



# Controls on arsenate, molybdate, and selenate uptake by hydrotalcite-like layered double hydroxides

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## ABSTRACT

Mill-scale neutralization of sulfatic and carbonic magnesium–aluminum–iron residues enriched with trace metal oxyanions often leads to the formation of mixed oxides, such as hydrotalcite-like layered double hydroxides (HT-LDHs). These compounds exert control on the migration of contaminants via sorption and are thus of environmental importance. This study evaluated various controls on arsenate, molybdate, and selenate uptake by HT-LDHs. Arsenate has a stronger affinity for the HT-LDHs than molybdate or selenate. HT-LDHs with both  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  as interlayer anions and  $\text{Fe}^{3+}$  as a substituting cation act as a better scavenger than  $\text{CO}_3^{2-}$ - and  $\text{Al}^{3+}$ -containing HT-LDHs. Greater uptake occurred when excess sorbates were made available, but the percent total uptake was reduced once surface saturation was attained. Sorbate uptake was negatively influenced by increasing pH and the presence of competing anions; the least uptake was observed in the presence of the large charge density  $\text{PO}_4^{3-}$  anion and at pH 10. X-ray diffractogram and Raman spectral studies provided evidence of interlayer occupancy of sorbed oxyanions. X-ray absorption and photoelectron spectroscopic data showed that the redox state of all sorbates remained unchanged and that there is strong binding between ferric iron and adsorbed arsenate that is absent between iron and either adsorbed molybdate or selenate. Partial oxyanion desorption occurred in a reverse order to their affinity for uptake, resulting in a 1.4–8.5% fractional release after 30 days.

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## 1. Introduction

Ground and surface water contamination by arsenic (As), molybdenum (Mo) and selenium (Se) is a serious environmental concern near abandoned mines and mine tailing discharge sites. Low-cost adsorptive removal techniques have been widely adopted to reduce the concentrations of these contaminants in such scenarios. Among the sorbents employed for this purpose (e.g., iron (oxyhydr)oxides, activated carbon), hydrotalcite-like layered double hydroxides (HT-LDHs) possess unique qualities as a result of their superior anion exchange properties (3.1–4.4 meq/g, Carriazo et al., 2007; 200–500 cmol/kg, Miyata, 1983; Forano et al., 2006) and reactive interlayer space. HT-LDHs are a natural sink near mine drainage sites (Ardau et al., 2007; Douglas et al., 2012), have been employed in landfill liners for radioactive wastes (Roh et al., 2000; Correa and Gómez, 2006), and have been used successfully as an efficient contaminant scavenger (Seida et al., 2001; Gillman, 2006; Douglas et al., 2010).

Although a few studies report better removal in acidic pH (e.g., Terry, 2004; Yang et al., 2005), HT-LDHs typically undergo partial dissolution below pH 5–6 (Yang et al., 2005; Das et al.,

2006). The adsorbed contaminants mostly occupy the interlayer space, either by partly displacing the existing interlayer anions ( $\text{A}^{n-}$ ) or becoming a part of the structure. Calcinated HT-LDHs demonstrate better retention of both trace metals (e.g., Lazaridis et al., 2004; Cocheci et al., 2009; Gutiérrez et al., 2009) and anions (e.g., Das et al., 2006) because of the ‘reformation effect’ (Cavani et al., 1991; Forano et al., 2006) and high surface area. Considering the artificial preparation, generation cost, and their absence in natural environments, detailed studies of uncalcinated HT-LDHs will provide better information with respect to uptake mechanisms that occur in natural settings.

$\text{MgAlCO}_3$ -type HT-LDHs have been extensively studied with respect to their contaminant uptake behavior (e.g., Lazaridis et al., 2004; Terry, 2004; Gillman, 2006; Cocheci et al., 2009; Gutiérrez et al., 2009), while limited research has been conducted on  $\text{MgFeCO}_3$ -type HT-LDHs (e.g., Seida et al., 2001; Das et al., 2002; Nishida et al., 2004; Türk et al., 2009),  $\text{MgFeSO}_4$ -type HT-LDHs have yet to undergo detailed characterization. Uptake of contaminants (e.g., As(V), Mo(VI), and Se(IV)) as charge balancing anions can occur during HT-LDH formation (e.g., Frost et al., 2005; Palmer et al., 2008; Liu et al., 2009; Palmer and Frost, 2011). The binding mechanism of trace metals within the structure of HT-LDHs is however poorly understood, but is generally believed to be due to interlayer incorporation (Grover et al., 2009; Türk et al., 2009; Palmer and Frost, 2011). Research on contaminant uptake after the precipitation of HT-LDHs is limited

