Sorption of oxyanions on nanocrystalline Mg/Al layered double hydroxides : sorption characteristics, mechanisms, and matrix interferences

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NANYANG
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**SORPTION OF OXYANIONS ON NANOCRYSTALLINE
MG/AL LAYERED DOUBLE HYDROXIDES: SORPTION
CHARACTERISTICS, MECHANISMS, AND MATRIX
INTERFERENCES**

GOH KOK HUI
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
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SUMMARY

Inorganic oxyanions have high solubilities in aqueous phase at the circumneutral to alkaline pH values typical of most subsurface environment. A number of these oxyanions are toxic to both humans and wildlife at mg/L level or even at $\mu\text{g/L}$ level. Sorption technology is regarded as one of the most promising technologies for removing oxyanions from water because it is inexpensive, versatile, and appropriate for small systems. Layered double hydroxide (LDH) has been recently explored as a potential sorbent for oxyanion removal but most of the investigated LDHs were prepared from conventional methods which produced unstable large LDH particles with aggregated crystallines. The LDH technology may be enhanced by engineering a new breed of nanocrystalline LDH for oxyanion removal since nanocrystalline materials have been proved to demonstrate several unique characteristics such as large surface area and high specificity.

In this study, a nanocrystalline Mg/Al LDH with nitrate intercalation (FCHT-LDH) was prepared by fast coprecipitation with subsequent hydrothermal treatment method. Several analytical techniques were employed to characterize the LDH samples. The sorption ability of FCHT-LDH for a variety of oxyanions (i.e. arsenate, borate, chromate, molybdate, selenate, and vanadate) and oxyhalides (i.e. bromate, chlorate, iodate, and perchlorate) were evaluated. Interactions of oxyanions and oxyhalides with FCHT-LDH were investigated using a combination of sorption/desorption studies and microscopic techniques such as X-ray photoelectron spectrometry (XPS), extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and CHNS/O. The sorption results suggested that the sorption characteristics of oxyanions and oxyhalides on FCHT-LDH were governed by their ionic potentials and molecular structures. Oxyanions which have ionic potentials higher than 7 nm^{-1} were found to be more readily sorbed by FCHT-LDH than oxyhalides with ionic potentials lower than 5 nm^{-1} . Trigonal oxyhalides generally showed a lower degree of specificity for FCHT-LDH than the tetrahedral oxyanions. Monovalent oxyhalide sorption on FCHT-LDH was likely occurred via anion exchange mechanism with subsequent formation of outer-sphere surface

complexes whereas polyvalent oxyanion sorption mechanisms on FCHT-LDH were possibly attributable to both anion exchange and ligand exchange reactions, resulting in the coexistence of outer-sphere and inner-sphere surface complexes.

The predominant nature of arsenate interaction with FCHT-LDH was studied through stoichiometric calculations, nitrate displacement investigation, comprehensive sorption/desorption experiments, and analyses with several microscopic techniques. FCHT-LDH exhibited a high arsenate sorption capacity of 114 cmol/kg and the reaction was satisfactorily described by Elovich model. Nevertheless, arsenite sorption on FCHT-LDH was comparatively low mainly due to the presence of uncharged and singly charged arsenite species which were unfavorable for the sorption reaction. The observed nitrate-arsenate molar displacement ratio, increased interlayer spacing, and decreased nitrogen content in the interlayer region revealed the predominance of anion exchange mechanism in arsenate sorption by FCHT-LDH. However, slight pH increase during arsenate sorption equalization and the presence of ~25% irreversibly sorbed arsenate signified the occurrence of ligand exchange process as the secondary sorption mechanism. This specific sorption process possibly involved the formation of inner-sphere arsenate complexes with a monodentate mononuclear configuration at the aluminum center, limited the regenerated sorption capacity of FCHT-LDH.

The influences of co-existing species on the sorption of oxyanions by FCHT-LDH were investigated by conducting the experiment in the presence of natural organic matter (NOM) and common anions such as nitrate, silica, sulfate, carbonate and phosphate. The adverse effects of co-existing anions were found to be more significant on the monovalent oxyhalide with lower ionic potential than the polyvalent oxyanion with higher ionic potential. Based on the degrees of influences on the arsenate sorption by FCHT-LDH, the co-existing anions can be arranged in the increasing order of nitrate < silica $\leq$ sulfate < carbonate < phosphate. Among the competitive anions, nitrate and silica (ionic potential $\leq 5 \text{ nm}^{-1}$) showed negligible and moderate competitive effects on arsenate sorption whereas sulfate, carbonate, and phosphate (ionic potential $> 5 \text{ nm}^{-1}$) exhibited moderate to significant competitive effects on arsenate sorption. Besides obstructing the surface of FCHT-LDH, NOM can also inhibit arsenate sorption by competing with arsenate for sorption sites, and

settling out FCHT-LDH from aqueous solution at alkaline condition and subsequently reducing the available sorption sites. The presence of these co-existing species did not cause significant effect on the dissolution of metals from the FCHT-LDH.

Various types of LDHs were prepared using different synthetic routes and assessed for their ability to remove arsenate from the aqueous solution. LDHs prepared by the alternative synthetic routes generally showed higher arsenate sorption capacities than those prepared by the conventional synthetic routes, mainly due to their lower carbonate content, larger surface area, better porosity characteristic, and nanocrystalline property. Solid LDH microspheres were successfully prepared via a fast coprecipitation-hydrothermal-spray drying process. The morphology and particle size of the prepared microspheres were dependent on the process parameters including inlet air temperature, compressed air flow rate, suspension feed concentration, and addition of surfactant. The LDH microspheres prepared in this study exhibited effective arsenate removal and easy recovery by gravity, but a relatively slow sorption rate. The SEM-EDX analysis revealed the occurrence of arsenate sorption in the internal surface sites of the LDH microspheres and demonstrated the mineral stability and reusability of the microspheres.

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LIST OF PUBLICATIONS

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Goh, K.H., Lim T.T., Dong, Z.L., 2009. Removal of arsenate from aqueous solution by nanocrystalline Mg/Al layered double hydroxide: sorption characteristics, prospects, and challenges. Water Science and Technology. 61(6), 1411-1417.

Goh, K.H., Lim T.T., Dong, Z.L., 2009. Enhanced arsenic removal by hydrothermally treated nanocrystalline Mg/Al layered double hydroxide with nitrate intercalation. Environmental Science and Technology. 43(7), 2537-2543.

Lim T.T., Goh, K.H., Goei, R., Dong, Z.L., 2009. Mechanistic and thermodynamic studies of oxyanion sorption by various synthetic Mg/Al layered double hydroxides. Water Science and Technology. 59(5), 1011-1017.

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Lim, T.T., Goh, K.H., Goei, R., Dong, Z.L., 2008. Synthesis of layered double hydroxides by different routes and their oxyanion sorption mechanisms and thermodynamics. IWA Chemical Industries 2008 International Conference, 9-11 November 2008, Beijing, China.

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Lim, T.T., Goh, K.H., Dong, Z.L., 2007. Synthesis and characterization of nano-scale clay anion exchanger and its application in removing arsenic from aqueous system. 4th International Conference on Ion Exchange ICIE 07, 15-19 October 2007, Chiba University, Japan.

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ABBREVIATIONS

$1/n$	heterogeneity factor
ΔG°	Gibbs free energy
ΔH°	standard enthalpy change
Δq	normalized standard deviation
ΔS°	standard entropy change
μ	ionic potential
α	Elovich constant related to the sorption rate
β	Elovich constant related to the surface coverage
χ^2	Chi-square
v_s	activity coefficient of the sorbed anion
v_e	activity coefficient of the anion in solution
a	average metal-metal distance inside the brucite-like sheets
a_e	activity of the anion in solution at equilibrium
a_s	activity of sorbed anion
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Hallender
c	interlayer distance regulated by the size and charge of the anion placed between the brucite-like sheets
c'	basal spacing
C_e	concentration of anion at equilibrium
C_0	initial concentration of anion
C_s	surface concentration of anion
CHNS/O	Carbon, hydrogen, nitrogen, sulfur, and oxygen
CN	average coordination number
CTAB	cetyltrimethylammonium bromide
DBPs	disinfection byproducts
DOC	dissolved organic carbon
DSC	differential scanning calorimetry
DTA	differential thermal analysis
E_a	activation energy

EDX	energy dispersive X-ray spectrometry
E_h	redox potential
EM	electrophoretic mobility
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
GFAAS	graphite furnace atomic absorption spectrophotometer
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
fwhm	full-width at half maximum
HASB	hard and soft acids and bases
HRTEM	high resolution TEM
HTlc	hydrotalcite-like compounds
IC	ion chromatograph
ICP-OES	inductively coupled plasma-optical emission spectrometer
ICSD	inorganic crystal structure database
IEP	isoelectric point
K_c	thermodynamic equilibrium constant
K_{eq}	apparent equilibrium exchange constant
K_{ex}	equilibrium exchange constant
K_F	Freundlich constant related to the sorption capacity
K_L	Langmuir sorption constant
k_{m1}	rate constant of modified multiplex model
k_{m2}	rate constant of modified multiplex model
LDH	layered double hydroxide
M^{2+}	divalent cation
M^{3+}	trivalent cation
MCL	maximum contaminant level
NMR	nuclear magnetic resonance
NOM	natural organic matter
n	number of data points
PCD	particle charge detector
PCS	photon correlation spectroscopy
pK_a	acid dissociation constant

pzc	point of zero charge
q_e	amount of anion sorbed at equilibrium
q_m	sorption capacity
$q_{t,exp}$	experimental values
$q_{t,cal}$	values calculated by the model
r	molecular radius
R	universal gas constant or average interatomic distance
R^2	linear coefficients of determination
R_L	separation factor
SAED	selected area electron diffraction
SDS	sodium deodecyl sulfate
SEM	scanning electron microscope
T	temperature
TEM	transmission electron microscope
TG	thermogravimetry
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectrometry
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
z	ionic charge

Chapter 1 Introduction

1.1 Background

Elevated levels of inorganic oxyanions such as arsenate, chromate, selenate, vanadate, etc. have been found in the natural environment (soils, groundwaters, and surface waters), drainage, and wastewaters (Qian et al., 2000; Li and Bowman, 2001; Yokoi et al., 2004; Dermou et al., 2005; Naeem et al., 2007) as a result of weathering and dissolution processes, geothermal activity, and a number of anthropogenic sources (as illustrated in Figure 1.1). These oxyanions have high solubilities in aqueous phase at the circumneutral to alkaline pH values typical of most subsurface environment. They are also less susceptible to sorption since most natural materials have negative surface charges. The occurrence of these oxyanions has raised potential health and regulatory concerns due to their toxic and carcinogenic properties. For instance, tens of thousands of people have already suffered from symptoms such as skin lesion, hyperkeratosis, liver cancer, etc. due to their exposure to arsenic-contaminated waters (Berg et al., 2001).

Figure 1.1 Groundwater and surface water contaminated by oxyanions like arsenate originated from natural and anthropogenic inputs (SWEHSC, 2007).

Among the removal strategies, sorption technology is considered to be one of the most appealing methods for oxyanion removal because it is cost-effective, versatile, and simple to operate (Jang et al., 2006). This technology is suitable for small system and requires relatively small footprints (Figure 1.2). A number of studies have been performed to remove oxyanions using sorbents such as activated carbon, agricultural by-products, clay minerals, biosorbents, and so on (Dupont and Guillon, 2003; Teixeira and Ciminelli, 2005; Bhattacharyya and Gupta, 2006; Mohan and Pittman Jr, 2006).

Figure 1.2 A sorption system installed for use in a small community (Dennis and Simms, 2004).

Layered double hydroxides (LDHs) have been recently developed and investigated for effective oxyanion removal (Alvarez-Ayuso and Nugteren, 2005; Yang et al., 2005; Goh et al., 2008) owing to their large surface area, high anion exchange capacity, good thermal stability, and ability to reconstruct the calcined LDH to its original layered structure through its “memory effect” (Cavani et al., 1991; Li and Duan, 2005). LDHs are mixed metal hydroxides containing positively charged brucite-like sheets with intercalated anions in the hydrated interlayer regions. They have a relatively weak interlayer bonding and consequently exhibit an excellent ability to exchange its interlayer anion for oxyanion in the bulk solution. Among the intercalated anions, nitrate appears to be a suitable candidate because it is highly exchangeable and thus most easily being exchanged with oxyanion according to the sequence of anion exchange capacity (Miyata, 1980; Auerbach et al., 2004). Several

hypotheses have been proposed to describe the removal mechanisms of contaminants from aqueous medium to LDHs: (1) interlayer anion exchange governed by the charge-balancing anions in the interlayer and the layer charge density, (2) external surface adsorption, and (3) intercalation of guest anions through reconstruction reaction.

Nanoscale inorganic particles and their agglomerates potentially offer excellent opportunities conducive to selective removal of a wide range of target contaminants from water. For example, nanoparticles can effectively sorb dissolved heavy metals or metalloids like oxyanions, act as strong solid phase oxidizing or reducing agents, and impart magnetic activity (Cumbal et al., 2003). Most of the LDHs investigated for oxyanion sorption have been prepared from conventional coprecipitation methods (Lazaridis et al., 2001; You et al., 2001a; Gillman, 2006; Goh et al., 2008) which produce unstable large LDH particles with aggregated crystallites (Zhao et al., 2002). Nanocrystalline materials demonstrate several unique characteristics such as large surface area and high specificity that make them excellent functional materials for water treatment applications. A recent study (Pena et al., 2006) has suggested that nanocrystalline TiO_2 exhibited high affinity for arsenic. Therefore, it is of worthy to engineer a new breed of nanocrystalline LDH using a scientifically sound synthesis method for the removal of arsenate and other environmentally significant oxyanions.

1.2 Motivation and knowledge gap

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 and vanadate, and oxyhalides such as bromate, chlorate, iodate, and perchlorate remains scarce. Some studies have indicated that LDHs have greater affinities for polyvalent anions than monovalent anions (Dutta and Puri, 1989; You et al., 2001a) but the interrelation between LDHs and valences of anions was yet to be elucidated. Although the oxyanion sorption performances of LDHs under various environmental conditions were studied thoroughly, the interactions between oxyanions and LDHs were investigated to a much less extent. This knowledge is

particularly crucial to the nanocrystalline LDH since it has much larger specific surface area and is more chemically reactive compared with the large LDH particles prepared by the conventional methods. Understanding of LDH interaction with oxyanions at the solid/aqueous interface is of paramount importance as it will allow the accurate prediction of the sorptive properties of the sorbent and subsequently lead to the optimization of the sorption and regeneration processes.

It has been suggested that arsenic can be removed by LDHs via anion exchange mechanism, but remains hypothetical at best (Lazaridis et al., 2002; Yang et al., 2005; Gillman, 2006). Thus far insufficient experiments are performed to demonstrate the ion exchange stoichiometry for LDH and to provide direct evidence of the occurrence of anion exchange mechanism. Therefore it is rather difficult to quantitatively assess the impact of anion exchange property of LDH on arsenic removal. It has been reported by Wang et al. (2008a) that arsenate sorption by LDH can occur through surface adsorption and interlayer anion exchange depending on the interlayer nitrate orientation. However, the predominant mechanism was not clearly identified. The quantification of the contributions of the different mechanisms (e.g. anion exchange and adsorption) to arsenate removal will greatly promote the thorough understanding of arsenic interaction with LDH.

Prior to successful application of LDHs in water treatment, one of the pertinent issues needs to be addressed is the interference in the oxyanion-LDH interaction caused by the co-existing species present in the aqueous matrix. These species may directly compete for available surface binding sites or indirectly alter the electrostatic charge on the LDH surface. Nitrate, silica, sulfate, carbonate, and phosphate are among the anions that commonly present in natural water bodies including groundwater, surface water, and seawater (Jain and Loeppert, 2000; Su and Puls, 2001; Katsoyiannis and Zouboulis, 2002). Natural organic matter (NOM) is also ubiquitously exist in natural waters and it tends to sorb onto mineral surfaces like LDH and thus may impact arsenate sorption either favorably or adversely. However, there has been no systematic study on the influence of NOM on the sorption of arsenate by LDHs. The influence of each of these species needs to be evaluated to infer the potential

limitation of LDHs in remediation of arsenate-contaminated waters that may contain significant amounts of co-existing species.

Recently, it has been reported that materials prepared by alternative synthetic routes such as sol-gel method can exhibit larger surface area and more uniform pore size distribution (Aramendia et al., 2002; Valente et al., 2007) and spray drying method can produce submicron- to micron-sized particles with a spherical shape that are more monodisperse (Okuyama et al., 2006), compared to those obtained by the conventional routes. Therefore, preparing LDHs by these alternative synthetic routes can potentially improve their structural and textural properties as well as their technical feasibility. For example, the micron-sized LDH particles produced by spray drying may offer the possibility of enhanced performances by minimizing separation and recovery problems in practical application. It is therefore necessary to study the characteristics and sorption performances of LDHs obtained by these alternative synthetic routes while the relevant literature remains sparse.

1.3 Objectives and scopes of work

The focus of the present study is on the sorption of oxyanions having different molecular properties by nanocrystalline Mg/Al LDH to better understand the principles of sorption reaction and the solid/liquid interactions on the particle surface. The specific objectives and scopes of work of this research are described as follows:

- i. To evaluate the sorption performance of nanocrystalline LDH for various oxyanions and oxyhalides, investigate their sorption characteristics and thermodynamics on the LDH, and determine the plausible mechanisms and surface structures for the sorbed anions at the solid/aqueous interface.
- ii. To assess arsenate binding by nanocrystalline LDH through anion exchange mechanism using both macroscopic and microscopic techniques, unravel the predominant nature of the interaction between the LDH and arsenate, and quantify the contributions of the different mechanisms to arsenate removal.
- iii. To investigate the influences of various co-existing species including natural organic matter (NOM) and common oxyanions such as nitrate, silica, sulfate,

carbonate, and phosphate on the sorption of several toxic oxyanions (arsenate, chromate, vanadate and bromate) by nanocrystalline LDH.

- iv. To compare the arsenate sorption performance of the LDHs prepared using the alternative synthetic routes and the conventional synthetic routes, develop micron-sized LDH microspheres, and evaluate their arsenate sorption capacity and recovery.

