel method (SG) have been explored with the aim to improve structural and textural properties (Aramendia et al. 2002; Xu et al. 2006; Valente et al. 2007). A few reports have demonstrated that LDHs prepared by FCHT method can produce more stable and homogeneous LDH particles (Xu et al. 2006) whereas SG method can exhibit higher surface area and more uniform pore size distribution (Aramendia et al. 2002; Valente et al. 2007) compared to those obtained by the conventional routes. These unique properties may lead to better oxyanion removal efficiency. The objectives of this study were to (1) investigate the sorption performance of LDHs for various oxyanions; (2) compare the characteristics of arsenate sorption by the LDHs prepared with the alternative routes and the conventional routes; and (3) study the sorption mechanism and thermodynamics.

MATERIALS AND METHODS

Materials

All the chemicals were analytical grade and the stock solutions of arsenate, borate, chromate, molybdate, perchlorate, selenate, and vanadate were prepared with ultrapure water using Na$_2$HAsO$_4$.7H$_2$O (Sigma, 99.4°/o), Na$_2$B$_4$O$_7$.10H$_2$O (Hayashi Pure Chemical, 99°/o), K$_2$CrO$_4$ (Merck, 99.5°/o), Na$_2$MoO$_4$.2H$_2$O (J.T.Baker, 100°/o), KClO$_4$ (BDH, 99°/o), Na$_2$SeO$_4$ (Sigma, 99°/o), and Na$_3$VO$_4$ (Aldrich, 99.9°/o), respectively.

Synthesis and characterization of LDHs

To prepare LDH by the conventional coprecipitation method, Mg(NO$_3$)$_2$.6H$_2$O (HiMedia Laboratories, 99°/o) and Al(NO$_3$)$_3$.9H$_2$O (Fluka Chemika, 98°/o) with Mg$^{2+}$ :Al$^{3+}$ molar ratio of 2:1 were dissolved in decarbonated ultrapure water (DW) and then added dropwise into NaOH solution. The resulting slurry was aged, centrifuged, washed with DW, and dried. The material obtained was denoted as COP-LDH. A part of the COP-LDH was calcined at 500°C for 5 h (denoted as CAL-LDH). The LDH produced by the conventional ion exchange method (denoted as IE-LDH) was purchased from Sinopharm Chemical.
To prepare LDH by fast coprecipitation with hydro-thermal treatment method, a mixed salt solution containing 16 mmol Mg(NO$_3$)$_2$.6H$_2$O and 8 mmol Al(NO$_3$)$_3$.9H$_2$O was rapidly added into NaOH solution under vigorous stirring and nitrogen purging. The LDH precipitate was obtained via several separation and washing with DW, and then dispersed in DW. The suspension was transferred into a Teflon-lined stainless steel autoclave and then placed in oven for hydrothermal treatment at 80°C for 16 h. The final precipitate (denoted as FCHT-LDH) was subsequently dried. In synthesizing LDH using sol-gel method, 30 mmol magnesium ethoxide (Strem Chemical, 98%/o) was dissolved at 80°C under vigorous stirring in ethanol (Fluka, 99%/o) with addition of HCl for complete dissolution. The solution was then added dropwise to 15 mmol aluminium acetylacetonate (Merck, 95%/o) dissolved in ethanol. The mixture was stirred and refluxed at 80°C for 1 h and the pH of the mixture was adjusted to ~10. A gel was thus formed and refluxed for 15 h at the same temperature under continuous stirring (denoted as SGRF-LDH). Part of the gel was solvothermally treated in an autoclave at 100°C for 5 h (denoted as SGST-LDH). After aging, the gel was washed several times with ethanol and then DW, and finally dried. Part of the SGRF-LDH and SGST-LDH was calcined at 500°C for characterization and sorption tests.

The elemental analysis of the LDHs was carried out using ICP-OES of Perkin Elmer Optima 2000 after microwave-assisted digestion. The CHNS/O analyzer (Perkin Elmer 2400 Series II) was used to determine carbon and nitrogen content in the LDHs. The BET surface area and porosity characteristics were determined using Quanta-Chrome Autosorb-1 Analyzer. The composition and phase purity of the LDH samples were analyzed by Bruker AXS (D8 Advance) X-ray diffractometer (XRD). Fourier transform infrared spectroscopy (FTIR) spectra were collected on a Perkin Elmer 2000 FTIR spectrometer. The morphologies of the LDHs were obtained by transmission electron microscopy (TEM, JEOL JSM-2010F).