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with respect to As(V) (Nishida et al., 2004; Yang et al., 2005; Chang et al., 2007; Türk et al., 2009) and Se(VI) (You et al., 2001) and, to the best of our knowledge, non-existent for Mo(VI). Hence, the present study was undertaken to evaluate conditions that govern As(V), Mo(VI), and Se(VI) uptake by HT-LDHs and understand the possible binding mechanisms using data gathered from geochemical, X-ray diffractogram, spectroscopic, and synchrotron techniques.

## 2. Materials and methods

### 2.1. Synthesis of HT-LDHs

Four types of HT-LDHs (MgFeCO<sub>3</sub>-, MgFeSO<sub>4</sub>-, MgAlCO<sub>3</sub>-, and MgAlSO<sub>4</sub>-types) were synthesized by co-precipitation at ambient temperature and pressure conditions using analytical grade (>99%) salts of MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·15H<sub>2</sub>O, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O as cationic sources and NaOH with or without Na<sub>2</sub>CO<sub>3</sub> as the anion source, as detailed elsewhere (Paikaray and Hendry, 2012). The HT-LDHs were dried and stored at room temperature after their synthesis.

### 2.2. Uptake experiments

Before use, all pieces of glassware were preconditioned in 10 vol.% HNO<sub>3</sub> for ~4 h, then, rinsed 3–5 times and immersed for 6–8 h in Milli-Q H<sub>2</sub>O followed by drying at room temperature (RT). As(V), Mo(VI), and Se(VI) stock solutions were prepared from analytical grade salts of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, and Na<sub>2</sub>SeO<sub>4</sub>, respectively, immediately prior to use. Uptake experiments were carried out in polyethylene (PE) reactor vials for 24 h, which is considered an adequate time for most trace metals to reach equilibrium (e.g., You et al., 2001; Carriazo et al., 2007; Chang et al., 2007; Grover et al., 2009; Türk et al., 2009).

The effect of HT-LDH type on uptake was evaluated using the four synthesized sorbents. For each sorbent, 0.25 g as a finely ground powder was added to 50 mL PE reactor vials with 25 mL of sorbate (As(V), Mo(VI), or Se(VI); at a concentration of 50 mg/L) and equilibrated for 24 h on a wrist shaker. The solid and aqueous phases were separated by filtration (Whatman 42) and stored for further analysis. The initial and final pH remained almost constant at 9.5 ± 0.5–10.5 ± 0.5 depending on the HT-LDH type. The sorbent demonstrating the maximum sorbate uptake was investigated in detail.

A range of initial sorbate concentrations (0.1–100 mg/L) were combined with 0.25 g of sorbent and equilibrated for 24 h in PE reactor vials to evaluate the effect of sorbate concentrations on total uptake and uptake mechanism. The equilibrium pH values were constant at 9.50 ± 0.25. Similar equilibrium studies were conducted to evaluate the effect of competing anions using 1, 10, and 100 mg/L NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> as NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> salts, respectively; sorbate and sorbent loadings were 0.05 and 10 g/L, respectively. Consistent with above pH values, the equilibrium pH was 9.50 ± 0.25.

Due to the strong buffering nature of the used HT-LDH at pH ~ 9.5, the effect of aqueous pH was studied by equilibrating the pre-formed HT-LDH in Milli-Q H<sub>2</sub>O prior to contact with sorbates. The pH of reaction vessels containing 24 mL Milli-Q H<sub>2</sub>O and 0.25 g HT-LDH was adjusted using diluted HCl and NaOH to 6, 8, and 10; these pH values remained almost stable after ~8 h. To maintain consistency with the sorbate experiments above, 1 mL of 1250 mg/L As(V) or Mo(VI) stock solution was added to achieve 50 mg/L sorbate concentrations. Due to solubility challenges at such high Se(VI) concentrations, only 1 mL of 100 mg/L stock solution was added to achieve a concentration of 4 mg/L. The pH was frequently monitored and maintained at the desired value. The overall change in volume due to acid/base addition was ~1–2 mL.