1.4 The structure of the thesis

This thesis mainly consists of eight chapters:

- i. Chapter 1 provides a general introduction of background problem, LDH sorption technology and its ability to remove oxyanions, and the motivation for the study. The objectives and the structure of the thesis are also included in this chapter.
- ii. Chapter 2 presents a comprehensive review of the use of LDHs for oxyanion removal from waters and wastewaters. The scope of review encompasses background and sources of oxyanions, contamination by oxyanions and their impacts, available technologies for oxyanion removal, background of LDHs, composition and structure of LDHs, synthesis and characterization of LDHs, and sorption of oxyanions on LDHs. The specific review of sorption isotherms, sorption kinetics and diffusion-controlled models, factors affecting sorption of oxyanions on LDHs, desorption, regeneration, recovery, mechanistic studies, comparison of LDHs with other sorbents, and problems, improvement, and potential application of LDHs are also discussed in this Chapter.
- iii. Chapter 3 addresses the materials and methods used in this study as well as the experimental procedures.
- iv. Chapter 4 contains the results and discussion of the sorption of various oxyanions and oxyhalides having different molecular properties in the batch experiment by the nanocrystalline LDH. The sorption characteristics, thermodynamics, mechanisms, and surface structures are also examined.
- v. Chapter 5 presents the major findings associated with the assessment of arsenate sorption by nanocrystalline LDH through anion exchange mechanism using stoichiometric calculations, nitrate displacement investigation, and several

advanced analytical techniques. Other results include quantification of the contributions of the different mechanisms to arsenate removal, possible dominant arsenate-LDH surface complex, reusability of the regenerated LDH, etc.

- vi. Chapter 6 shows the influences of common anions and NOM on the sorption of arsenate by nanocrystalline LDH. The effects of these co-existing species on arsenate sorption were investigated as functions of time, concentration, and pH.
- vii. Chapter 7 describes the preparation and characterization of LDHs obtained by various synthetic routes, and their performances in arsenate removal. The effects of various fabrication process parameters on the characteristics of the LDH microspheres are also presented.
- viii. Chapter 8 outlines the main conclusions derived from this study and the recommendations for the future work.

Chapter 2 Literature Review

2.1 Oxyanions and their chemistry

Oxyanions or oxoanions are chemical compounds with the generic formula $A_xO_y^{z-}$, where A represents a chemical element and O represents an oxygen atom. Oxyanions are usually formed by a large majority of the chemical elements (Greenwood and Earnshaw, 1997). Oxyhalides are the oxyanions that are formed by halogens. The formulae of oxyanions are determined by the octet rule whereas the structures of oxyanions can be rationalized in terms of the number of polyhedral units with sharing of corners or edges between polyhedra. For example, arsenite, arsenate, bromate, chromate, vanadate, etc. are among the harmful oxyanions/oxyhalides that can endanger human as well as ecosystem over a long period of time.

Arsenic is ubiquitous in the earth's crust, with an average abundance of approximately 3 mg/kg (Violante et al., 2006). Arsenic exists in the -3, 0, +3, and +5 oxidation states. Inorganic forms of arsenic, i.e. arsenite (As(III)) and arsenate (As(V)), most often exist in natural waters. Organic arsenic forms may be produced by biological activity in surface waters, but are rarely quantitatively important. Arsenite can appear in the forms of H_3AsO_3 , $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} while arsenate mainly appears as H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} (O'Neill, 1995). In oxygenated water systems, arsenates are the dominant species, whereas under more reducing conditions, arsenite species are the predominant speciation form (Montgomery, 1985). The dissociation constants for arsenious (H_3AsO_3) and arsenic (H_3AsO_4) acids in aqueous solution are given below:

Dissociation of Arsenite

Dissociation of Arsenate

Redox potential (E_h) and pH control arsenic speciation. Figure 2.1 illustrates the Eh-pH diagram for various arsenate and arsenite compounds. Arsenate dominates at circumneutral pH and atmospheric conditions. Conversely, in mildly reducing conditions such as the prevailing environment in most groundwaters, arsenite exists predominantly.

Figure 2.1 The E_h -pH diagram for arsenic at 25 °C and 1 atm (Montgomery, 1985).

The bromate anion (BrO_3^-) is a bromine-based oxyanion. It exists as a number of salts, the most industrially important being potassium (KBrO_3) and sodium bromates (NaBrO_3). Once in solution, bromate is highly stable at room temperature, does not volatilize, and does not removed by boiling. Bromate can form through both a molecular ozone (O_3) pathway and a hydroxyl radical ($\text{OH}\cdot$) pathway depending on the dissolved organic carbon (DOC), Br^- content, and pH of the water (Amy and

Siddiqui, 1998). $\text{OH}^\bullet$ is a secondary oxidant formed upon O_3 decomposition and its pathway is more dominant under higher pH conditions and higher NOM concentrations. For the molecular ozone pathway, Br^- is first oxidized by dissolved ozone to hypobromite ion (OBr^-), which is then further oxidized to BrO_3^- (Haag and Holgné, 1983):

The aforementioned reaction demonstrates the formation of BrO_3^- through an intermediate species, OBr^- , which is in equilibrium with hypobromous acid (HOBr). The reaction therefore exhibits a pH dependency, i.e. there is greater BrO_3^- formation at higher pH, where OBr^- is the dominant bromine species. Molecular ozone theory indicates that BrO_3^- formation is directly driven by dissolved ozone. In contrast, $\text{OH}^\bullet$ theory suggests that dissolved ozone plays only an indirect role by decomposing O_3 to produce hydroxyl radicals, which further react with bromine species to produce BrO_3^- (Amy and Siddiqui, 1998).

Hexavalent chromium exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion (HCrO_4^-), and chromate ion (CrO_4^{2-}), depending on the pH. H_2CrO_4 predominates at pH less than 1, HCrO_4^- at pH between 1 and 6, and CrO_4^{2-} at pH above about 6 (Mohan and Pittman Jr, 2006). The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) forms when the concentration of chromium exceeds approximately 1 g/L. Chromate and dichromate ions are regarded as the most soluble, mobile and toxic forms of hexavalent chromium in the environment. Vanadium occurs in +3, +4, and +5 oxidation states in aqueous solution (Naeem et al., 2007). In freshwaters, vanadium(V) exists almost exclusively as monomeric species, either as free vanadate or as ligated complexes. Under strongly basic conditions, above a pH of about 12, vanadate exists as the trianionic species, VO_4^{3-} (Tracey et al., 2007). Under moderately basic conditions (pH 8.2-12), it predominantly presents as the dianionic compound, HVO_4^{2-} . The principal form is the monoanionic derivative from pH 8.2 until close to a pH of 3, when it is protonated to become neutral.

2.2 Sources of oxyanions

As aforementioned, the source of oxyanions can be due to both natural and anthropogenic inputs. Parent rock materials contribute to the natural sources of arsenic. Arsenic is often concentrated in magmatic sulfides and iron ores. Arsenic can be mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions, and other anthropogenic activities. Soil erosion and leaching have contributed to 612×10^8 and 2380×10^8 g/year of arsenic, respectively, in dissolved and suspended forms in the oceans (Mohan and Pittman Jr, 2007). Most environmental arsenic problems are the result of mobilization under natural conditions. However, anthropogenic sources such as mining activities, industrial activities, combustion of fossil fuels, use of arsenic pesticides and crop desiccants, and use of arsenic additives to livestock feed have created additional impacts.

Hexavalent chromium (Cr(VI)) scarcely occurs naturally and usually has an anthropogenic origin. Industrial sources of Cr(VI) include leather tanning, cooling tower blowdown, electroplating, anodizing baths, etc. (Mohan and Pittman Jr, 2006). Molybdenum occurs naturally in various ores and its compounds are used primarily in the production of metal alloys (Namasivayam and Sangeetha, 2006b). Selenium exists in the subsurface environment due to the dissolution of selenium-bearing minerals and anthropogenic sources such as wastewater from coal burning power plants (Peak et al., 2006) whereas vanadium is introduced into the environment through activities such as combustion of fossil fuels and production of phosphoric acid (Naeem et al., 2007).

Borate, another oxyanion, enters the environment through inputs from boron in silts present in the aquifer or in the systems of urban and industrial wastes. The urban wastes mainly originate from the detergents and cleaning products while the industrial wastes come from a wide range of different activities as well as several chemical products used in agriculture (del Mar de la Fuente García-Soto and Camacho, 2006). Oxyhalides such as bromate, chlorate, and iodate are known disinfection byproducts (DBPs) of drinking water treatment, namely, ozone and chlorine dioxide processes. On the other hand, environmental contamination of perchlorate has primarily been

associated with industrial and military activities; however, perchlorate has also been shown to occur naturally (Parette and Cannon, 2005; Snyder et al., 2005).

2.3 Contamination of water by oxyanions and their impacts

Oxyanions have been detected in the natural waters with concentrations ranging from $\mu\text{g/L}$ to mg/L , and occasionally can reach up to significant higher levels according to the nature of the process used. For example, arsenic concentrations in some contaminated waters have been found ranging from $< 1.0 \mu\text{g/L}$ to $> 1000 \mu\text{g/L}$ (Liu et al., 2008). High arsenic concentrations (up to several hundreds of mg/L) have also been reported in some river waters and groundwaters as a result of inputs from geothermal, mining, and agricultural sources (Smedley and Kinniburgh, 2001).

A number of oxyanions like arsenate, chromate, selenate, etc. are identified as toxins and potential carcinogens. These oxyanions can be harmful to both humans and wildlife at either $\mu\text{g/L}$ or mg/L levels. Several diseases have already been related to arsenic poisoning such as skin lesion, hyperkeratosis, melanosis, and various types of cancers (Berg et al., 2001; Mukherjee et al., 2005). The main regions of the world affected by arsenic contamination are shown in Figure 2.2, which also indicates the scale of chronic human exposure. The largest population at risk among these countries with known arsenic contamination is in Bangladesh, followed by West Bengal in India. As triggered by the risk concern of carcinogenic arsenic, the U.S. EPA. has revised the Maximum Contaminant Level (MCL) for arsenic in drinking water from $50 \mu\text{g/L}$ to $10 \mu\text{g/L}$ with a compliance date of January 22, 2006 (U.S.EPA., 2001).

Borate has been reported to stunt plant growth, cause virulence for reproduction, and cause disease in the nervous system of animals (Wang et al., 2006a) whereas acute exposure to chromate has resulted in nausea, diarrhea, liver and kidney damages, dermatitis, internal hemorrhage, and respiratory problems (Hayes, 1988; Mohan et al., 2006). Molybdate and selenate are considered essential micronutrients at low levels, however chronic exposure at high levels can result in damage to kidney and liver tissues (Kapoor et al., 1995; Namasivayam and Sangeetha, 2006b). Harmful effects on

the circulatory system and disturbance on the metabolism including that of plants have been reported as a result of exposure to vanadate (Namasivayam and Sangeetha, 2006a). Bromate, chlorate, and iodate have been shown to cause cancer, whereas perchlorate is well-known for having direct action on the thyroid gland by inhibiting the production of thyroid hormones (Parette and Cannon, 2005; Snyder et al., 2005). Since oxyanion contamination is a serious environmental problem and poses a clear public health risk for many countries, there is an urgent need for an effective and economical technique for their removal from water.

Figure 2.2 Worldwide distribution of arsenic contaminated regions, sources of arsenic, and numbers of people at risk of chronic exposure (Garelick and Jones, 2008).

2.4 Available technologies for oxyanion removal

The current technologies available for controlling oxyanions in the environment generally include chemical reduction and precipitation, ion exchange, membrane filtration, biological treatment, and sorption (U.S.EPA., 2002; Rubel, 2003; Amy et al., 2005; Esmaeili et al., 2005; Galan et al., 2005; Jang et al., 2006; Mohan and Pittman Jr, 2006; Miřtová et al., 2007; Montes-Hernandez et al., 2009). Majority of these methods are currently still in the laboratory evaluation and development stages. Although some of them can theoretically reduce oxyanions to below compliance level, each has its technical limitations.

The chemical reduction with subsequent precipitation approach is among the most widely used conventional processes for the removal of oxyanions such as chromate and perchlorate. This method is highly effective in removing chromate and perchlorate from water. However, it has shortcomings such as consumption of significantly higher amount of reagents, generation of higher volume of sludges that pose a potential hazard to the environment due to landfill leachate, and difficult recovery of metals (e.g. Chromium) for reuse (Hu et al., 2005).

Though ion exchange and membrane filtration can effectively remove some of the oxyanions, they are more expensive for both initial and ongoing operating costs than other reported technologies. In addition, ion exchange performance is strongly dependent on the types of resin used and the ion exchange resin usually has a short operational life span. Membrane filtration, on the other hand, requires sophisticated operation and maintenance (Mohan and Pittman Jr, 2007). Biological process may be effective, but it has disadvantages such as time consuming, unpredictable performance, and sensitive to seasonal variation (Parvin Huq et al., 2007).

Sorption technology is regarded as one of the most attractive processes for removal of contaminants from water because it is economical and flexible in design and operation. This technology is often appropriate for small system and requires relatively small footprints. To date, various conventional and nonconventional sorbents have been used for removing oxyanions including activated carbon (Mohan and Pittman Jr, 2006), zeolites (Shevade and Ford, 2004), agricultural by-products and seeds (Dupont and Guillon, 2003), fibers (Greenleaf et al., 2006), clay minerals and metal oxides (Garcia-Sanchez et al., 2002; Bhattacharyya and Gupta, 2006), industrial waste and by-products (Makris et al., 2006), biosorbents (Teixeira and Ciminelli, 2005), alginate–goethite beads (Zouboulis and Katsoyiannis, 2002; Lazaridis and Charalambous, 2005), etc. However, a good number of them are not selective and some have low sorption and regeneration efficiencies. Sorption using activated alumina may be an effective method for oxyanion removal, particularly arsenate, due to its high removal efficiency. Nonetheless, it incurs high capital and operation costs (Atkins, 2001). In this regard, LDHs have good potential for use as a new sorbent

since they are simple and economical to prepare, offer a large interlayer space to host the guest anions, and can be easily recycled. Many studies have been devoted to investigate their ability to remove a diverse number of anions in recent years.

2.5 Background, property, and application of LDHs

Clays are one of the most common natural earth minerals and have been utilized by human being for centuries. Clays are very versatile materials and they find applications in varying areas. In recent decades, a class of anionic clays known as layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTlc) has attracted substantial attention from both industry and academia. Although LDHs exist as naturally occurring minerals, they are also relatively simple and inexpensive to synthesize. The structure of LDHs is based on positively charged brucite-like sheets and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions. LDHs have relatively weak interlayer bonding and as a consequence exhibit excellent ability to capture organic and inorganic anions. The most interesting properties of LDHs include large surface area, high anion exchange capacity (2-3 meq/g) that is comparable to those of anion exchange resins, and good thermal stability (Bish, 1980; Cavani et al., 1991; Vaccari, 1998).

LDHs have been studied for their potential use in a wide range of important areas, i.e. catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical science, and environmental application (Cavani et al., 1991; Newman and Jones, 1998; Rives, 2001; Li and Duan, 2005; Evans and Duan, 2006). LDHs have been applied in catalyzing the production of basic chemicals (Morioka et al., 2001; Tsyganok et al., 2003), catalyzing redox processes (Monzón et al., 1999; Nishimura et al., 2000), and catalyzing acid-base processes (Tichit et al., 1998; Roelofs et al., 2001) with improved activity and improved recuperation of immobilized catalysts (Sels et al., 2001). For applications in photochemistry, photodimerization and photoisomerization of the interlayer anions occurred in the LDHs could yield useful photoresponsive materials (Shichi et al., 1996; Shimizu et al., 2006). LDHs have also been investigated for their use as electrode for alkaline secondary cells (Jayashree and

Vishnu Kamath, 2002; Chen et al., 2003) and nanocomposite polymer electrolytes (Liao and Ye, 2004). In medical applications, LDHs have been potentially used in pharmaceutical formulations (Gardner, 1985) and development of new delivery systems in biomedical science (Rahman et al., 2004). Moreover, LDHs have been used as heat retention additives in plastic films (Evans and Duan, 2006), flame retardants (Shi et al., 2005; Wang et al., 2005), stabilizing agents for polymers (Van Der Ven et al., 2000; Lin et al., 2005), and precursors to magnetic materials (Sugimoto, 1999).

Besides the abovementioned applications, there has also been considerable interest in using LDHs to remove environmental contaminants since environmental protection has emerged as an important issue in the recent decades. Significant progress has been achieved in the research and development of LDH application in environmental protection, such as their use as environmental catalysts in removing organic and inorganic wastes (Corma et al., 1997; Shannon et al., 1997; Kannan, 1998; Kannan and Swamy, 1999; Palomares et al., 1999; Pérez-Ramírez et al., 1999; Palomares et al., 2004; Rahman et al., 2004). LDHs have also been used as a novel membrane-like materials to partition pyrene from a methanol-water solution containing the polycyclic aromatic hydrocarbon (Dutta and Robins, 1994). Indeed, increasing interest has recently been diverted to evaluating the ability of LDHs to remove inorganic contaminants such as oxyanions (e.g. arsenite, arsenate, chromate, phosphate, selenite, selenate, borate, etc.) and monoatomic anions (e.g. fluoride, chloride, bromide, and iodide) from aqueous solutions by the process of adsorption and ion exchange. This is because LDHs have exhibited a great potential to efficiently remove harmful oxyanions attributing to their superior characteristics as mentioned in the preceding discussion.

The following review presents several aspects of LDHs, i.e. their composition and structure, synthesis, and characterization, with specific emphasis on their ability to sorb oxyanions from aqueous solution. Most of the studies cited in this review have been conducted under controlled experimental conditions. Several factors that play important roles in the sorption process such as pH, competitive anions, temperature, LDH particle size, etc. have also been systematically reviewed. In general, this review

focuses on the following issues that arise: (1) the extent to which the sorption efficiencies of LDHs can be achieved under specific conditions, (2) the recyclability of LDHs that can be attained by various desorption and regeneration methods and the possible ways for recovery of the oxyanions, (3) the mechanisms that are responsible for the sorption and desorption of oxyanions on LDHs, and (4) the main concerns and suggested solutions with regard to the practical application of LDHs in water and wastewater treatments, e.g. stability of LDHs, physical form of LDHs, separation of LDHs, etc.