**Sorption experiments**

The oxyanion solutions used for the sorption experiments were prepared by dilution from the stock solutions with ultrapure water. NaNO$_3$ was used as the background electrolyte.
All the experiments were performed using the batch sorption technique at 25°C and at pH 9.5 (near the natural pH of the LDH suspension), unless otherwise stated.

**Sorption performance of LDHs on various oxyanions**

In this experiment, the sorption efficiencies of FCHT-LDH and IE-LDH on various oxyanions were investigated. The sorption experiment was performed in a single oxyanion system by adding a predetermined dose of LDH into 0.2 mM oxyanion in a 50 mL centrifuge tube. The suspension was reacted for 24 h to allow complete equilibrium. The suspension in each tube was then centrifuged, filtered, and the concentrations of oxyanions were determined by ICP-OES. The maximum sorption capacity \(q_m\) of FCHT-LDH for the oxyanions was also determined.

**Arsenate sorption behavior of various LDHs**

The arsenate sorption behaviors of LDHs prepared by the conventional routes (IE-LDH, COP-LDH, and CAL-LDH) and the alternative routes (FCHT-LDH, SGRF-LDH, and SGST-LDH) were explored. The equilibrium isotherms were determined by reacting LDH with arsenate of concentrations ranging from 0.013 to 0.667 mM. The LDH and oxyanion solutions were agitated for 24 h, subsequently centrifuged, filtered, and the concentrations of arsenate were analyzed. An independent experiment investigating the effect of temperature on arsenate sorption by FCHT-LDH was also carried out. The time-dependent sorption experiment was performed by adding LDH into 0.2mM arsenate 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 arsenate concentrations were determined. Selected solids remaining at the end of the experiment were characterized by XRD and FTIR.

**Anion exchange experiment**

The anion exchange of arsenate for interlayer nitrate of FCHT-LDH was investigated as a function of initial arsenate concentration and reaction time without NaNO\(_3\) addition. The concentrations of arsenate were determined by ICP-OES whereas the concentrations of the released nitrate were analyzed by Ion Chromatograph (IC, Dionex ICS-1000). For
data analysis, LDH-phase concentrations were calculated as the difference in aqueous-phase concentrations before and after anion exchange equilibrium. The nitrate/arsenate anion exchange ratio was calculated by dividing the aqueous-phase concentration of nitrate by the LDH-phase arsenate concentration.

**RESULTS AND DISCUSSION**

**Characterization of the LDHs**

The molar ratios of Mg/Al in the synthesized LDHs were generally in good agreement with the values in the starting salts (Table 1). The CHNS/O analyses indicated the presence of N and C in most LDHs, implying the coexistence of both nitrate and carbonate in the interlayer spaces (except for SG-LDHs). The pore sizes of all the LDHs fall in the meso size range, showing their mesoporous behavior. The surface areas, pore volumes, and pore sizes of FCHT-LDH and SGST-LDH were the highest among the investigated LDHs. This was possibly due to the effective prevention of LDH particle aggregation during hydrothermal or solvothermal treatment.

The XRD patterns of all the LDHs are illustrated in Figure 1(a). A single phase corresponding to hydrotalcite-like compounds (ICSD 81963) can be identified for all the LDHs. FCHT-LDH, SGRF-LDH, and SGST-LDH showed a poorer crystallinity compared to the LDHs prepared by the conventional routes, they however demonstrated smaller crystallite size and higher interlayer spacing (indicated by c value). The peak positions of the FTIR spectra for all the LDHs were close despite very small shifts, implying that the structures of these LDHs were similar (Figure 1(b)). The FTIR spectra of COP-LDH, CAL-LDH, and FCHT-LDH showed a peak at -1,384 cm\(^{-1}\) whereas the spectra of IE-LDH exhibited a slightly strong peak at 1,360 cm\(^{-1}\), showing the presence of nitrate and carbonate, respectively, and these findings consistent with the result of CHNS/O analysis. TEM images (figures not shown) confirmed that the LDHs prepared by the alternative routes, particularly FCHT-LDH and SGST-LDH clearly exhibited the characteristic LDH platelet structure with a uniform size (40–100nm). High resolution TEM (HRTEM) images (figures not shown) of these LDHs showed that they consisted of nanocrystalline grains of 5 to 6 nm diameters.
**Sorption performance of LDHs on various oxyanions**