### 2.3. Desorption experiments

To characterize the strength of sorbate binding on HT-LDH, sorbents with greatest uptake were allowed to equilibrate in Milli-Q H<sub>2</sub>O for 30 days in the absence of any competing anions. The sorbent load was maintained at 10 g/L in three separate closed PE reactor vials; pH changes were noted for 30 days and ~1 mL of the aqueous phase was collected at defined time intervals to determine the concentration of desorbed sorbates.

### 2.4. Analytical techniques

The final As, Mo, and Se aqueous concentrations were measured by inductively coupled plasma-mass spectrophotometry (ICP-MS, Perkin-Elmer Elan 5000) with B, P, and S2 lens settings at 45 and RF power at 1000 W. The solid phase loading 'q<sub>e</sub>' was determined by mass balance:  $q_e = (C_i - C_{eq}) / (M/V)$ , where C<sub>i</sub> and C<sub>eq</sub> are the initial and equilibrium sorbate concentrations (mg/L), respectively, M is the mass (g), and V is the solution volume (L). NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> concentrations were measured by ion chromatography (IC).

Powdered slurries of the HT-LDHs with and without sorbates prepared using methanol were mounted on glass slides and dried for ~30 min at RT before X-ray diffraction (XRD) by a PANalytical Empyrean X-ray diffractometer at 40 kV and 45 mA with a Co Kα radiation source (λ = 1.78901 Å). The runs were performed between 10 and 80° 2θ at a 0.02°/s step size and 80 s step time. The XRD peaks were indexed using PowderX software and compared with reports in the literature.

Raman spectra of the powdered HT-LDHs were obtained using a Renishaw InVia Raman spectrophotometer equipped with a solid state laser diode at 785 nm and 1200 lines/mm grating. The instrument was calibrated by an internal Si wafer (~520 cm<sup>-1</sup>) before sample measurements. A 50× Leica PLAN objective lens was focused on the particles and the spectra obtained were between 100 and 1500 cm<sup>-1</sup>. Multiple acquisitions (3 to 5) were collected to improve the signal to noise ratio, and the average was reported.

Freshly prepared powdered samples of As(V)-, Mo(VI)-, and Se(VI)-loaded HT-LDHs (9.8, 8.8, and 8.6 mg/g, respectively) were mounted on Kapton® tape over a Teflon® sample holder for X-ray absorption spectroscopic (XAS) analysis at the HXMA-06ID-1 beamline (2.9 GeV and ~250 mA), Canadian Light Source, Saskatoon. The energy source is a superconducting wiggler equipped with a double-crystal Si(111) monochromator and Rh-coated collimating mirror. The higher harmonics in the beam were suppressed by detuning the second monochromator to 50% of the fully-tuned beam intensity. The monochromator step size was reduced to 0.5 eV in the X-ray absorption near-edge spectroscopy (XANES) region and to 0.05 Å<sup>-1</sup> in the extended X-ray absorption fine structure (EXAFS) region. Data were collected in fluorescence mode at ambient conditions using 32-element solid-state germanium with simultaneous measurement of As, Mo, and Se reference spectra for energy calibration. For all three samples, 3–4 scans were collected and averaged to increase the signal-to-noise ratio and the data were then modeled using IFFFIT (Ravel and Newville, 2005). The k<sup>3</sup>-weighted and Fourier transformed (FT) EXAFS spectra of the As, Mo, and Se K-edge were all fitted with ab initio phase and amplitude functions generated with FEFF version 6L included in IFFFIT (Rehr et al., 1992).

X-ray photoelectron spectroscopic (XPS) measurements on As(V)-, Mo(VI)-, and Se(VI)-loaded HT-LDHs (9.8, 8.8, and 8.6 mg/g, respectively) were performed on an AXIS 165 spectrometer (Kratos Analytical) at the Alberta Centre for Surface Engineering and Science (ACES), University of Alberta. The base pressure in the analytical chamber was lower than 5 × 10<sup>-8</sup> Pa. A monochromatic Al Kα source (hν = 1486.6 eV) was used at a power of 210 W. The analysis spot was 400 × 700 μm and the take-off angle was 90°. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f

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