2.6 Composition and structure of LDHs

LDHs are a class of two-dimensional nanostructured anionic clays. The structure of LDHs is based on cadmium iodide-type layered hydroxide (e.g., brucite, $\text{Mg}(\text{OH})_2$), where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been isomorphously replaced by trivalent cations, giving positively charged sheets. The net positive charge is compensated by anions in the interlayer region between the brucite-like sheets. Some hydrogen bonded water molecules may occupy the free space in this interlayer (Cavani et al., 1991; Li and Duan, 2005; Evans and Duan, 2006). The structure of LDHs and a typical octahedral unit are depicted in Figure 2.3. The basal spacing (c') is the total thickness of the brucite-like sheet and the interlayer region. The octahedral units of M^{2+} or M^{3+} (sixfold coordinated to OH^-) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding.

LDH Structure **Octahedral Unit**

Figure 2.3 Schematic representation of the LDH structure.

LDHs can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively; the value of x is equal to the ratio of $M^{3+}/(M^{2+}+M^{3+})$, whereas A is the anion of valence n . The identities of M^{2+} , M^{3+} , x , and A^{n-} may be varied over a wide range, thus giving rise to a large class of isostructural materials with varied physicochemical properties (Evans and Duan, 2006). The parent material of these anionic clays is the naturally occurring mineral hydrotalcite which has the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$.

Different stacking arrangements of the brucite-like sheets have been observed. The brucite-like sheets can be either stacked with two layers per unit cell in hexagonal symmetry (manasseite), or with three layers per unit cell in rhombohedral symmetry (hydrotalcite), or in less symmetrical arrangements (Carrado et al., 1988). In general,

LDHs of rhombohedral symmetry have mainly been found. M^{2+} (Mg^{2+} , Fe^{2+} , Co^{2+} , etc.) and M^{3+} (Al^{3+} , Cr^{3+} , Fe^{3+} , etc.) ions that have similar ionic radius to that of Mg^{2+} can be accommodated in the holes of the close packed configuration of OH groups in the brucite-like sheets to form LDHs. In addition, LDHs containing more than two species of the second cation have been reported (Nunan et al., 1989; Kooli et al., 1995). Another class of LDHs, which contains monovalent and trivalent matrix cations such as $[LiAl_2(OH)_6]^+A^-\cdot mH_2O$, has also been prepared (Besserguenev et al., 1997; Nayak et al., 1997; Williams et al., 2004; Kottegoda and Jones, 2005). The charge density and the anion exchange capacity (number and arrangement of the charge balancing anions in the interlayer) of the LDHs may be controlled by varying the M^{2+}/M^{3+} ratio. The most common anion found in the natural occurring LDHs is carbonate. In practice, however, a broad spectrum of charge-balancing anions may be incorporated, namely halides, oxyanions, silicates, polyoxometalate anions, complex anions, and organic anions (Newman and Jones, 1998).

2.7 Synthesis of LDHs

LDHs can be considered as a class of materials that are simple to synthesize in the laboratory, although not always as pure phases. In general, there are several approaches to prepare LDHs. Recently, a thorough review has been prepared by He et al. (2005) on the preparation of LDHs.

The simplest and most commonly used method is coprecipitation method. In this method, aqueous solutions of M^{2+} and M^{3+} containing the anion that is to be incorporated into the LDHs are used as precursors, of which Mg and Al are the most frequently used metal precursors. In order to ensure simultaneous precipitation of two or more cations, it is necessary to carry out the synthesis under conditions of supersaturation. There are generally two types of coprecipitation conditions, namely coprecipitation at low supersaturation and coprecipitation at high supersaturation. Coprecipitation at low supersaturation is performed by slow addition of mixed solutions of divalent and trivalent metal salts in the selected ratio into a reactor containing an aqueous solution of the desired interlayer anion. A second solution of

an alkali is then added into the reactor simultaneously at such a rate as to maintain the desired pH for coprecipitation of the two metallic salts.

Conversely, coprecipitation at high supersaturation requires the addition of a mixed salt solution to an alkaline solution containing the desired interlayer anion. Coprecipitation at high supersaturation generally gives rise to less crystalline materials compared to those with low supersaturation, due to the formation of large number of crystallization nuclei. After precipitation at low and high supersaturation, a thermal treatment process is performed to increase the yields and the crystallinity of the materials. This is followed by an aging process conducted for a period ranging from a few hours to several days (Cavani et al., 1991; He et al., 2005).

A synthesis method of LDHs involving separate nucleation and aging steps has been proposed by Zhao et al. (2002). This method involves a very rapid mixing and nucleation process in a colloid mill, followed by a separate aging process. As compared to the conventional coprecipitation process, this method results in a slightly higher degree of crystallinity of the LDH materials, smaller crystallites with a higher aspect ratio, and a narrower distribution of crystallite sizes, owing to the extreme forces to which the nucleation mixture is subjected in the colloid mill.

A number of studies have reported the synthesis of LDHs using urea hydrolysis method (Costantino et al., 1998; Ogawa and Kaiho, 2002; Oh et al., 2002). The optimum conditions to prepare the LDHs with a good crystal quality in a relatively short time using this method have been suggested to involve dissolving solid urea in a 0.5 M solution of the chosen metal chlorides to give a urea/metal ion molar ratio of 3.3. The compounds prepared using this method display homogeneous sizes and platelet-like primary particles with well-defined hexagonal shapes, which may be very interesting from the viewpoint of nanotechnology since LDHs offer nanosize two-dimensional spaces for the creation of functional materials (Costantino et al., 1998).

LDHs can also prepared by ion exchange method. This method is useful when the coprecipitation method is inapplicable, e.g. when divalent or trivalent metal cations or the anions involved are unstable in alkaline solution. In this method, the guests are

exchanged with the anions present in the interlayer regions of LDHs to produce specific anion pillared LDHs (Morel-Desrosiers et al., 2003). Another common method to produce LDHs is rehydration or reconstruction using structural “memory effect”. This method involves calcination of LDHs to remove the interlayer water, interlayer anions, and the hydroxyl groups, resulting in mixed metal oxides. It is interesting to note that the calcined LDH is able to regenerate the layered structure when they are exposed to water and anions (Marchi and Apesteguía, 1998; Rocha et al., 1999; Erickson et al., 2005). In addition, the anions included need not be the same species originally present in the interlayer of the uncalcined LDHs, and therefore this is an important method to synthesize LDHs with desired inorganic or organic anions to fulfill specific application requirements.

Hydrothermal synthesis method is usually used when organic guest species with low affinity for LDHs are required to be intercalated into the interlayers, and when the ion exchange and coprecipitation methods are not applicable. This method has been shown effective because only the desired organic anions can occupy the interlayer space under the hydrothermal condition since insoluble magnesium and aluminium hydroxides are used as the precursors and other anions are absent (Ogawa and Asai, 2000). In the synthesis of nanoscale LDHs, an innovative aerogel method that produced nanobinary and nanoternary LDHs with enhanced chemical activities has been published (Choudary et al., 2005). The key features of this method are homogenization of metal organic precursors in methanol-toluene mixture, controlled hydrolysis, gelation, hydrothermal treatment, and finally supercritical drying of solvent. The resulted LDHs displayed large surface areas and small particle sizes (Carnes et al., 2002; Choudary et al., 2005). A novel method involving fast coprecipitation followed by controlled hydrothermal treatment under different conditions that produced stable homogeneous nanoscale LDH suspensions has also been reported (Xu et al., 2006a; Xu et al., 2006b).

2.8 Characterization of LDHs

Several techniques have been used to characterize LDHs. The routine analyses that are most frequently used are X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Other routine analyses include thermogravimetry (TG), differential scanning calorimetry (DSC), differential thermal analysis (DTA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Some specific characterization techniques are electron spin resonance (ESR), nuclear magnetic resonance (NMR), X-ray absorption spectroscopy (XAS), Mössbauer spectroscopy, UV/VIS spectroscopy, etc.

X-ray patterns generated by XRD are normally obtained using randomly oriented powdered samples. The typical X-ray patterns of LDHs, as shown in Figure 2.4, contain sharp basal (00 l) reflections at low 2θ values correspond to successive orders of basal spacing c' . On the other hand, relatively weak non-basal reflections are observed at higher values of 2θ . The true c value is a multiple of c' and depends on the layer stacking sequence. The interlayer spacing observed in Figure 2.3 is the difference between basal spacing c' and the brucite-like sheet thickness of about 4.8 Å. The interlayer spacing is always dependent on the size and orientation of the charge balancing anion. The ratio of M^{2+}/M^{3+} of the LDHs may be deduced from the parameter a of the unit cell, which is calculated by the formula $a = 2d(110)$, where $d(110)$ is the d-spacing of the 110 reflection. The measurement of $d(110)$ together with the elemental analysis techniques, allows the prediction of an approximate chemical formula for the LDHs (Cavani et al., 1991; Newman and Jones, 1998).

Figure 2.4 Typical X-ray pattern of LDHs.

FTIR spectroscopy is another useful tool for the characterization of LDHs, involving the vibrations in the octahedral lattice, the hydroxyl groups, and the interlayer anions. These methods can be used to identify the presence of the charge balancing anion in the interlayer, the type of bonds formed by the anions and their orientations (Cavani et al., 1991). Raman spectroscopy can be seen as complementary to infrared spectroscopy and both are often used together to characterize LDHs. The major difference between these two techniques is that Raman spectroscopy depends on the changes in polarizability of molecules, whereas infrared spectroscopy depends on the changes in dipole moments of molecules (Frost, 1996).

The thermal properties of the LDHs are commonly studied using TG, DSC, and DTA, while the morphologies of the LDHs are usually observed by using SEM and TEM. TEM image as illustrated in Figure 2.5 shows that the LDHs are smooth, well-shaped in hexagonal form, and overlapping crystals. For most transition metal ions that have unpaired electrons, the corresponding LDHs can show their own ESR signals. Several transition metal-containing LDHs have been examined by ESR spectroscopy, some investigating the effect of metal substitution in LDHs (Velu et al., 1999), the thermal composition of LDHs (Ukrainczyk et al., 1994; Moujahid et al., 2002), and the arrangement of anions in the interlayer region (Auerbach et al., 2004). NMR spectroscopy has been used to study the protons with very different mobilities in LDHs, monitor the decomposition process of LDHs, examine the dynamic and

structural behavior of interlayer and externally sorbed anions, and identify the coordination of metal cations in LDHs (Auerbach et al., 2004).

Figure 2.5 TEM image of LDHs (Goh et al., 2008).

XAS provides powerful means for assessing the local ordering of the cations in the brucite-like sheet (Intissar et al., 2002), the local ordering of the anions in the interlayer region of LDHs (Evans and Slade, 2005), and the orientation of organic guests in the interlayer region of LDHs. Another specific technique known as Mössbauer spectroscopy has been applied to a range of Fe-containing LDHs, specifically examining the difference in the Fe^{3+} local environment between two types of LDHs and studying the reduction reaction of LDH-derived oxides (Auerbach et al., 2004). A number of studies have reported on the use of UV/VIS spectroscopy in the characterization of LDHs, e.g. Roussel et al. (2001) used UV/VIS spectroscopy to examine the formation of LDHs while Velu et al. (1999) utilized UV/VIS spectroscopy to investigate the spectral changes with Mn loading in Mn-containing LDHs. Neutron scattering has been used by Kagunya et al. (1998) to investigate the vibrational modes of LDHs and the properties of water sorbed on LDHs.

Other physicochemical methods include elemental analysis, CHNS/O analysis, N_2 adsorption-desorption analysis, and photon correlation spectroscopy (PCS). Very little works have reported on the pH_{pzc} (pH of point of zero charge) and the acid buffer capacity of LDHs. A few published pH_{pzc} values of LDHs have been shown in Table 2.1.

Table 2.1 Reported pH_{pzc} values of LDHs in the literature

Types of LDHs	pH_{pzc}	Method	Reference
Uncalcined Mg/Al LDHs	12.0-12.5	--	Han et al. (1998)
Uncalcined Mg/Fe LDHs	8.9	Particle Charge Detector (PCD-03-pH) by polyelectrolyte titration method	Das et al. (2002)
Uncalcined chloride-Mg/Al/Fe LDHs	10.9-11.1	Potentiometric Titration	Li et al. (2003a)
Uncalcined Mg/Fe LDHs	8.7	Particle Charge Detector (PCD-03-pH) by polyelectrolyte titration method	Das et al. (2004)
Uncalcined chloride-Li/Al LDHs	7.2	Malvern Zetasizer 3000	Liu et al., (2006)
Uncalcined chloride-Zn/Al LDHs	10.4-11.0	Potentiometric Titration	Jiao and Hou (2007)
Uncalcined chloride-Zn/Al/Fe LDHs	9.3-10.0	Potentiometric Titration	Jiao and Hou (2007)

2.9 Sorption of oxyanions on LDHs

Besides the large surface area and high anion exchange capacity of LDHs, their flexible interlayer region that is accessible to anionic species as well as polar molecular species is another important feature promising their high removal efficiencies of contaminants. In general, three different mechanisms have been proposed to control the removal of contaminants from aqueous medium to the LDHs, namely surface adsorption, interlayer anion exchange, and reconstruction of calcined LDH precursors by the memory effect (Li and Duan, 2005). The surface adsorption involves the adhesion of the contaminants to the surface of LDHs, thus allowing the formation of a molecular or atomic film. The anion exchange process of LDHs is

mainly influenced by the charge-balancing anions in the interlayer and the layer charge density. The memory effect of LDHs will be discussed in greater detail in subsequent section since it is one of their most attractive features as a sorbent. In the past few years, many reports on the sorption of various contaminants on LDHs have been published. The contaminants include oxyanions (Kang et al., 1999; Toraishi et al., 2002; Zhang and Reardon, 2003; Wang et al., 2006b; Yang et al., 2006; Ay et al., 2007), monoatomic anions (Liu et al., 2006a; Lv et al., 2006a; Lv et al., 2006b; Paredes et al., 2006), cations (Lehmann et al., 1999; Seida et al., 2001; Lazaridis, 2003), organics (Zhu et al., 2005; Bruna et al., 2006; Li et al., 2006), and gas (Cantu et al., 2005; Ritter et al., 2005).

Thus far, the oxyanions investigated are arsenite, arsenate, chromate, dichromate, phosphate, selenite, selenate, borate, nitrate, perrhenate, pertechnetate, iodate, molybdate, and vanadate. Table 2.2 shows the ionic radius of various oxyanions. The ionic radius of the oxyanions listed fall in the range of 0.19-0.26 nm. The ion exchange would reach its maximum when the interlayer region is large enough for the oxyanions to fit into the region for exchange process. The list of oxyanions which have been investigated for their sorption characteristics with various LDHs is presented in Table 2.3.

Table 2.2 Ionic radius of various oxyanions

Oxyanion	Ionic radius (nm)	Reference
Arsenite (AsO_2^-)	0.211	David (2003)
Arsenate (AsO_4^{3-})	0.248	Gmelin (1954); Wilkinson et al. (1987)
Borate (BO_3^{3-})	0.191	Claude (2004)
Bromate (BrO_3^-)	0.214	David (2003)
Chlorate (ClO_3^-)	0.208	David (2003)
Carbonate (CO_3^{2-})	0.189	David (2003)
Chromate (CrO_4^{2-})	0.240	Gmelin (1954); Wilkinson et al. (1987)
Iodate (IO_3^-)	0.218	David (2003)
Molybdate (MoO_4^{2-})	0.246	Gmelin (1954); Wilkinson et al. (1987)
Nitrate (NO_3^-)	0.200	David (2003)
Perchlorate (ClO_4^-)	0.240	Moyer and Bonnesen (1997)
Perrhenate (ReO_4^-)	0.260	Stephan et al. (2004)
Pertechnetate (TcO_4^-)	0.252	Stephan et al. (2004)
Phosphate (PO_4^{3-})	0.238	Gmelin (1954); Wilkinson et al. (1987)
Selenite (SeO_3^{2-})	0.239	Claude (2004)
Selenate (SeO_4^{2-})	0.243	Stephan et al. (2004)
Sulfate (SO_4^{2-})	0.230	Gmelin (1954); Wilkinson et al. (1987)
Vanadate (VO_4^{3-})	0.260	Jenkins and Thakur (1979)

Table 2.3 List of oxyanions investigated for their sorption characteristics with various LDHs

Oxyanion	Types of LDHs	Reference
Arsenite	Uncalcined carbonate-LDHs	Manju and Anirudhan (2000)
Arsenite	Uncalcined chloride-LDHs, uncalcined carbonate-LDHs, and calcined LDHs	You et al. (2001b)
Arsenite	Uncalcined and calcined Mg/Al LDHs	Yang et al. (2005)
Arsenite	Calcined Mg/Al LDHs and calcined Mg/Fe LDHs	Ye et al. (2005)
Arsenite	Uncalcined nitrate-LDHs, uncalcined chloride-LDHs, and uncalcined carbonate-LDHs	Gillman (2006)
Arsenite	Uncalcined and calcined Mg/Al LDHs	Shibata and Murayama (2006)
Arsenate	Calcined Mg/Al LDHs	Kovanda et al. (1999)
Arsenate	Uncalcined and calcined Mg/Al LDHs	Lazaridis et al. (2002); Doušová et al. (2003); Bhaumik et al. (2005)
Arsenate	Uncalcined Mg/Al LDHs	Bryan et al. (2003)
Arsenate	Uncalcined and calcined Mg/Fe/Al LDHs	Carja et al. (2005)
Arsenate	Uncalcined Mg/Al LDHs	Kiso et al. (2005); Peng et al. (2005); Romanova et al. (2005)
Arsenate	Uncalcined and calcined Mg/Al LDHs	Yang et al. (2005)
Arsenate	Uncalcined nitrate-LDHs, uncalcined chloride-LDHs, and uncalcined carbonate-LDHs	Gillman (2006)
Arsenate	Uncalcined chloride-Li/Al LDHs	Liu et al., (2006)