Figure 2 shows the sorption efficiencies of various oxyanions on FCHT-LDH and IE-LDH. It can be seen that FCHT-LDH can remove oxyanions more effectively and achieved significantly higher removal efficiency than IE-LDH for all the oxyanions, mainly due to its lower carbonate content, higher surface area, larger pore volume, and larger pore size in comparison to IE-LDH. These results showed that almost 100% of trivalent vanadate, divalent arsenate, divalent chromate, divalent molybdate, and divalent selenate was removed by FCHT-LDH whereas monovalent borate and perchlorate sorbed by FCHT-LDH were only about 50% and <10%, respectively. This suggested that oxyanions with higher valence could be readily removed by FCHT-LDH than the lower-valence oxyanions. Among the divalent oxyanions, chromate had the highest sorption capacity, followed by selenate, molybdate, and arsenate. Interestingly, chromate had the smallest ionic radius while arsenate had the largest ionic radius among these oxyanions (Goh et al. 2008), indicating that smaller oxyanion can be better accommodated in LDH. Zhang & Reardon (2003) have reported that the mobility of anions in the LDH interlayer was dependent on the strength of their bonding to the hydroxide layers, which in turn was dependent on ionic radius. Therefore it could be deduced that the selectivity of FCHT-LDH was governed by both the valency and the ionic radius of the oxyanion.

**Conventional routes versus alternative routes**

The equilibrium isotherms for arsenate sorption on various LDHs were examined. Two commonly used isotherm models, Freundlich isotherm and Langmuir isotherm, have been used to fit the experimental data. Langmuir isotherm was found suitable for describing the sorption of arsenate on all the LDHs (Figure 3(a)). The arsenate maximum sorption capacity for LDHs prepared by the alternative routes, especially FCHT-LDH and SGST-LDH was more than 100 cmol/kg, much higher than those prepared by the conventional routes. The higher arsenate sorption capacity on FCHT-LDH and SGST-LDH could be due to their low carbonate content, higher surface area, and better porosity characteristics. In addition, these LDHs are nanocrystalline materials that often show reactivity that is not observed in bulk materials. They have enhanced surface chemical reactivity toward
incoming sorbates, which is attributed to their extremely large surface areas, small crystallite size, unique morphology and porous nature (Jadhav et al. 2005). Arsenate sorption reached an equilibrium within 0.5 h for the LDHs prepared by the conventional routes while sorption rate was slower for the LDHs prepared by the alternative routes (approximately 3 h) (Figure 3(b)). These observations suggested that arsenate sorption on the LDHs prepared by the conventional routes (except for CAL-LDH) was mainly anion exchange. Conversely, arsenate sorption on FCHT-LDH and SG-LDHs may involve anion exchange and surface adsorption.

**Sorption mechanisms**

Figure 4(a) demonstrates the findings of a series of experiments performed at a fixed FCHT-LDH load with increasing initial arsenate concentration. They are presented in an $n$ vs $C_0/m$ plot, which provides a simple manner of characterizing the exchange properties of LDHs (Costantino et al. 2000). The amount of exchanged arsenate was found to increase linearly with $C_0/m$ at low initial concentrations. The slope of 0.996 confirmed that the linear relationship between the exchanged arsenate and initial arsenate concentration. The value of $n_{\text{max}}$, i.e. 114 cmol/kg, was in accordance with the maximum exchange capacity estimated from the stoichiometry of the exchange reaction, thus suggesting that the arsenate sorption by FCHT-LDH was mainly due to an anion exchange mechanism. Figure 4(b) shows that nitrate released steadily with time from FCHT-LDH with simultaneous arsenate sorption. The pH of the system was ~9.5 and HAsO$_2^-$ was the dominant arsenate species. The nitrate/arsenate anion exchange ratio ranged from 2–3 throughout the reaction time. These results further supported the presence of an anion exchange relationship. In addition, it can be seen from Table 1 nd Figure 1(a) that the (003) plane moved to lower 2θ angle from nitrate-LDH ($d$(003) = 7.84 Å) to arsenate-LDH ($d$(003) = 7.97 Å) after FCHT-LDH reacted with arsenate, indicating that a larger anion (i.e. arsenate) had resided in the LDH interlayer region. FTIR spectra provided another evidence for the anion exchange process (Figure 1(b)). After removal of arsenate, the band assigned to interlayer nitrate (1,384 cm$^{-1}$) became weaker and significant As-O vibrations (830 cm$^{-1}$) were observed. It is also worth noting
that ~ 24% of arsenate was not desorbed in an independent desorption study, further suggesting the occurrence of a secondary sorption mechanism.