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Oxyanion	Types of LDHs	Reference
Arsenate	Uncalcined and calcined Mg/Al LDHs	Shibata and Murayama (2006)
Arsenate	Conditioned calcined Mg/Al LDHs	Yang et al. (2006)
Arsenate	Uncalcined and calcined Mg/Fe LDHs	Carja et al. (2008)
Arsenate	Calcined carbonate-Mg/Al LDHs	Dadwhal et al. (2009)
Arsenate	Uncalcined chloride-Mg/Al LDHs and uncalcined carbonate-Mg/Al LDHs	Violante et al. (2009)
Arsenate	Uncalcined nitrate-Mg/Al LDHs	Wang et al. (2009b)
Chromate	Calcined Mg/Al LDHs	Rhee et al. (1997); Lazaridis and Asouhidou (2003); Martinez-Gallegos and Bulbulian (2004)
Chromate	Uncalcined and calcined Mg/Al, Ni/Al, and Zn/Cr LDHs	Goswamee et al. (1998)
Chromate	Uncalcined chloride-Zn/Al LDHs	Houri et al. (1998)
Chromate	Uncalcined chloride-Mg/Al, chloride-Zn/Al, and chloride-Zn/Cr LDHs	Houri et al. (1999)
Chromate	Calcined Mg/Al LDHs	Kovanda et al. (1999)
Chromate	Uncalcined Mg/Al LDHs (commercial)	Lehmann et al. (1999); Terry (2004)
Chromate	Uncalcined carbonate-Mg/Al LDHs	Manju et al. (1999); Chen et al. (2004); Lazaridis et al. (2004)
Chromate	Uncalcined and calcined Mg/Al LDHs	Lazaridis et al. (2001); Ye et al. (2004); Alvarez-Ayuso and Nugteren (2005); Bakhti and Ouali (2005); Shibata and Murayama (2006)

Oxyanion	Types of LDHs	Reference
Chromate	Uncalcined hydroxide-Ca/Al LDHs and carbonate-Ca/Al LDHs	Zhang and Reardon (2003)
Chromate	Uncalcined Mg/Fe LDHs	Das et al. (2004)
Chromate	Uncalcined and calcined Zn/Al/Zr and Mg/Al/Zr LDHs	Das et al. (2004b)
Chromate	Uncalcined and calcined Mg/Al LDHs	Martinez-Gallegos et al. (2004)
Chromate	Uncalcined Ni/Fe LDHs	Prasanna et al. (2006)
Chromate	Uncalcined Li/Al LDHs	Wang et al. (2006b)
Phosphate	Uncalcined and calcined Mg/Al LDHs	Shin et al. (1996); Lazaridis (2003); Bakhti and Quali (2006)
Phosphate	Uncalcined chloride-Zn/Al LDHs	Badreddine et al. (1999)
Phosphate	Uncalcined Mg/Fe and Ca/Fe LDHs	Seida and Nakano (2001); Seida and Nakano (2002)
Phosphate	Uncalcined Mg/Al LDHs	Kameda et al. (2002); Nomura et al. (2003); Frost et al. (2006)
Phosphate	Uncalcined and calcined Mg/Mn LDHs	Tezuka et al. (2004a)
Phosphate	Calcined Mg/Mn LDHs	Chitrakar et al. (2005)
Phosphate	Uncalcined Mg/Al, Mg/Fe, and Ni/Fe LDHs	Chitrakar et al. (2006)
Phosphate	Uncalcined and calcined Mg/Al, Zn/Al, Ni/Al, Co/Al, Mg/Fe, Zn/Fe, Ni/Fe, and Co/Fe LDHs	Das et al. (2006)
Phosphate	Uncalcined Mg/Al LDHs (commercial)	Kuzawa et al. (2006)
Selenite	Uncalcined chloride-Mg/Al and chloride-Zn/Al LDHs	You et al. (2001a)

Oxyanion	Types of LDHs	Reference
Selenite	Uncalcined Mg/Fe LDHs	Das et al. (2002)
Selenite	Uncalcined carbonate-Mg/Al LDHs (commercial)	Tsuji (2002)
Selenite	Uncalcined and calcined Zn/Al/Zr and Mg/Al/Zr LDHs	Das et al. (2004b)
Selenite	Uncalcined and calcined Mg/Al LDHs	Yang et al. (2005)
Selenite	Uncalcined and calcined Mg/Al LDHs	Shibata and Murayama (2006)
Selenite	Uncalcined Mg/Al, Zn/Al, and Zn/Fe LDHs	Mandal et al. (2009)
Selenate	Uncalcined chloride-Mg/Al and chloride-Zn/Al LDHs	You et al. (2001a)
Selenate	Uncalcined Mg/Al LDHs	Bryan et al. (2003)
Selenate	Uncalcined hydroxide-Ca/Al LDHs and carbonate-Ca/Al LDHs	Zhang and Reardon (2003)
Selenate	Uncalcined and calcined Mg/Al LDHs	Yang et al. (2005)
Borate	Uncalcined hydroxide-Ca/Al LDHs and carbonate-Ca/Al LDHs	Zhang and Reardon (2003)
Borate	Uncalcined Mg/Al and Mg/Fe LDHs	Ferreira et al. (2005; 2006)
Borate	Uncalcined and calcined Mg/Al LDHs	Shibata and Murayama (2006)
Borate	Uncalcined and calcined nitrate-Mg/Al LDHs	Ay et al. (2007)
Nitrate	Uncalcined chloride-Mg/Al, Co/Fe, Ni/Fe, and Mg/Fe LDHs	Tezuka et al. (2004b)
Nitrate	Uncalcined chloride-Ni/Fe LDHs	Tezuka et al. (2005)
Nitrate	Uncalcined Zn/Al LDHs	Frost and Musumeci (2006)
Perrhenate	Uncalcined Mg/Al LDHs	Kang et al. (1996)

Oxyanion	Types of LDHs	Reference
Perrhenate	Calcined Mg/Al LDHs	Kang et al. (1999)
Perrhenate	Uncalcined Mg/Al LDHs	Bryan et al. (2003)
Pertechnetate	Uncalcined Mg/Al LDHs	Kang et al. (1996)
Pertechnetate	Calcined Mg/Al LDHs	Kang et al. (1999)
Pertechnetate	Uncalcined M(II)-M(III) LDHs; M(II)=Co, Ni, Cu, Fe, Cd, Pd, and Mn, and M(III)=Al, Fe, Cr, V, Y, Yb, La, Ga, and Bi	Wang and Gao (2006)
Iodate	Uncalcined carbonate-Mg/Al LDHs (commercial) and nitrate-Mg/Al LDHs	Toraishi et al. (2002)
Molybdate	Uncalcined hydroxide-Ca/Al LDHs and carbonate-Ca/Al LDHs	Zhang and Reardon (2003)
Vanadate	Calcined Mg/Al LDHs	Kovanda et al. (1999)

2.9.1 Sorption isotherms and sorption capacities

Sorption isotherm is pivotal to the design of sorption systems because it describes how sorbates interact with sorbents and this information is essential in optimizing the use of sorbents. Table 2.4 summarizes the reported sorption capacities of LDHs for various oxyanions in the single-oxyanion aqueous system. The affinities of LDHs for oxyanions can be generally grouped into the following ranges: 0.1-87.5 mg/g LDHs for arsenite (as As(III)); 5-615 mg/g LDHs for arsenate (as As(V)); 9-160 mg/g LDHs for chromate (as Cr(VI)); 7.3-81.6 mg/g LDHs for phosphate (as P); 29-270 mg/g LDHs for selenite (as Se); 14-20 mg/g LDHs for borate (as B); and 2.3-4.6 mg/g LDHs for nitrate (as N). The common sorption isotherms employed to represent equilibrium LDHs-oxyanion sorption data follow the order of Langmuir > Freundlich > Modified Langmuir > Redlich-Peterson ~ Sips.

It is also evident from Table 2.4 that the oxyanion sorption on LDHs is strongly influenced by the calcination process during LDH synthesis. For example, the sorption of arsenate increases from 105 mg/g to 615 mg/g when LDHs are calcined

(LDH dosage = 1 g/L) (Lazaridis et al., 2002; Kiso et al., 2005). For chromate, the sorption capacities of the calcined LDHs (LDH dosage ranging from 1 to 10 g/L) are generally reported as more than 50 mg/g (Goswamee et al., 1998; Lazaridis et al., 2001; Lazaridis and Asouhidou, 2003; Martinez-Gallegos et al., 2004; Ye et al., 2004; Alvarez-Ayuso and Nugteren, 2005), whereas the chromate sorption capacities of the uncalcined LDHs (LDH dosage ranging from 1 to 4 g/L) are usually reported as less than 25 mg/g (Houri et al., 1998; 1999; Manju et al., 1999; Lazaridis et al., 2004; Terry, 2004; Alvarez-Ayuso and Nugteren, 2005). In the case of phosphate sorption on LDHs, the calcined LDHs also show generally higher sorption capacities (34-82 mg/g, except one report) than the uncalcined LDHs (29-47 mg/g). The greater sorption capacities of the calcined LDHs may be attributed to their larger surface area of 198-287 m²/g compared to 5-84 m²/g for the uncalcined LDHs.

Table 2.4 Sorption characteristics of various oxyanions with LDHs

Oxyanion	Types of LDHs (calcination temperature in parenthesis)	Synthesis method ^a	Surface area (m ² /g)	Sorption capacity (mg/g); isotherm ^b	C ₀ (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model ^c	Reference
Arsenite	Uncalcined carbonate-LDHs			L	75	pH 8.5; room Room		F	Manju and Anirudhan (2000)
Arsenite	Calcined Mg/Fe LDHs	C		87.5					Ye et al. (2005)
Arsenite	Uncalcined chloride-LDHs	C		0.086 ^d	0.432 ^d		1:200		Gillman (2006)
Arsenate	Calcined Mg/Al LDHs (450 °C)			L		Neutral; 20			Kovanda et al. (1999)
Arsenate	Uncalcined Mg/Al LDHs	C		32.6; R-P, L, F	10-70	Natural; 30	1:1000		Lazaridis et al. (2002)
Arsenate	Calcined Mg/Al LDHs (500 °C)	C		615; R-P, L, F	50-700	Natural; 30	1:1000		Lazaridis et al. (2002)
Arsenate	Calcined Mg/Al LDHs (450 °C)	C		99.6 ^d	149.8 ^d	Neutral; 20	1:1000		Doušová et al. (2003)
Arsenate	Calcined Mg/Fe LDHs (450 °C; high N ₂ flow)	C	287.4	202 ^d	206 ^d	pH 6.5; 25	1:1000		Carja et al. (2005)
Arsenate	Uncalcined chloride-Mg/Al LDHs			105; ML		Neutral			Kiso et al. (2005)
Arsenate	Uncalcined Mg/Al LDHs	H		F				LP-S	Peng et al. (2005)
Arsenate	Calcined Mg/Al LDHs (500 °C)	C	198	5.609 ^d ; F, L	0.01-0.2 ^d	pH 4.2-5.4; 25	1:8333	M	Yang et al. (2005)
Arsenate	Uncalcined chloride-Li/Al LDHs	C	18.8	24.2 ^d ; L	3-150 ^d	pH 5	1:400		Liu et al. (2006)
Arsenate	Calcined Mg/Al LDHs (500 °C, conditioned)	C and CO		~5.25 ^d ; S	0.06-0.3 ^d	pH ~6.7; 25	1:25000		Yang et al. (2006)

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Oxyanion	Types of LDHs (calcination temperature in parenthesis)	Synthesis method ^a	Surface area (m ² /g)	Sorption capacity (mg/g); isotherm ^b	C ₀ (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model ^c	Reference
Chromate	Calcined Mg/Al LDHs (450 °C)	C		117.7 ^d ; F	0-1570 ^d	Room	1:100	F	Goswamee et al. (1998)
Chromate	Uncalcined chloride- Zn/Al LDHs	C		23.3 ^d	6.7- 134.5 ^d				Houri et al. (1998; 1999)
Chromate	Calcined Mg/Al LDHs (450 °C)			L		Neutral; 20			Kovanda et al. (1999)
Chromate	Uncalcined Mg/Al LDHs (commercial)		34.8	~160	200	pH 4	1:1000		Lehmann et al. (1999)
Chromate	Uncalcined carbonate- Mg/Al LDHs			23.2				F	Manju et al. (1999)
Chromate	Calcined Mg/Al LDHs (500 °C)	C		110	10.4 ^d		1:1000		Lazaridis et al. (2001)
Chromate	Calcined Mg/Al LDHs			120; F			1:1000	P-F, M- S, E F	Lazaridis and Asouhidou (2003)
Chromate	Uncalcined Mg/Fe LDHs	C	62	L		30-60			Das et al. (2004)
Chromate	Calcined Mg/Al/Zr (450 °C)	C	200	24; L	60	pH 6; 30	1:2000		Das et al. (2004b)
Chromate	Uncalcined carbonate- Mg/Al LDHs	C	84	17; F		pH 6; 30	1:1000	S	Lazaridis et al. (2004)
Chromate	Calcined Mg/Al LDHs (500 °C)	C		78 ^d		20	1:200		Martinez-Gallegos et al. (2004)
Chromate	Uncalcined Mg/Al LDHs (commercial)			~9 ^d ; F	5-40	pH 2.0- 2.1; 24	1:250	P-F	Terry (2004)
Chromate	Calcined Mg/Al LDHs			73					Ye et al. (2004)
Chromate	Uncalcined Mg/Al LDHs	C		16.3; L	11-57	Natural; 22	1:500		Alvarez-Ayuso and Nugteren (2005)

Chapter 2

Oxyanion	Types of LDHs (calcination temperature in parenthesis)	Synthesis method ^a	Surface area (m ² /g)	Sorption capacity (mg/g); isotherm ^b	C ₀ (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model ^c	Reference
Chromate	Calcined Mg/Al LDHs (500 °C)	C		128; L	57-448	Natural; 22	1:500		Alvarez-Ayuso and Nugteren (2005)
Chromate	Uncalcined nitrate- Ni/Fe LDHs	H	71.2	93.6 ^d		pH 8.2; 22-25	1:250		Prasanna et al. (2006)
Phosphate	Uncalcined chloride- Mg/Al LDHs			29.2 ^d					Shin et al. (1996)
Phosphate	Uncalcined Ca/Fe LDHs	C		28.8; L	1-1500	pH 8.4	1:2000		Seida and Nakano (2002)
Phosphate	Calcined Mg/Al LDHs (500 °C)	C		81.6 ^d ; S, L, F		pH 7- 7.5; 30	1:4000	LP-F	Lazaridis (2003)
Phosphate	Calcined Mg/Mn LDHs (300 °C)	C and AO		34.1 ^d		pH 8			Tezuka et al. (2004a)
Phosphate	Calcined Mg/Mn LDHs (300 °C)	C		7.3; F	0.3	Room	1:40000		Chitrakar et al (2005)
Phosphate	Calcined Mg/Al LDHs	C		49.6 ^d	2.5-50			F-R	Bakhti and Ouali (2006)
Phosphate	Calcined Mg/Al LDHs	C	210	44; L, F	50	pH 6; 30	1:2500	F	Das et al. (2006)
Phosphate	Uncalcined Mg/Al LDHs (commercial)			47.3; ML		pH 8.6; 25			Kuwaza et al. (2006)
Selenite	Uncalcined Mg/Al LDHs	C		270 ^d ; L	624.1 ^d	pH 9; 25	1:2500		You et al. (2001a)

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Oxyanion	Types of LDHs (calcination temperature in parenthesis)	Synthesis method ^a	Surface area (m ² /g)	Sorption capacity (mg/g); isotherm ^b	C ₀ (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model ^c	Reference
Selenite	Uncalcined Mg/Fe LDHs	C		L		pH 6	1:1000		Das et al. (2002)
Selenite	Calcined Mg/Al/Zr (450 °C)	C	251	29; L		pH 6; 30	1:2000		Das et al. (2004b)
Borate	Uncalcined Mg/Al LDHs	C		~14					Ferreira et al. (2005)
Borate	Uncalcined Mg/Al LDHs	C	5	14; L	0-50	pH 9; 25	1:400		Ferreira et al. (2006)
Borate	Uncalcined nitrate- Mg/Al LDHs	C	17.3	~20		pH 9; 30	1:83.3		Ay et al. (2007)
Nitrate	Uncalcined chloride- Ni/Fe LDHs	H		2.3 ^d	0.42 ^d	Room	1:1000		Tezuka et al. (2004b)
Nitrate	Uncalcined chloride- Ni/Fe LDHs	H		4.6 ^d ; F	0.56 ^d	Room	1:10000		Tezuka et al. (2005)
Iodate	Uncalcined nitrate- Mg/Al LDHs	C		444.2 ^d		25	1:100		Toraishi et al. (2002)

Note: All studies are performed in batch mode; All concentrations are defined as elemental concentration; C₀ = Initial concentration; S/L = Solid/Liquid.

^aSynthesis method: C, coprecipitation; H, hydrothermal; CO, conditioned; AO, air oxidation.

^bIsotherm (arranged in descending order in terms of ‘best-fit’ in the table): L, Langmuir; F, Freundlich; R-P, Redlich–Peterson; ML, Modified Langmuir; S, Sips/ Langmuir-Freundlich.

^cKinetic model (arranged in descending order in terms of ‘best-fit’ in the table): F, first-order kinetics; P-F, pseudo-first-order kinetics; F-R, first-order reversible kinetics; LP-F, Lagergren pseudo-first-order kinetics; LP-S, Lagergren pseudo-second-order kinetics; M-S, modified second-order kinetics; S, second-order kinetics; E, Elovich kinetics; M, *m*th-order kinetics (Yang et al., 2005).

^dCalculated from the publication.

2.9.2 Sorption kinetics and diffusion-controlled models

A few studies have reported on the time-dependent sorption of arsenite and arsenate on LDHs (You et al., 2001b; Lazaridis et al., 2002; Yang et al., 2005). Although the initial arsenate sorption process by uncalcined and calcined LDHs was fairly fast, it took 2-3 d to completely reach equilibrium (Yang et al., 2005). A similar phenomenon was observed for the arsenite sorption on calcined LDHs, whereby the sorption only reached a quasi-equilibrium after 20 h (You et al., 2001b). However, the arsenate sorption on uncalcined LDHs only needed about 8 h to reach equilibrium according to Lazaridis et al. (2002).

The chromate sorption on LDHs was a rapid process according to several reported studies (Das et al., 2004b; Alvarez-Ayuso and Nugteren, 2005; Bakhti and Ouali, 2005). For chromate sorption on calcined LDHs, an equilibrium time at 20 min and 2 h have been reported by Bakhti and Ouali (2005) and Das et al. (2004b), respectively. The chromate sorption on uncalcined LDHs has been found to reach equilibrium within 1 h, for various chromate dosages (Alvarez-Ayuso and Nugteren, 2005).

The studies investigating phosphate and selenite sorption have shown that 70% of phosphate was sorbed by calcined LDHs within 1 d and the sorption only reached equilibrium after 3 d (Chitrakar et al., 2005) whereas selenite sorption by uncalcined LDHs was a rapid process, and the sorption equilibrium time increased with the selenite loading (You et al., 2001a). The sorption of boron on LDHs was relatively fast initially and then saturation was gradually reached after a few hours (Ferreira et al., 2006; Ay et al., 2007).

In general, most of the time-dependent sorption studies have shown a fast initial oxyanion sorption by LDHs followed by a slower process to reach complete equilibrium. Three mechanisms are believed to be involved during the oxyanion sorption by LDHs, i.e. (i) external mass transfer such as boundary layer/film diffusion between the external surface of the sorbent particles and the surrounding fluid phase; (ii) intraparticle transport within the particle; and (iii) sorption (reaction at phase boundaries).

Among the models used to analyze the experimental results of oxyanion sorption by LDHs, first-order kinetics and pseudo-first-order-kinetics are the most widely used (Table 2.4). Besides these models, diffusion-controlled models such as Homogeneous Diffusion Model (HDM) and Shrinking Core Model (SCM) have been used by Lazaridis et al. (2004) to describe chromate sorption and desorption kinetics on LDHs. Classical Homogeneous Surface Diffusion Model (HSDM) and Bidisperse Pore Model (BPM) have been utilized by Yang et al. (2006) to describe the sorption kinetics of arsenate on LDHs. When HSDM is used to fit the experimental kinetic data, the estimated diffusivity values are dependent on the particle size. On the other hand, when BPM is applied to the same data, it predicts an intracrystalline diffusivity, which is invariable with the particle size.

Apparently, a variety of kinetic models seem to be possible if they are determined empirically such as curve fitting through experimental data. One should note that the merit of the fit is purely mathematical, and can be influenced by random errors in data acquisition and artifacts in the sorption experiments. Besides, another possible cause for the discrepancies in the proposed kinetic models among the published literature is that some researchers might pre-qualify a few possible kinetic models, and derived the most possible one merely on the basis of curve fitting.

To avoid obtaining the “disguised kinetic models”, the time-dependent sorption experiment must be rigorously conducted with good protocol of quality control, and the experimental system has to be well defined. Future study should also pay adequate attention on factors that can mask the observed kinetics, especially the mass-transfer processes. Therefore, one must always ascertain that the experimental data are free of external mass transport limitations by providing sufficient solid-to-liquid ratio and agitation during sorption equilibration. Data analysis should be done on adequate set of data, and with mechanistic examination of the sorption process when suggesting representative kinetic model.

2.9.3 Factors affecting sorption of oxyanions on LDHs

There are several factors that can influence oxyanion sorption by LDHs, as outlined in the following reviews.

2.9.3.1 pH

The pH effect on the oxyanion sorption by LDHs is dependent on the types of oxyanions and the types of LDHs. In general, the sorption of oxyanions such as arsenate, chromate, phosphate, and selenite by LDHs tends to decrease with increasing pH, with a few exemptions reported in the published literature. The surface of the LDHs is negatively charged when $\text{pH} > \text{pH}_{\text{pzc}}$. Therefore, in the higher pH range, the oxyanions will be repelled by the LDH surface. For $\text{pH} < \text{pH}_{\text{pzc}}$, the LDH surface is positively charged, favoring sorption of the oxyanions. However, at a very low pH, i.e. $\text{pH} \ll \text{pH}_{\text{pzc}}$, the stability of the LDH structures is impaired and this decreases the oxyanion sorption. At a higher pH ($\text{pH} \gg \text{pH}_{\text{pzc}}$), the oxyanion sorption may be affected due to the increasing competitive effect of OH^- for sorption on LDHs.

The arsenate sorption on uncalcined chloride-Li/Al LDHs has been reported as sensitive to changes in pH between 4 and 7 (Liu et al., 2006) whereas arsenate and selenite sorption on uncalcined Mg/Al LDHs could be sensitive to changes in a wider pH range of 2-11 (Yang et al., 2005). For chromate sorption on uncalcined Mg/Al LDHs, a few studies have discovered that high sorption occurred at about pH 2 (Manju et al., 1999; Terry, 2004), whereas low sorption observed at pH values higher or lower than 2 (Terry, 2004). However, another study carried out on chromate has reported that high chromate sorption by uncalcined carbonate-Mg/Al LDHs was favored at pH 6 (Lazaridis et al., 2004). The decline of chromate sorption by LDHs with increasing pH was found to be independent of chromate speciation (Das et al., 2004a; Das et al., 2004b).

Phosphate removal by LDHs has been reported to reach maximum at pH 5 by Das et al. (2006) and pH 7–9 by others (Kameda et al., 2002; Chitrakar et al., 2005). The removal of phosphate by LDHs was also studied from the viewpoint of the pH buffering effect by Seida and Nakano (2001; 2002). They revealed that the pH buffering effect of LDHs worked effectively to enhance the phosphate removal through dissolution-coagulation and/or dissolution-precipitation process.

A significant selenite sorption by uncalcined Mg/Fe LDHs was observed even at $\text{pH} \geq \text{pH}_{\text{pzc}}$, which indicated that the interaction between the surface sites and selenite was not necessarily of the electrostatic type alone; rather it was a combined effect of both chemical and electrostatic in nature (Das et al., 2002). Two different phenomena were discovered for the pH influence on nitrate sorption by uncalcined LDHs, (i) sorption was nearly constant over a pH range between 5 and 10 (Tezuka et al., 2004b); and (ii) sorption reached maximum at pH 8, with low sorption in the regions outside pH 6-9 (Tezuka et al., 2005). The sorption of boron on uncalcined Mg/Al and Mg/Fe LDHs was pH independent according to Ferreira et al. (2006).

The discrepancies on the reported pH influences on oxyanion sorption may be due to several reasons. One important reason is improper pH control throughout the sorption equilibration period, and another reason is pH adjustment whereby complimentary anions (chloride, nitrate, and sulfate) of the added acid may influence the sorption of oxyanions of interest especially when pH has to be adjusted to less than 5. For example, to adjust pH to 3 from the initial pH 8 for LDHs, one would have to introduce at least 10^{-3} M of the complementary anions of the acid added; a greater amount would be added in most cases to overcome the acid buffering capacity of LDHs. The interference arising from sorption competition might not be taken into consideration by some of the previous investigators when they reported their results. In addition, some of the reported sorption studies using LDHs did not indicate clearly whether the pH values shown were initial pH or the equilibrium pH, and whether pH was maintained throughout the sorption equilibration period.

2.9.3.2 Competitive anions

There are many published literature reporting on the effects of competitive anions on oxyanion sorption by LDHs, and anion affinity or anion intercalation capability of LDHs (Goswamee et al., 1998; You et al., 2001a; You et al., 2001b; Das et al., 2004a; Tezuka et al., 2004a; Kiso et al., 2005; Yang et al., 2005; Das et al., 2006).

The effects of competing anions on arsenite sorption by LDHs were found to reduce in the order $\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$ (You et al., 2001b),

while the interfering effects of competing anions on arsenate sorption by LDHs were reported to follow the order $\text{HCO}_3^- > \text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$ (Kiso et al., 2005) and $\text{HPO}_4^{2-} > (\text{HCO}_3^- \text{ and } \text{CO}_3^{2-}) > \text{SO}_4^{2-} > \text{NO}_3^-$ (Yang et al., 2005). Yang et al. (2005) observed that the competing ions had stronger effect on the arsenate sorption on the uncalcined LDHs than on the calcined LDHs. For selenite sorption on uncalcined chloride-Mg/Al LDHs, the effects of competing anions were reported to follow the order $\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^-$ (You et al., 2001a; Yang et al., 2005). Sorption behavior of chromate in the presence of various competing anions has been also studied (Goswamee et al., 1998; Das et al., 2004a). For example, the amount of chromate released from LDHs by different competing anions followed the order $\text{CO}_3^{2-} > \text{Cl}^- > \text{water}$ (Goswamee et al., 1998). In the phosphate sorption by LDHs, the divalent anions were observed to have a profound interfering effect compared to the monovalent anions (Das et al., 2006).

A few studies have been carried out to investigate the effect of seawater matrix on the oxyanion sorption by LDHs (Tezuka et al., 2004a; Tezuka et al., 2004b; Chitrakar et al., 2005). The results showed that the calcined Mg/Mn LDHs and the uncalcined Ni/Fe LDHs had remarkably high selectivity for the sorption of phosphate (Chitrakar et al., 2005) and nitrate (Tezuka et al., 2004b; 2005) despite the existence of overwhelming Cl^- , SO_4^{2-} , and CO_3^{2-} in the seawater.

Overall, it could be deduced from the published literature that the anions of higher valence have a more significant interfering effect than the monovalent anions in the sorption of oxyanions by LDHs. Among the divalent anions, HPO_4^{2-} appears to be the most competitive anion that retards the sorption of other oxyanions by LDHs. Unfortunately most of the studies investigating the effects of competing anions on oxyanion sorption by LDHs have not reported the pH of the system, thus the speciation of the competing species existed in the sorption system is not clear.

2.9.3.3 Dosage of sorbent

Applying an optimum dosage of suitable sorbent for sorbate removal in a batch sorption system is crucial for its cost-effective application. A dose of 2 g/L calcined Mg/Al LDHs was reported sufficient to reach the maximum percentage removal

(99.5%) for chromate concentrations in the range of 57-239 mg/L, while for the higher concentrations of chromate (351 and 448 mg/L), a dose of 5 g/L was required to reach maximum percentage removal of 97.5% (Alvarez-Ayuso and Nugteren, 2005). In another study, at least 4 g/L of uncalcined Mg/Al LDHs was found to be required for maximum chromate removal of 96% from an initial concentration of 5 mg/L and 20 mg/L (Terry, 2004). The effect of LDH dosage on boron sorption has also been investigated (Ferreira et al., 2006; Ay et al., 2007). The amount of boron sorbed from an initial concentration of 18 mg/L reached a maximum sorption at around 92% when 2.5 g/L uncalcined Mg/Al LDHs was used (Ferreira et al., 2006). At a high initial boron concentration of 250 mg/L, the maximum sorption (> 95%) was achieved at a rather high dose of 12 g/L uncalcined nitrate-Mg/Al LDHs (Ay et al., 2007).

2.9.3.4 Temperature

A change in temperature will change the equilibrium capacity of the sorbent for particular sorbate. Usually, the sorbate uptake decreases with increasing temperature due to the exothermic nature of the simple sorption reaction. The arsenate sorption on both calcined and uncalcined LDHs was reported as an exothermic process (Yang et al., 2005). Das et al. (2006) observed that the percentage of phosphate sorption by calcined Mg/Al LDHs decreased with increasing temperature from 30 °C to 60 °C. The negative value of ΔH° obtained confirmed the exothermic nature of sorption. The positive value of ΔS° reflected the affinity of LDHs toward phosphate in aqueous medium and suggested some structural changes in the sorbate and sorbent. In the case of selenite removal by uncalcined Mg/Fe LDHs, the sorption process was also observed as exothermic (Das et al., 2002).

However, a number of studies have reported that the sorption of oxyanions by LDHs appeared to be an endothermic process (Das et al., 2004a; Chitrakar et al., 2005; Tezuka et al., 2005; Yang et al., 2005). Examples of reported endothermic processes are sorption of selenite on calcined carbonate-Mg/Al LDHs (Yang et al., 2005), phosphate sorption on calcined Mg/Mn LDHs (Chitrakar et al., 2005), and nitrate sorption on uncalcined Ni/Fe LDHs (Tezuka et al., 2005). The endothermic nature could be due to increased reactivity of the surface sites with temperature (Das et al.,

2004). However, it was unclear whether the observed endothermic sorption processes could have been masked by the increased rate of intraparticle diffusion of oxyanions into the pores of LDHs at higher temperatures that gave rise to observed increase in their sorption.

Others have reported insignificant influence of temperature on the oxyanion sorption by LDHs. For example, chromate sorption by the uncalcined Mg/Al LDHs (Terry, 2004) and selenite sorption by the uncalcined carbonate-Mg/Al LDHs (Yang et al., 2005) have been reported as temperature-independent.

2.9.3.5 Nature of precursor metals and crystallinity of LDHs

The nature of the LDH precursor metals including different combinations of the metals, atomic ratio of the metals, metal-metal distance in the brucite-like sheet, etc. and the crystallinity of LDHs can significantly influence the sorption of guest oxyanions. For example, the nature and the content of bivalent and trivalent metal ions in LDHs were found to influence the chromate sorption (Goswamee et al., 1998). In their study, calcined Mg/Al LDHs with higher Al^{3+} content showed higher sorption capacity compared with those with lower Al^{3+} content, while sorption was higher in the calcined Mg/Al LDHs than the calcined Ni/Al LDHs and calcined Zn/Cr LDHs.

According to Wang and Gao (2006), the sorption of pertechnetate on uncalcined LDHs was correlated with the basal spacing $d(003)$ of the materials, which decreased with the radii of both divalent and trivalent cations. The sorption seemed to take place at the edge sites of LDH layers, and it reached a maximum when the layer spacing was just large enough for a pertechnetate to fit into a cage space among three adjacent octahedra of metal hydroxides at the edge. Moreover, the sorption of pertechnetate also increased with the crystallinity of the materials. For a given choice of metal cations and interlayer anions, the best crystalline LDH phase was generally obtained with an $\text{M}^{2+}/\text{M}^{3+}$ ratio of 3:1. The results reported by Wang and Gao (2006) indeed help to establish a general structure–property relationship that will guide engineering LDH materials for removal of a specific oxyanion.

2.9.3.6 Layer charge and interlayer anion charge

It is generally believed that the oxyanion sorption by LDHs can be enhanced by increasing anion exchange capacity of the LDHs. This may be achieved by incorporating more trivalent cations or higher valent cations in the brucite-like sheet which can subsequently increase its net positive charge in the brucite-like sheet (layer charge). Lower chromate sorption capacity of the uncalcined Ni/Fe LDHs was however obtained with a higher layer charge (Prasanna et al., 2006). This was probably due to the higher electrostatic attraction between the A^{n-} species and the brucite-like sheet, causing the A^{n-} species a poorer leaving group during anion exchange process with chromate.

A number of publications have reported the possibility of synthesizing LDHs containing tetravalent cations (Bhattacharyya et al., 1997; Velu et al., 1997; Velu et al., 1998; Velu et al., 1999b; Velu et al., 1999c; Tichit et al., 2002). In particular, incorporation of Zr^{4+} into LDH layers and the sorption of chromate and selenite on Zr^{4+} -incorporated LDHs have been investigated by Das et al. (2004b). They found that Zr^{4+} -incorporated LDHs increased the sorption capacity by up to 20%. Nevertheless, others have suggested that the Zr^{4+} ions may not actually be incorporated in the LDH layers in these materials and that they are in fact mixed phases (Intissar et al., 2003; Intissar et al., 2004). These controversial findings highlight the needs for a comprehensive investigation of the material structure and the corresponding sorption mechanisms. For example, X-ray absorption near edge structure (XANES) and Mössbauer spectroscopies could be used to verify the incorporation of tetravalent cations into the LDH structure.

The charge and species of the interlayer anion can also affect the sorption of guest oxyanions. Prasanna et al. (2006) discovered that carbonate-Ni/Fe LDHs did not exhibit any chromate sorption compared to nitrate-Ni/Fe LDHs. This could be due to the strong electrostatic forces of carbonate attraction to the host lattice, or formation of prismatic interlayer sites that strongly accommodate carbonate ions with their planes parallel to the layers.

2.9.3.7 Calcination and memory effect

Another key factor affecting the oxyanion sorption by LDHs is the calcination and memory effect during the synthesis of LDHs. When LDHs were thermally decomposed below 200 °C, only surface water and interstitial water were lost; between 250 and 450 °C, both carbon dioxide and water from the dehydroxylation were lost (Sato et al., 1986). At 450-500 °C, calcined LDHs would lose their layer structure and form highly active composite metal oxides with high thermal stability, large surface area, basic properties, small crystal size, and high stability against sintering even under extreme conditions (Li et al., 2005). This calcined product can reconstruct its original layer structure with rehydration and sorption of various anions. However, Miyata (1980) cautioned that segregation of the solid solution to spinels would take place at above 800 °C, resulting in incapable reconstruction of LDHs. Overall, the calcination temperature is the key parameter to be controlled in this process. It must be high enough to eliminate most of the carbonate anions, since their presence will inhibit significant incorporation of guest oxyanions, but low enough to permit the layer reconstruction.

Numerous studies have reported that oxyanion sorption by calcined LDHs was considerably higher than the sorption by uncalcined LDHs (Goswamee et al., 1998; Lazaridis et al., 2001; Alvarez-Ayuso and Nugteren, 2005; Carja et al., 2005; Yang et al., 2005). The differences in behavior between calcined and uncalcined LDHs may be linked to several reasons: (i) increased surface area of the calcined products (Carja et al., 2005; Yang et al., 2005); (ii) increased porosity as a result of the calcination process (Lazaridis et al., 2001; Carja et al., 2005); and (iii) fewer carbonate anions in the interlayer of the calcined LDHs than the uncalcined LDHs (Yang et al., 2005).

The significant difference in the sorptive behavior among the calcined and the uncalcined LDHs can also be due to the different mechanisms of the anion sorption. For the calcined material, the sorption mechanism involves the rehydration of mixed metal oxides and concurrent intercalation of oxyanions into the interlayer to reconstruct the LDHs. For the uncalcined material, the sorption process is primarily due to the ion exchange of the interlayer anions.

2.9.3.8 Particle size

LDH particle sizes are commonly not characterized in most of the published research works investigating oxyanion sorption on LDHs. This particular characteristic is indeed an important parameter in diffusion-controlled models. Particle size is also a key consideration for the application of LDHs in flow-through columns, where pressure drops and particle carryover are of concerns.