**Arsenate sorption thermodynamics**

Figure 5 presents the equilibrium sorption isotherms of arsenate at 25, 35, 45, and 55°C. The equilibrium capacity was observed to increase with the increase of temperature, implying the interaction between arsenate and FCHT-LDH was endothermic in nature. Thermodynamic parameters such as Gibbs free energy ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) were calculated using the following equations:

\[
\Delta G^\circ = -RT \ln K_c
\]
\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

where $R$ is universal gas constant, $T$ is temperature (K), and $K_c$ is the thermodynamic equilibrium constant and it can be obtained using the method of Khan & Singh (1987). The negative $\Delta G^\circ$ value (−6.43 kJ/mol) obtained in this study indicated that the arsenate removal was a spontaneous process. The positive value of $\Delta H^\circ$ (3.73 kJ/mol) confirmed the endothermic nature of anion exchange process (Lv et al. 2009). The positive value of $\Delta S^\circ$ (0.03 kJ/mol.K) revealed the increased randomness at the solid/solution interface for the anion exchange between arsenate and FCHT-LDH.

**CONCLUSIONS**

Oxyanions with higher valence and smaller ionic radius were more readily removed by LDH compared to those with lower valence and larger size. LDHs prepared by the alternative routes can generally remove oxyanions more effectively and achieved higher removal efficiencies than those prepared by the conventional routes for all the investigated oxyanions. Among the LDH preparation routes, fast coprecipitation with hydrothermal treatment (FCHT) method appeared to be the most efficient method by producing LDH with the highest arsenate sorption capacity, mainly due to its lower carbonate content, higher surface area and nanocrystalline property. Anion exchange mechanism was found to be the primary reaction that governed the arsenate sorption by
FCHT-LDH and the occurrence of anion exchange process was supported by anion exchange measurements, XRD and FTIR analyses. However, a secondary sorption mechanism might also occur concurrently. The positive value of $\Delta H^0$ in the thermodynamic analysis confirmed the endothermic nature of anion exchange process in the removal mechanism.

ACKNOWLEDGEMENTS

K. H. Goh is grateful to Singapore Millennium Foundation (SMF) and Nanyang Technological University for the provision of financial support during this study.
REFERENCES


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Figure 2 Sorption efficiencies of various oxyanions on FCHT-LDH ($q_m$ of FCHT-LDH for oxyanion is presented in cmol/kg).

Figure 3 (a) Equilibrium isotherms for arsenate on various LDHs and (b) time-dependent sorption of arsenate on various LDHs.

Figure 4 (a) Exchanged arsenate as a function of the initial concentration (no added nitrate) and (b) arsenate remained and nitrate released as a function of reaction time.

Figure 5 Equilibrium isotherms of arsenate by FCHT-LDH at different temperatures ($pH = 9.5$, time = 24 h, dose = 0.4 g/L) and the curves are non-linear regression with Langmuir model.
<table>
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<tr>
<th>Types of LDH</th>
<th>Composition</th>
<th>Structural property</th>
<th>Lattice parameter</th>
<th>Crystal sizea (nm)</th>
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<tbody>
<tr>
<td></td>
<td>Mg²⁺/Al³⁺ molar ratio</td>
<td>C (wt %)</td>
<td>N (wt %)</td>
<td>S² (m²/g)</td>
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<td>IE-LDH</td>
<td>3.1/1</td>
<td>9.2</td>
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<td>1.8</td>
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<td>FCHT-LDH (As(V)-loaded)</td>
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</table>

* BET surface area; † BJH pore volume; ‡ BJH pore size; a = 2 × d(110); c = 3 × d(003); †† Average value calculated from FWHM of peak (003) and (006) using Scherrer Equation; ** Rehydrated LDH; †† Calcined sample; n/a, data not available.
Figure 1
Figure 2
Figure 3
Figure 4

(a) $R^2$ (slope) = 0.996

FGHT-LDH
Time = 24 h
As(V) = 0.013–0.667 mM
$m$ = LDH load = 0.4 g l$^{-1}$
$n$ = As(V) exchanged per gram of LDH
$C_o$ = Initial As(V) concentration

(b) pH = 9.5

FGHT-LDH
- As(V) in solution
- Nitrate released

As(V) concentration (mM)
Nitrate concentration (mM)

Time (min)
Figure 5