A few studies have reported that decreasing the particle size of the LDHs has a dramatic effect on the oxyanion sorption rate but not on the oxyanion sorption capacity (Lazaridis et al., 2004; Yang et al., 2006). Examples include arsenate sorption on the calcined Mg/Al LDHs (Yang et al., 2006) and chromate sorption on the uncalcined carbonate-Mg/Al LDHs (Lazaridis et al., 2004). The experiment performed by Yang et al. (2006) showed that arsenate sorption capacity was independent of the LDH particle size (ranging from 53 μm to 300 μm). The relatively higher sorption rate with smaller sorbent particle may be attributed to the fact that smaller particles yield large surface area and require shorter intraparticle diffusion time to reach sorption equilibrium.

2.9.4 Desorption, regeneration, and recovery

The desorption/regeneration of sorbents is the most difficult and expensive part of a sorption technology. It may account for > 70% of the total operating and maintenance cost for a sorption system. A successful desorption/regeneration process should restore the sorbent similar to its initial properties for effective reuse. For sorbates, they can be recovered either for reuse or for proper disposal, depending on their market demand.

2.9.4.1 Desorption

Various alkaline solutions and salt solutions or the mixture of these solutions have been successfully used to desorb oxyanion-loaded LDHs. More than 85% of arsenite and chromate can be desorbed from the uncalcined carbonate-LDHs using 0.1 M NaOH (Manju et al., 1999; Manju and Anirudhan, 2000). The desorption of arsenate

and selenite was dependent on the anion species and their concentrations in the desorbing solutions (Yang et al., 2005). The abilities of various anions to desorb arsenate from calcined Mg/Al LDHs were reported to follow the order $\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$ and $\text{HCO}_3^- > \text{NO}_3^-$, while the order was $\text{SO}_4^{2-} > \text{HPO}_4^{2-} > \text{CO}_3^{2-}$ and $\text{HCO}_3^- > \text{NO}_3^-$ for selenite desorption, which were consistent with their competitiveness in the sorption by LDHs. The sorbed selenite was found to be desorbed completely from uncalcined chloride-Mg/Al LDHs with aqueous carbonate species (You et al., 2001a). The effective desorption of phosphate from the LDHs could be achieved using a mixed solution of NaCl and NaOH (Chitrakar et al., 2005; Kuzawa et al., 2006) and a good phosphate sorption has been exhibited even after seven cycles of the sorption/desorption (Chitrakar et al., 2005).

2.9.4.2 Regeneration

A number of studies have shown that oxyanion-loaded LDHs could be regenerated with chloride and carbonate solutions or with subsequent calcination (Shin et al., 1996; Kovanda et al., 1999; Lazaridis et al., 2004; Bhaumik et al., 2005; Peng et al., 2005; Kuzawa et al., 2006). Lazaridis et al. (2004) showed that chromate-loaded uncalcined LDHs could be fully regenerated by Na_2CO_3 in ~20 min and these regenerated LDHs exhibited consistent sorption capacity over 10 cycles of sorption and desorption. Arsenate-loaded Mg/Al LDHs can also be regenerated by the carbonate solution (Peng et al., 2005). Successful regeneration of LDHs with chloride solutions has been demonstrated by Bhaumik et al. (2005) and Kuzawa et al. (2006). Kuzawa et al. (2006) reported that phosphate-loaded LDHs was effectively regenerated with MgCl_2 solution and the sorption capacity after 10 regenerations was 60% of the initial one.

A few LDH regeneration studies have been performed by incorporating calcination process (Shin et al., 1996; Kovanda et al., 1999). Kovanda et al. (1999) reported that the sorbed oxyanions (arsenate, chromate, and vanadate) were released from the calcined Mg-Al LDHs by anion exchange in a carbonate solution and the LDHs were regenerated with subsequent calcination. The sorption capacity of the LDHs gradually reduced after a few cycles of regeneration. They concluded that the change in the sorption capacity was mainly governed by the ability of the calcined LDHs to regenerate the layered crystal structure during the rehydration process.

2.9.4.3 Recovery of sorbates

Thus far only limited research works have reported on the recovery of oxyanions such as arsenate, phosphate, and chromate from spent LDHs (Gillman, 2006; Kuzawa et al., 2006; Wang et al., 2006b). Gillman (2006) reported that the minute amount of arsenic in the arsenic-loaded LDHs could be easily recovered by saturating arsenic-loaded LDHs with phosphate, in order to convert them into valuable phosphatic fertilizers. Kuzawa et al. (2006) proposed a scheme whereby the desorbed phosphate in the spent desorption solution could be recovered as calcium phosphate precipitate by addition of CaCl_2 , and the remaining spent desorption solution could also be reused after supplementing additional NaOH (Figure 2.6).

Figure 2.6 Schematic diagram of the system for phosphate removal/recovery, regeneration of LDHs, and regeneration of desorption solution (proposed by Kuzawa et al., 2006).

Wang et al. (2006b) showed that chromate could be potentially recovered from chromate-loaded Li/Al LDHs by resuspending them in hot water to enhance simultaneous Li^+ deintercalation from Li/Al LDH structures in aqueous solution and chromate desorption. Through this technique, chromate could be recovered from the solution and the solid product, i.e., gibbsite, could be recycled for further uses.

2.9.5 Mechanistic studies

Mechanistic study of oxyanion sorption is of paramount importance in the understanding of the sorbate-sorbent interaction, which can lead to the optimization of the sorption process and the subsequent desorption/regeneration process. Mechanistic studies of oxyanion sorption by LDHs have been carried out with either assistance of the state-of-the-art analytical equipments, or the postulation from comprehensive experimental observations on sorption characteristics.

For example, Liu et al. (2006) deduced from the EXAFS analysis that the superior arsenate sorption by chloride-Li/Al LDHs was mainly resulted from the additional positive charge brought by the occupation of the Li cations in the vacant octahedral holes within $\text{Al}(\text{OH})_3$, which transformed the surface of $\text{Al}(\text{OH})_3$ layers into active sorption sites. Another example is the application of Raman spectroscopy in identifying the intercalation of phosphate species into the uncalcined LDHs, and exploring the pH effect on the phosphate intercalation into the LDHs (Frost et al., 2006).

Recently, Wang et al. (2006b) developed a mechanistic model to describe the sorption and desorption of chromate on/from chloride-Li/Al LDHs (Figure 2.7) in four steps:

- i. In Step 1, chromate in the solution is sorbed rapidly through ion exchange, and the Cl^- on the surface of LDHs or at the edge of interlayer is replaced by the sorbed chromate.
- ii. In Step 2, the Cl^- at the edge of the interlayer and the Li^+ from the brucite-like sheets start diffusing out to the bulk solution.
- iii. In Step 3, the deintercalation of Li/Al LDHs due to the increasing release of Li^+ results in the desorption of both chromate (on the basal surfaces or/and edges of LDHs) and Cl^- (in the interlayers).
- iv. In Step 4, the desorption rate of the chromate gradually decreases until the reaction reaches equilibrium.

Figure 2.7 A proposed mechanism for the sorption and desorption of chromate in Li/Al LDHs (modified from Wang et al., 2006).

2.9.6 Comparison of the sorption capacity of LDHs with various sorbents

A comparison of the sorption capacity of LDHs with various sorbents is presented in Table 2.5. The sorbents are categorized based on the medium, that is, classifying the sorbents as aluminas, biomaterials, carbon-based materials, clays, iron-based minerals/materials, LDHs, resins, sands, silicas, waste materials, zeolites, and other minerals/materials. Aluminas such as activated alumina, carbon-based materials such as activated carbon, and resins such as Amberlite IRA-743 have been used in commercial scale to remove certain oxyanions.

Direct comparison of LDHs with other sorbents is difficult because of the different experimental conditions (e.g. pH and temperature) and different solution matrices being tested (e.g. surface water, drinking water, real wastewater, and simulated wastewater). Keeping these caveats in mind, several salient generalizations can be drawn:

- i. LDHs have relatively high sorption capacities for most of the commonly found oxyanions as compared to other sorbents. Some sorbents, including carbon-based materials, resins, and silicas have demonstrated outstanding oxyanion sorption capacities, especially for arsenite, arsenate, and borate. Nevertheless, the high production cost of these sorbents will definitely increase the cost for large-scale production. Low-cost sorbents developed from wastes, i.e. fly ash and orange juice residue have also shown remarkable sorption capacities, but only limited for arsenite and arsenate removal.
- ii. The larger surface area of the sorbent may not promise greater oxyanion sorption capacity, as indicated by the performance of activated carbon in arsenate and selenite removal.
- iii. The optimum pH value for most of the other sorbents is relatively low, especially for the sorption of chromate (majority in the range of pH 1-4). It would be an advantage for employing LDHs, if the sorption process occurs at circumneutral pH.

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Table 2.5 Comparative evaluation of LDHs and various sorbents for oxyanion removal

Sorbent	Surface area (m ² /g)	Sorption capacity (mg/g)							C ₀ (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO ₄ ⁻)				
<u>Aluminas</u>												
Activated alumina	116-118	3.5	15.9						0.8-4.9 for As(III); 2.9-11.5 for As(V)	pH 7 for As(III); pH 5.2 for As(V); 25 pH 5.2; 30		Lin and Wu (2001)
Alumina						127.8 ^a						Parida and Gorai (2003)
<u>Biomaterials</u>												
Biomass		13.2							1-10	pH 2; 28		Teixeira and Ciminelli (2005)
Bio-polymeric beads				15.6						pH 5; 28		Sekhar et al. (1998)
Chitosan			58	0.83					86.7 ^a 400	pH 6; 25 pH 4; 25		Baipai et al. (2004)
				11.3		34.5				pH 3 for Cr(VI); pH 4 for Se(VI); 25		Mcafee et al. (2001)
												Qian et al. (2000)
<u>Carbon-based materials</u>												
Activated carbon	522 1210		3.1	186.1					0.025-0.2 5-200	pH 5; 24 pH 3; 40		Chuang et al. (2005)
	1200						1.4		28-100			Khezami and Capart (2005)
Char carbon	36.5	89	34.5						193-992 for As(III); 157-737 for As(V)	pH 2-3; 25		Rajaković and Ristić (1996)
ZnCl ₂ activated coir pith carbon						1.7 ^a			10-40	pH 4; 35	Des. ~50% (after 1 cycle)	Pattanayak et al. (2000)
Bituminous granular activated carbon	925							2.42	2	; 20		Namasivayam and Prathap (2004)
Clays	15.6			13.9						pH 4.6; 25		Chen et al. (2005)
												Bhattacharyya and Gupta (2006)

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Sorbent	Surface area (m ² /g)	Sorption capacity (mg/g)							C ₀ (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO ₄ ⁻)				
<u>Iron-based minerals/materials</u>												
Bead cellulose loaded with iron oxyhydroxide		99.6	33.2							pH 7; 25		Guo and Chen (2005)
Ferrihydrite			68.8						0-150	pH 7		Lafferty and Loeppert (2005)
Goethite	39	22	4						0-60	pH 9; 22		Lenoble et al. (2002)
Haematite		0.2							1-10	pH 2.8-5		Singh et al. (1988)
Hydrous ferric oxide	200	28	7						0-60	pH 9; 22		Lenoble et al. (2002)
Nanoscale zero-valent iron	37.2	2.5								pH 7; 35		Kanel et al. (2005)
Maghemite nanoparticles	178			19.2					5-200	pH 2-3; 25	Des. 87.7% (after 1 cycle)	Hu et al. (2005)
<u>LDHs</u>												
Calcined LDHs		87.5 ¹			26.6 ^{a2}					pH 7-7.5 for PO ₄ ³⁻ ; room for As(III); 30 for PO ₄ ³⁻		¹ Ye et al. (2005); ² Lazaridis (2003)
Nanoscale LDHs			85	61.9					1-50 for As(V); 1-50 for Cr(VI)	pH 9.5; room	Des. ~76% (after 1 cycle); Reg. ~78% (after 1 cycle)	This study
Uncalcined LDHs						270 ^{a1}	~20 ²		624.1 ^a for Se(IV)	pH 9; 25 for Se(IV); 30 for B		¹ You et al. (2001a) ² Ay et al. (2007)
<u>Resins</u>												
Monoclinic hydrous zirconium oxide (Zr resin)	373	112.4	89.9						74.9 ^a	pH 9-10 for As(III); pH 4-6 for As(V); 25	Des. 99% (after 1 cycle)	Suzuki et al. (2001)
Ion exchange resin IRN97H				58.1					~20	pH 3.8; 25		Rengaraj et al. (2003)
Lewatit M610 anion exchange resin				22.1					20-100	pH 5; 25		Gode and Pehlivan (2005)

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Sorbent	Surface area (m ² /g)	Sorption capacity (mg/g)							C ₀ (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO ₄ ⁻)				
Amberlite IRA-743 resin							2.5		25	pH 9; 30		de la Fuente García-Soto and Muñoz Camacho (2005)
Diaion CRB 01 resin							3 ^a		20	; 30		Kabay et al. (2004)
Polymer supported amino-bis(cis-propane 2,3-diol)							18		~95 ^a	natural; room	Des. 53.3% (after 1 cycle)	Bicak et al. (2005)
<u>Sands</u>												
Aluminium-oxide-coated sand						1.1			63.2-142.1 ^a	pH 4.8; 25		Kuan et al. (1998)
<u>Silicas</u>												
Amino-functionalized mesoporous silicas (MCM-41)	310		119.8						0-1500	pH 6; 25	Reg. 91% (after 1 cycle)	Yoshitake et al. (2003)
Ammonium-functionalized MCM-48	750				15 ^a				100-700	; 5	Reg. 94% (after 5 cycles)	Saad et al. (2007)
Glucamine-modified MCM-41	250						8.7 ^a		50-200		Des. 83% (after 1 cycle)	Kaftan et al. (2005)
Polyolfunctionalized SBA-15	224						6.8 ^a		20-250	; 30		Wang et al. (2006a)
<u>Waste materials</u>												
Fly ash			27.8									Diamadopoulos et al. (1993)
	4.4			1.8					2-10	pH 2; 30		Banerjee et al. (2004)
Orange juice residue		70.4	67.4							pH 7-11 for As(III); pH 2-6 for As(V); 30		Ghimire et al. (2002)
			19						100-600			Lee et al. (1999)
Activated sludge				18.9					50-500	pH 1; 25		Aksu et al. (2002)
Sawdust				1.5					0-100			Sumathi et al. (2005)
Blast furnace slag	0.4					2.1 ^a			500	pH 8.5		Oguz (2004)
Weak anion exchanger prepared from lignocellulosic residue	111.3					23.7 ^a			10-300	pH 5; 30	Reg. 87.3% (after 4 cycles)	Anirudhan et al. (2006)

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Sorbent	Surface area (m ² /g)	Sorption capacity (mg/g)							C ₀ (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO ₄ ⁻)				
Fe(III)/Cr(III) hydroxide sludge	147.4					15.6			12.4-37.3 ^a	pH 6.5; 32	Des. < 15% (after 1 cycle)	Namasivayam and Prathap (2006)
Manganese nodule leached residues	109.2					54.6			60	pH 5; 30	Des. 28.5% (after 1 cycle)	Dash and Parida (2007)
Aluminum-based drinking-water treatment residuals								0.03 ^a	10-200	; 23		Makris et al. (2006)
<u>Zeolites</u>												
Shirasu-zeolite (SZP ₁)	15.6		65.9						97.4 ^a	pH 3-10; 24	Reg. 85% (after 2 cycles)	Xu et al. (2002)
Zeolite	500					25.9 ^a				; 25	Des. 56% (after 1 cycle)	Onyango et al.(2007)
<u>Other minerals/ materials</u>												
Manganese dioxide		44										Chen et al. (1999)
Titanium dioxide	330	59.9	37.5							pH 7; 25		Pena et al. (2005)
Aluminum oxide hydroxide						~11.4 ^a			95			Tanada et al. (2003)

Note: Des. = Desorption efficiency; Reg. = Regeneration efficiency.

^aCalculated from the publication.

2.10 Problems, improvement, and potential application of LDHs

2.10.1 Stability of LDHs

For a sorption medium in a practical context, one of the important considerations is sorbent stability. To date, only a few well-documented studies have reported the mineral stability of LDHs during the sorption and regeneration processes. If the precursor metals in the brucite-like sheets are to be released into the solution, it would be important to ensure that they exist below the levels harmful to the environment, or otherwise the LDHs should be free of toxic metals. Though some of the precursor metals are not currently regulated, they potentially pose health concern if used for drinking water treatment. In fact, many laboratory sorption studies that used LDHs synthesized with heavy metals such as Zn, Cr, Ni, Mn, Co, Cu, Cd, etc., did not report sorbent stability, though mineral dissolution could be significant under aggressive environments. This may therefore raise skepticism over the practical application of these LDHs. Ferreira et al. (2006) reported that the amount of Mg^{2+} released from the LDHs increased with decreasing pH. Their results have provided some important perspectives: (1) sorption performed below circumneutral pH induces metal release, and (2) the nature of the precursor metals incorporated in the brucite-like sheets determines the extent of the metal release.

2.10.2 Design of LDH sorption systems

LDHs may be used in a dispersed powder form or in a fixed-bed granular form. The potential uses are the removal of trace oxyanions from surface water and groundwater and as final polishing process in advanced wastewater treatment systems.

2.10.2.1 Powdered LDHs

If LDHs are applied in the powder form for their large surface area and rapid oxyanion sorption rate, it may present appreciable problems in the subsequent solid/liquid separation process, e.g. blockage of the filter that causes pressure drops. For efficient powdered LDH application, sorptive flotation constitutes an interesting

option because it combines the advantages of greater sorption capacity and faster sorption kinetics of the sorbents, without running into the solid/liquid separation problems which occur with the dead-end filtration. In this way, treated water is produced as underflow and a foam concentrate is also generated. Recovery of oxyanions is also possible from the foam concentrate and, if required, the fine sorbents may be recycled after oxyanion desorption. The sorptive flotation system has been demonstrated by Lazaridis et al. (2001; 2002) for promising arsenate and chromate removal and effective particles separation (Figure 2.8). In another study, a ‘porous pot’ technique integrated with powdered LDHs for arsenic removal has been demonstrated by Gillman (2006) and satisfactory results were obtained. He estimated that the production cost of LDHs could be about US\$0.12 per day for a family consuming 20 L of drinking water, suggesting that LDHs might be an attractive sorbent for water treatment in less-developed regions.

Figure 2.8 Flow diagram of the sorptive flotation system (Lazaridis et al., 2002).

2.10.2.2 Granular LDHs

Apart from using sorptive flotation for separating suspended powdered LDHs, it would be a good alternative to use granular LDHs in fixed-bed filter, especially where continuous application is required. Granular LDHs that are amenable to separation could be produced by harnessing LDHs and their aggregates within polymeric beads. While the LDH granules retain their intrinsic sorption/desorption properties, the

robust polymeric support offers adequate mechanical strength, durability, and favorable hydraulic properties in the flow-through systems. Granular LDH flow-through systems may be designed to operate in a conventional downflow filtration mode or in an upflow mode. Though a few studies have indicated that the LDH granules are able to reduce relatively high concentrations of oxyanions to levels that would be acceptable in practice (Gillman, 2006; Kuzawa et al., 2006), additional studies may be required to further confirm the physical stability of the LDHs. The possibility of hybridizing LDHs with other potential mechanically- and chemically-stable materials should also be explored.

In short, two important considerations should be borne in mind concerning the design of LDH sorption systems: (1) the influent turbidity should be as low as possible since sorption is a process for removing dissolved oxyanions and (2) reliable values for design parameters such as volume of LDHs required to achieve the desired effluent quality and rate of LDH saturation, could only be obtained through pilot plant investigation.

Chapter 3 Materials and Methods

3.1 Materials

3.1.1 Chemicals

All chemicals used in the experiments were analytical grade and the solutions of oxyanions, i.e. arsenite, arsenate, borate, chromate, molybdate, selenate, and vanadate were prepared using NaAsO_2 (Merck, Assay 98.5%), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma, Assay 99.4%), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Hayashi Pure Chemical, Assay 99%), K_2CrO_4 (Merck, Assay 99.5%), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (J.T.Baker, Assay 100%), Na_2SeO_4 (Sigma, Assay 99%), and Na_3VO_4 (Aldrich, Assay 99.9%), respectively. Oxyhalides like bromate, chlorate, iodate, and perchlorate were prepared from NaBrO_3 (Merck, Assay 98%), KClO_3 (Merck, Assay 99%), KIO_3 (Hayashi Pure Chemical, Assay 99.5%), and KClO_4 (BDH, Assay 99%) compounds.

Purified magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Assay 99%) was obtained from HiMedia Laboratories Pvt. Ltd., aluminum nitrate nanohydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Assay 98%) from Fluka Chemika, sodium hydroxide (NaOH , Assay 97%) from Scientific Resources, magnesium ethoxide ($\text{Mg}(\text{OC}_2\text{H}_5)_2$, Assay 98%) from Strem Chemical, aluminium acetylacetonate ($\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$, Assay 95%) from Merck, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99%) from Fluka Chemika, and hydrochloric acid (HCl , Assay 37-38%) from Merck. Three surfactants were obtained as assay-grade from commercial sources and were used as received: pluronic F127, sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB).

Five types of commonly found anions were used as received: sodium nitrate (NaNO_3 , Merck, Assay 99.5%), sodium metasilicate enneahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, Hayashi Pure Chemical), sodium sulphate anhydrous (Na_2SO_4 , BDH, Assay 99%), sodium carbonate anhydrous (Na_2CO_3 , Merck, 99.5%), and sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, Merck). Natural organic matter (NOM, represented by humic acid)

was obtained from Aldrich. Milli-Q ultrapure water (18.2 MΩ•cm) was used for all the experiments, and the water was adequately purged with N₂ before use.

3.1.2 LDHs prepared using alternative synthetic routes

3.1.2.1 Fast coprecipitation with subsequent hydrothermal treatment method

A nanocrystalline Mg/Al LDH intercalated with nitrate was prepared by fast coprecipitation followed by hydrothermal treatment method (hereinafter denoted as FCHT-LDH) modified from Xu et al. (2006). In this method, a mixed salt solution containing 16 mmol of Mg(NO₃)₂·6H₂O and 8 mmol of Al(NO₃)₃·9H₂O was rapidly added (within 5 s) into 40 mL of 1.4 M NaOH under vigorous stirring, and under nitrogen purging to avoid, or at least minimize, the contamination by atmospheric CO₂. The precipitate was centrifuged, washed several times with ultrapure water, and subsequently dispersed in 40 mL of ultrapure water. This aqueous suspension was then hydrothermally treated in a stainless steel autoclave with a Teflon lining (Parr Instrument) under autogenous pressure, at 80 °C for 16 h. After cooling, the product was freeze-dried to avoid aggregation. The LDH samples were kept in a desiccator over fused silica gel in order to avoid adsorption of atmospheric CO₂ and moisture from the atmosphere. The preparation of FCHT-LDH can be generally represented by the following reaction, assuming no contamination of CO₂:

3.1.2.2 Sol-gel method

In synthesizing LDH using sol-gel method, 30 mmol magnesium ethoxide was dissolved at 80 °C under vigorous stirring in ethanol with addition of HCl for complete dissolution. The solution was then added dropwise to 15 mmol aluminium acetylacetonate 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 ultrapure water, and finally dried. Part of the SGRF-LDH and SGST-LDH was calcined at 500 °C for characterization and sorption tests.

3.1.3 LDHs prepared using conventional synthetic routes

3.1.3.1 Conventional coprecipitation and calcination methods

To prepare LDH by the conventional coprecipitation method, 60 mmol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 30 mmol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with $\text{Mg}^{2+}:\text{Al}^{3+}$ molar ratio of 2:1 were dissolved in 50 mL of ultrapure water. This mixture was then added dropwise into 200 mL of a 1.05 M NaOH solution under vigorous stirring and under nitrogen purging. The resulting slurry was aged at 60 °C for 18 h. The precipitate was subsequently centrifuged, washed thoroughly with ultrapure water, dried at 105 °C, and finally stored in dessicator. 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).

3.1.3.2 Conventional ion exchange method

The commercial hydrotalcite (hereinafter referred to as IE-LDH) $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$, used in this study was purchased from Sinopharm Chemical. This commercial LDH was produced by the conventional ion exchange method. In this method, divalent carbonate was exchanged with the univalent chloride present in the interlayer region of the preformed LDHs and the reaction is depicted as follows:

3.1.4 LDH microspheres prepared by spray drying method

A mixed salt solution containing 16 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 8 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was rapidly added into 1.4 M NaOH solution under vigorous stirring and nitrogen purging, and followed by several cycles of separation and washing with

ultrapure water. The aqueous suspension was subjected to hydrothermal treatment and subsequently spray-dried in a spray dryer model SD-05 (Lab-plant, UK), with concurrent flow regime. In the spray dryer, the LDH particles aggregated to form semisolid LDH microspheres. The drying chamber has a diameter of 215 mm and a height of 500 mm. The main components of the system are the feed system of the drying material, constituted by a peristaltic pump, a two fluid atomizer (inlet orifice diameter of 0.5 mm), and an air compressor; a feed system of the drying gas, constituted by a blower and an air filter; a temperature control system of the drying gas; and a product collection system (cyclone). Figure 3.1 shows a schematic diagram of the spray dryer used. The gas humidity was measured at inlet and at exhaust of the spray dryer by means of a traceable thermo-hygrometer. Various operating factors influencing the characteristics of spray-dried LDH microspheres such as inlet air temperature, suspension feed concentration, addition of surfactant, etc. were investigated and it is elaborated in Chapter 7.

Figure 3.1 Schematic diagram of the spray dryer used (Rattes and Oliveira, 2007).

3.2 Analytical methods

3.2.1 Characterization

The elemental analysis of the LDHs was carried out using inductively coupled plasma-optical emission spectrometer (ICP-OES) of Perkin Elmer Optima 2000DV after microwave-assisted digestion of LDHs (EPA Method 3052), in order to determine the actual Mg:Al ratios of the LDH samples. The CHNS/O analyzer (Perkin Elmer 2400 Series II) was used for simultaneous determination of carbon and nitrogen content in the samples.

The nitrogen adsorption-desorption experiments were carried out using QuantaChrome Autosorb-1 analyzer. Prior to measurements, all samples were outgassed at 200 °C under nitrogen flow for several hours. The adsorption multipoint data were obtained at -195.8 °C and relative pressure of 760 mmHg. Specific surface area was calculated from the adsorption isotherm according to Brunauer-Emmett-Teller (BET) method, and the pore size distribution and pore volume were calculated from desorption isotherm by Barrett-Joyner-Hallender (BJH) methods. Photon correlation spectroscopy (PCS) was performed using Malvern Zetasizer Nano ZS to analyze the particle size distribution of the samples from 0.6 to 6000 nm, in which the peak position and the width at half-maximum were automatically calculated. The mean size and size distribution of the samples from 0.05 to 550 µm were measured using a Malvern Mastersizer MicroPlus based on the principle of laser diffraction. The crystallographic information of the samples was examined by X-ray diffraction (XRD). The XRD patterns were collected at a scanning rate of 0.4°/min from $2\theta = 5^\circ$ to $2\theta = 80^\circ$ with Co K α radiation ($\lambda = 1.54 \text{ \AA}$) on a Bruker AXS (D8 advance) X-ray diffractometer operated at 40 kV voltage and 40 mA current. The average crystallite sizes of the samples were estimated by using Debye-Scherrer equation from the full-width at half maximum (fwhm) of some intense peaks (Cheetham and Day, 1987).

Fourier transform infrared spectroscopy (FTIR) analysis was conducted on a Perkin Elmer 2000 FTIR spectrometer. The samples were prepared using the potassium bromide (KBr) pellet technique by mixing the powdered solids with KBr in about

1:100 ratio to get transparent pellet auto supported on the different solids at 10 ton pressure. Spectra were collected in transmission mode at a resolution of 4 cm^{-1} within $4000\text{--}370\text{ cm}^{-1}$, and 100 scans were recorded to ensure good signal to noise ratio.

Scanning electron microscope (SEM) images were obtained using a Carl Zeiss Evo 50 microscope whereas field emission scanning electron microscope (FESEM) images were obtained using a JEOL JSM-6340F microscope. A conductive layer of gold or platinum was deposited on the sample by a sputter coater to reduce surface charging during SEM or FESEM analysis. SEM combined with energy dispersive X-ray spectrometry (EDX) was performed on JEOL JSM-6360 microscope (equipped with EDX system JED-2300) with tungsten electron source and an operating voltage in the range of 0.5–30 kV. Some samples were analyzed by EDX in order to determine the elemental compositions through EDX elemental mapping.

Transmission electron microscope (TEM) images were obtained using a JEOL JEM-2100F microscope at an acceleration voltage of 200 kV. Prior to TEM imaging, the samples were dispersed in ethanol with ultrasonication for 10–20 min, and the droplet was dropped on a copper grid coated with carbon film. Selected area electron diffraction (SAED) patterns were also recorded in order to analyze qualitatively the crystallite size and the crystallinity of the samples. Field limiting apertures used for SAED were 5–60 μm in diameter.

The X-ray photoelectron spectrometry (XPS) analysis was performed using a Kratos AXIS Ultra spectrometer with a monochromatized Al $K\alpha$ X-ray source (1486.71 eV) operated at a reduced power of 150 W (15 kV and 10 mA). Binding energies were referenced to the C (1s) neutral C–C peak at 284.6 eV so as to compensate the effect of charging. Curve fitting of the spectra peaks was performed after a Shirley background subtraction by nonlinear least square fitting using a mixed Gaussian/Lorentzian function.

The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis on the samples reacted with chromate or vanadate were performed at the XDD beamline of the Singapore Synchrotron Light Source (SSLS, Singapore) where a Si(111) channel-cut monochromator is equipped. The

samples were ground into fine powders, dispersed evenly on a clear sticky-tape, placed in a stainless steel cell, and measured in transmission mode at the Cr and V K-edge, respectively, at room temperature. The scanned energy was from 90 eV below the K-absorption edge ($E_0 = 5.989$ keV for Cr and $E_0 = 5.465$ keV for V) to 750 eV above the edge. Standards Cr-foil, Cr_2O_3 , K_2CrO_4 , and K_2CrO_7 were used as references for samples with chromate, and for samples with vanadate V-foil, VO, V_2O_3 , VO_2 and V_2O_5 were analyzed. The EXAFS data were analyzed following the standard methods using the WINXAS code (Ressler, 1997).

3.2.2 Analysis of arsenate, borate, chromate, molybdate, selenate, and vanadate

The concentrations of the oxyanions such as arsenate, borate, chromate, molybdate, selenate, and vanadate were reported as their elemental concentrations in this study. Their concentrations were determined using an ICP-OES. Prior to analysis, the solution samples were filtered with 0.45 μm membrane filter and acidified with concentrated HNO_3 , and stored in acid-washed sample tubes. All samples were analyzed either immediately after experiment or after storage at 4 °C for a maximum of 48 h. The instrument was calibrated each time before use. All calibrations were prepared using at least five standards covering the range of sample concentrations. Linear coefficients of determination (R^2) for the standard curves were no less than 0.999. Each sample was injected three times, and the relative standard deviation (RSD) for the triplicate analysis was within 5%.

For measurements of arsenate concentrations at $\mu\text{g/L}$ level, graphite furnace atomic absorption spectrophotometer (GFAAS, Perkin Elmer SIMMA 6000) was used. Arsenic speciation analysis was performed using the method modified from Lim and Goh (2005). In this method, the species of arsenic were determined by subdividing the sample solutions into two parts; one for determination of arsenite and the other for determination of total arsenic (arsenite and arsenate).

3.2.3 Analysis of bromate, chlorate, iodate, and perchlorate

The concentrations of bromate, chlorate, iodate, and perchlorate were analyzed by ion chromatograph (IC, Dionex ICS-1000). This Dionex system was equipped with an AS-HV autosampler, a 4 mm AS15 column, a 4 mm AG15 guard column, and a 4 mm SRS[®] ULTRA II suppressor. For perchlorate analysis, the columns were replaced with AS16 column and AG16 guard column. The eluent concentration used for bromate, chlorate, and iodate analyses was 34 mM KOH whereas 50 mM KOH for perchlorate analysis.

3.2.4 Analysis of nitrate displaced and Mg and Al released

The interlayer nitrate displaced from LDH due to anion exchange process was quantified by IC whereas the Mg and Al released from LDH during the sorption and desorption processes were analyzed by ICP-OES, using similar procedures as described above.

3.3 Experimental procedures

3.3.1 Sorption reaction

All the glasswares used were soaked in diluted acid for overnight and then rinsed with ultrapure water before used. Analytical reagent grade chemicals and ultrapure water were used for preparation of all solutions throughout the study. The background electrolyte solution was prepared from NaNO₃. Unless otherwise stated, all the experiments were carried out using the batch sorption technique at 0.4 g/L LDH loading, at 25 °C, and at pH 9.5 (the natural pH of the LDH suspension).

Most sorption studies were performed in 50 ml polyethylene centrifuge tubes by subjecting LDH to a period of agitating with oxyanion solutions. The mixtures were then separated by centrifugation, filtration, and the oxyanion concentrations in the supernatant were then determined either by ICP-OES, GFAAS or IC. Part of the solid

remaining at the end of the sorption experiment was further characterized either by CHNS/O, XRD, FTIR, EDX, XPS, XANES, and EXAFS analyses. Triplicate determinations of the sorption results were performed for most of the experiments and only mean values were presented. A control experiment was also conducted in parallel to some experiments.

A few QA/QC measures were taken to minimize CO₂ dissolution during the sorption reaction. For example, all the experiments were carried out in the air-tight system. For some sorption experiments such as the kinetic experiments, the suspension in the container was purged with nitrogen, then sealed, and wrapped in Parafilm to ensure CO₂-free atmosphere for the reaction. On each sampling interval, the sample was extracted from the sealed container by the syringe needle through the Parafilm.

3.3.2 Sorption experiments of oxyanions and oxyhalides having different molecular properties on LDHs

The sorption efficiencies of FCNT-LDH and IE-LDH for various oxyanions (arsenate, borate, chromate, molybdate, selenate, and vanadate) and oxyhalides (bromate, chlorate, iodate, and perchlorate) were investigated in a single sorbate system by adding LDH into the solution of 0.2 mM anion in a 50 mL centrifuge tube. The suspensions were reacted for 24 h to enable complete equilibrium. The suspensions were subsequently centrifuged, filtered, and the concentrations of oxyanions were determined by ICP-OES whereas the concentrations of oxyhalides were determined by IC.

Two oxyanions (divalent chromate and divalent vanadate) and an oxyhalide (monovalent bromate) were selected for investigation of sorption isotherms, kinetics, pH effect, and ionic strength effect. Their selection was based on their environmental significance, different ionic charges, molecular structures, and molecular radii. In addition, they have only one predominant species at pH 9.5, thus reducing the number of dissolved anion species and possible adsorbing species, and subsequently minimizing ambiguity in the interpretation of sorption results.

Sorption isotherms of these anions were studied by contacting FCHT-LDH with 0.008-0.391 mM bromate solutions, 0.019-0.962 mM chromate solutions, and 0.020-0.982 mM vanadate solutions, respectively. The suspensions were reacted for 24 h at temperature-controlled shaker maintained at 25, 35, 45, and 55 °C. The suspensions were then centrifuged, filtered, and the concentrations of anions were analyzed. Sorption kinetic experiments were conducted by adding LDH samples into 0.4 mM bromate, chromate, and vanadate, respectively, and then stirring for 6 h with intermittent sampling. Sufficient agitation (250 rpm) was provided in order to avoid particle and solute gradients in the batch reactor which allowed the bulk diffusion to be neglected. Bromate, chromate, and vanadate sorption on FCHT-LDH were examined as a function of pH ranging from 4.5 to 11 and ionic strength of 0.005 M and 0.5 M NaNO₃. LDH samples were hydrated in 0.005 M and 0.5 M NaNO₃ solutions prior to the pH adjustment using either HNO₃ or NaOH solutions. An appropriate amount of bromate, chromate, or vanadate stock solution was added and the suspensions were then reacted with intermittent pH adjustment. The volume added for pH adjustment never exceeded 1% of the total volume. The use of buffer was intentionally avoided in this study in order to restrict the addition of foreign anions. The amount of the anion sorption was calculated as follows:

$$q_e \text{ (cmol/kg LDH)} = \frac{(C_0 - C_e)V}{M} \quad (3.3)$$

where q_e is the sorption loading of LDH at equilibrium (cmol/kg), C_0 (cmol /L) and C_e (cmol /L) are the initial and equilibrium concentration of anion, respectively, V is the volume of the solution added (L), and M is the mass of LDH added (kg).

3.3.3 Sorption experiments of arsenic on LDHs

The sorption isotherms were determined by contacting FCHT-LDH and IE-LDH with 0.013-0.667 mM arsenate solutions. The LDH and arsenate solutions were reacted in the centrifuge tubes for 24 h. For experiment investigating temperature effect on arsenate sorption by FCHT-LDH, the suspensions were reacted at temperature-controlled shaker at different temperatures. The suspension in each tube was centrifuged, filtered, and the concentrations of arsenate were determined by ICP-OES

or GFAAS. Kinetic experiments were performed by adding LDH samples into 0.2 mM arsenate solutions and stirred for 6 h, and at selected time intervals, 4 mL samples were extracted, filtered, and analyzed. To investigate the pH effect on arsenic sorption by FCHT-LDH, 20 mL of FCHT-LDH suspension and 20 mL of 0.46 mM arsenate or 0.2 mM arsenite solution, both with pre-adjusted pH (in the range of 5-11), were mixed and stirred for 4 h with intermittent pH adjustment.

3.3.4 Sorption experiments of oxyanions in co-existing anion and NOM solutions

The batch system was used to investigate the influences of the co-existing species on the sorption of oxyanions by FCHT-LDH. In the first part of this study, arsenate, bromate, chromate, or vanadate solutions containing different co-existing anions (i.e. nitrate, silica, sulfate, carbonate, and phosphate) were prepared by dissolving their sodium salts in 0.4 mM arsenate, bromate, chromate, or vanadate solutions, and their resultant anion/oxyanion ratios were 0, 1, 10, and 100. FCHT-LDH was then added to each of the solutions in centrifuge tubes and the suspensions were reacted for 24 h. After centrifugation and filtration, the concentrations of arsenate, chromate, and vanadate were determined by ICP-OES while the concentrations of bromate was determined by IC.

In the second part, the effects of anions and NOM of different concentrations on arsenate sorption by FCHT-LDH were examined as a function of reaction time and as a function of pH. The amount of Mg and Al released from FCHT-LDH at different pH in the presence of anions and NOM was also monitored. The initial arsenate concentration was 0.4 mM and the dosage of FCHT-LDH was 0.4 g/L. The procedures of experiments investigating on the reaction time and pH were similar to those described in the foregoing studies.

3.3.5 Sorption experiments of arsenate on LDHs prepared using conventional routes, alternative routes, and spray drying method

The arsenate sorption characteristics 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) as well as the spray drying method (LDH microspheres) were explored and compared. The sorption isotherms were determined by reacting LDH with arsenate of concentrations from 0.013 to 0.667 mM whereas the kinetic experiments were performed by adding LDH into 0.2 mM arsenate solution in a covered container with intermittent sampling. The samples extracted were filtered and the arsenate concentrations were determined.

3.3.6 Nitrate displacement experiment

The displacement of interlayer nitrate by arsenate was investigated as a function of arsenate loading and reaction time. A predetermined dose of FCHT-LDH was contacted with arsenate solutions of concentrations ranging from 0.013 to 0.667 mM for the former experiment whereas FCHT-LDH was added into 1 L of 0.2 mM arsenate solutions and stirred for 6 h with intermittent sampling at selected time intervals in the later. The concentrations of arsenate were determined by ICP-OES whereas the concentrations of the nitrate were analyzed by IC.

3.3.7 Electrophoretic mobility measurement

To better understand the interaction between oxyanion and FCHT-LDH surface, the electrophoretic mobility (EM) measurements were performed on a Zetasizer Nano ZS (Malvern Instrument). The pH of the suspension containing FCHT-LDH in 0.01 M NaNO_3 was adjusted to 4.5-13.5 using HNO_3 or NaOH solutions. The suspensions were reacted with or without oxyanions (i.e. bromate, chromate, and vanadate). The final pH and the EM of the mixed samples were measured.

3.3.8 Regeneration of LDH

The regeneration of FCHT-LDH was evaluated by reacting oxyanion-loaded FCHT-LDH in the regenerating solution at 1 g/L for 24 h. The regenerating solution used included 0.05 M and 0.1 M NaOH , 1 M NaNO_3 , 1 M $\text{Mg}(\text{NO}_3)_2$, a mixture of 1 M NaNO_3 and 0.1 M NaOH , and 0.1 M Na_2CO_3 . The amount of oxyanion desorbed was determined through analysis of oxyanion released into the solution whereas the amount of oxyanion uptake by the regenerated FCHT-LDH was determined through

analysis of oxyanion removed from the solution. For the regeneration of arsenate-loaded FCHT-LDH, four cycles of arsenate sorption-desorption were performed using the best-performing regeneration method.

3.4 Computation of equilibrium exchange constant

The equilibrium exchange constant, K_{ex} was determined to assess the extent of arsenate binding by anion exchange process. This parameter is useful for determining the state of ionic equilibrium at different ion concentrations. K_{ex} was computed by referring to the methods of Vanselow (1932) and Gaines and Thomas (1953). Based on these methods, K_{ex} was computed from the following equation:

$$\ln K_{ex} = \int_0^1 \ln K_{eq} d(LDH)_{As(V)} \quad (3.4)$$

where K_{eq} is the apparent equilibrium exchange constant and $(LDH)_{As(V)}$ is the equivalent fraction of arsenate on the LDH. One can determine $\ln K_{ex}$ by plotting $\ln K_{eq}$ vs $(LDH)_{As(V)}$ and integrating under the curve by summing the areas of the trapezoids using the relationship:

$$\frac{1}{2} \sum_{i=1}^{10} ((LDH)_{As(V)}^{i+1} - (LDH)_{As(V)}^i)(y^i + y^{i+1}) \quad (3.5)$$

where $(LDH)_{As(V)}^1 \dots (LDH)_{As(V)}^{10}$ are the experimental values of $(LDH)_{As(V)}$, $((LDH)_{As(V)}^{i+1} - (LDH)_{As(V)}^i)$ denotes the width of the i th trapezoid, and $y^1 \dots y^{10}$ represent the corresponding $\ln K_{eq}$ values (Sparks, 2003).

3.5 Kinetic analysis

Four possible kinetic models were used to fit the experimental data, including the commonly used pseudo-first order and pseudo-second order models, modified multiplex model, and Elovich model. The modified multiplex model (2007) is based on a combination of the pseudo-first order and pseudo-second order models:

$$\frac{dq_t}{dt} = k_{m1}(q_e - q_t) + k_{m2}(q_e - q_t)^2 \quad (3.6)$$

where q_t (cmol/kg) is the amount of oxyanion sorbed at time t , q_e (cmol/kg) is the amount of oxyanion sorbed at equilibrium, and k_{m1} (min^{-1}) and k_{m2} (g/mg/min) are the rate constants. Elovich equation is given as follows:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (3.7)$$

where α and β are the Elovich constants. The Elovich constant α is related to the sorption rate while β is related to the surface coverage. Two statistical parameters (R^2 and χ^2) and a normalized standard deviation (Δq) are evaluated to distinguish which can best represent the experimental results.

3.6 Statistical analysis

Statistical Chi-square (χ^2) value was determined using equation 3.8 whereas normalized standard deviation (Δq) was calculated according to equation 3.9.

$$\chi^2 = \sum \left[\frac{(q_{t,\text{exp}} - q_{t,\text{cal}})^2}{q_{t,\text{cal}}} \right] \quad (3.8)$$

where $q_{t,\text{exp}}$ and $q_{t,\text{cal}}$ are the experimental values and the values calculated by the model, respectively. Small number of χ^2 indicates that data from the model is close to

the experimental data whereas large number of χ^2 shows that data from model is different from the experimental data.

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}}) / q_{t,\text{exp}}]^2}{n-1}} \quad (3.9)$$

where n is the number of data points.

Chapter 4 Sorption Characteristics and Mechanisms of Nanocrystalline LDH for Various Oxyanions and Oxyhalides

4.1 Introduction

Oxyanions such as arsenate, chromate, selenate, vanadate, etc. and oxyhalides such as bromate, perchlorate, etc. are toxic to both humans and wildlife at either $\mu\text{g/L}$ or mg/L levels (Li and Bowman, 2001; Yokoi et al., 2004; Snyder et al., 2005; Wang et al., 2006a; Naeem et al., 2007). Among various anion treatment processes, sorption is considered to be one of the most promising technologies for anion removal from water because it is cost-effective, versatile, and simple to operate (Jang et al., 2006). In recent years, many conventional sorbents have been used to remove oxyanions and oxyhalides from water. However, most of them are not selective and some have low sorption and regeneration efficiencies. LDH has been explored as a potential sorbent for removing various oxyanions (Lazaridis et al., 2002; Yang et al., 2005; Goh et al., 2008), however the sorption study on emerging deleterious oxyanions such as borate, molybdate, vanadate, and oxyhalides such as bromate, chlorate, iodate, and perchlorate remains scarce.

Most of the LDHs investigated for oxyanion sorption were prepared from conventional coprecipitation methods (Lazaridis et al., 2002; Yang et al., 2005; Gillman, 2006; Goh et al., 2008; Wang et al., 2009b) which produced unstable large LDH particles with aggregated crystallites (Zhao et al., 2002). Nanocrystalline materials demonstrate several unique characteristics such as large surface area and high specificity that make them excellent functional materials for water treatment applications. A recent study (Pena et al., 2006) suggested that nanocrystalline TiO_2 exhibited high affinity for arsenic. Therefore, it is of worthy to engineer a new breed of nanocrystalline LDH for the removal of oxyanions.

Some studies have indicated that LDHs have greater affinities for polyvalent anions than monovalent anions (Dutta and Puri, 1989; You et al., 2001a) but the interrelation between LDHs and valences of anions was not clearly elucidated. Indeed a systematic investigation on the sorption of various oxyanions and oxyhalides considering the relationship between molecular properties of anions and their sorption characteristics on LDHs could serve as the basis for predicting the selectivity of LDHs towards a wide range of anions. Most previous studies have focused on the anion sorption performance of LDHs under various environmental conditions (Goh et al., 2008), comparatively little is known about the interaction between anions and LDHs. Knowledge of LDH interaction with oxyanions and oxyhalides at the solid/aqueous interface is of paramount importance as it will allow the accurate prediction of the sorptive properties of the sorbent and subsequently lead to the optimization of the sorption and regeneration processes. Recent advancements in analytical techniques such as XPS and EXAFS allow probing into the surface chemistry and detailed structural information of the sorbed complexes at the solid/aqueous interface. One recent EXAFS study revealed that arsenate sorbed on the internal and external surfaces of the LDHs by forming outer-sphere complexes (Wang et al., 2009b). Nonetheless, almost no detailed microscopic study has been performed to examine the interaction between LDHs and other environmentally significant anions including bromate, chromate, and vanadate. These insights are vital for improving the sorbent functionality through novel synthesis.

The objectives of this part of study were: (1) to evaluate the sorption performance of nanocrystalline Mg/Al LDH for various oxyanions (arsenate, borate, chromate, molybdate, selenate, and vanadate) and oxyhalides (bromate, chlorate, iodate, and perchlorate) on the basis of their molecular properties; (2) to investigate and compare the sorption characteristics and thermodynamics of oxyanion (i.e. divalent chromate and vanadate) and oxyhalide (i.e. monovalent bromate) on the LDH; and (3) to determine the plausible mechanisms and surface structures for the sorbed bromate, chromate, and vanadate at the LDH/aqueous interface using both macroscopic and microscopic techniques.

4.2 Experimental section

The materials and methods used in this part of study have been described in Chapter 3. The sorbents used were nanocrystalline Mg/Al LDH prepared by fast coprecipitation with hydrothermal method (FCHT-LDH) and commercial LDH prepared by ion exchange method (IE-LDH). The sorption experiments of FCHT-LDH and IE-LDH for various oxyanions and oxyhalides were conducted in two parts in a single-sorbate batch system.

In the first part, the sorption efficiencies of FCHT-LDH and IE-LDH for various oxyanions and oxyhalides were investigated by adding a predetermined dose of LDH into the solution of anion. The suspensions were reacted for 24 h and were subsequently centrifuged, filtered, and the concentrations of anions were determined by either ICP-OES or IC. In the second part, two oxyanions (divalent chromate and divalent vanadate) and an oxyhalide (monovalent bromate) were selected for investigation of sorption isotherms, kinetics, pH effect, ionic strength effect, and electrophoretic mobility. To provide more insights into the interactions of bromate, chromate, or vanadate with FCHT-LDH at the solid/aqueous interface, some selected samples were analyzed with CHNS/O, XRD, FTIR, XPS, XANES, and EXAFS. Desorption experiments were also performed by investigating the efficiencies of different regenerating solutions on the anion-loaded FCHT-LDHs.

4.3 Results and discussion

4.3.1 Characterizations

The molar ratios of $\text{Mg}^{2+}/\text{Al}^{3+}$ in all the LDHs were close to the stoichiometric ratios of their starting salts (Table 4.1). Almost no change of $\text{Mg}^{2+}/\text{Al}^{3+}$ ratios for the anion-loaded FCHT-LDHs demonstrated insignificant reduction in LDH crystallinity under the explored experimental condition. The CHNS/O analysis revealed the existence of N in FCHT-LDH, suggesting the successful intercalation of nitrate into the interlayer region. The higher C content in IE-LDH agreed with its composition while the

presence of a small amount of C in FCHT-LDH was likely originated from the atmospheric CO₂ and considered to pose insignificant effect to the anion exchange process. The surface area, pore volume, and pore size of FCHT-LDH were 127 m²/g, 0.31 cm³/g, and 8 nm, respectively, and they were higher than those of IE-LDH by 2-8 times.

Table 4.1 Composition and lattice parameters of the fresh and anion-loaded LDHs

Sample	Composition			Lattice parameter		
	Mg ²⁺ /Al ³⁺ (molar ratio)	C (wt %)	N (wt %)	a ^a (Å)	c ^b (Å)	Crystal size ^c (nm)
IE-LDH	3.1/1	9.2	1.4	3.04	22.67	21.5
FCHT-LDH (fresh)	2.0/1	0.7	3.3	3.04	23.53	5.9
Bromate-loaded (20 mg/L)*	1.9/1	0.8	2.1	3.05	23.51	11.5
Bromate-loaded (100 mg/L)	1.9/1	0.8	2.0	3.05	23.53	11.8
Chromate-loaded (20 mg/L)	1.9/1	0.6	0.8	3.05	23.65	8.3
Chromate-loaded (100 mg/L)	1.8/1	0.6	0.5	3.04	23.85	10.2
Vanadate-loaded (20 mg/L)	1.9/1	0.9	0.9	3.06	23.82	13.4
Vanadate-loaded (100 mg/L)	1.8/1	1.2	0.8	3.06	24.01	15.1

^aa = average metal-metal distance inside the brucite-like sheets = 2 × d(110); ^bc = interlayer distance regulated by the size and charge of the anion placed between the brucite-like sheets = 3 × d(003); ^cAverage value calculated from fwhm of peak (003) and (006) using Scherrer Equation; *Numbers in parentheses denote the initial concentration of anion used for sorption equilibration with FCHT-LDH.

A single LDH phase (ICSD 81963) can be identified for all the LDHs and no other crystalline phases were observed (Figure 4.1). The peaks recorded were due to crystalline planes of rhombohedral symmetrical (3R) LDH structure (Braterman et al., 2004). FCHT-LDH also showed a smaller crystallite size and a higher interlayer spacing (indicated by larger c value in Table 4.1) compared to IE-LDH. As shown in Figure 4.2, FTIR spectra of the FCHT-LDHs are typical of LDH material, as featured by a broad band at 3470 cm⁻¹ (ν_{OH} for OH stretching vibration of hydrogen-bonded groups in the brucite-like sheets and water in the interlayer space), a peak at 1637 cm⁻¹ (δ_{H₂O} for water bending vibrations of the interlayer water), a strong peak at 1384 cm⁻¹ (due to ν(NO₃⁻), NO₃⁻ intercalated in the interlayer space), and bands at 780, 667,

556, and 448 cm^{-1} (due to M-O vibrations and M-O-H bending). FCHT-LDH was observed as well-formed and overlapping plate-like particles characteristic of layered structure with a uniform size of 40-100 nm and comprised nanocrystalline grains (Figure 4.3).

Figure 4.1 XRD patterns of (a) fresh FCHT-LDH and various anion-loaded FCHT-LDHs: (b) bromate-loaded (20 mg/L), (c) bromate-loaded (100 mg/L), (d) chromate-loaded (20 mg/L), (e) chromate-loaded (100 mg/L), (f) vanadate-loaded (20 mg/L), and (g) vanadate-loaded (100 mg/L).

Figure 4.2 FTIR spectra of (a) fresh FCHT-LDH and various anion-loaded FCHT-LDHs: (b) bromate-loaded (20 mg/L), (c) bromate-loaded (100 mg/L), (d) chromate-loaded (20 mg/L), (e) chromate-loaded (100 mg/L), (f) vanadate-loaded (20 mg/L), and (g) vanadate-loaded (100 mg/L).

Figure 4.3 (a) TEM image of FCHT-LDH particles in a cluster (the inset on the top right is an individual FCHT-LDH particle and the inset on the bottom left is the high resolution TEM (HRTEM) image of FCHT-LDH) and (b) SEM image of FCHT-LDH particles.

4.3.2 Comparative sorption studies of oxyanions and oxyhalides having different molecular properties

Most oxyanions investigated in this study are divalent at pH 9.5 except borate whereas all of the oxyhalides are monovalent (Table 4.2). The molecular radii of the oxyanions (except borate) are generally more than 0.24 nm and their ionic potentials are about 8 nm^{-1} . The molecular radii of the oxyhalides range from 0.21 to 0.24 nm and their ionic potentials are less than 5 nm^{-1} . All the oxyanions are of tetrahedral structure while most oxyhalides are of trigonal pyramid structure. Anion selectivity is generally governed by the mobility of anions in the interlayer region of the LDH (Newman et al., 1999) which is likely dependent on the ionic charge, molecular radius, and molecular structure of the anion.

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Table 4.2 Molecular properties of various oxyanions and oxyhalides

Anion	Predominant species at pH 9.5	Ionic charge	Molecular structure	Molecular radius (nm)	Ionic potential (nm ⁻¹)	Reference (a: predominant species; b: molecular radius)
<u>Oxyanion</u>						
Arsenate ^c	HAsO ₄ ²⁻	2	tetrahedral	0.248 (AsO ₄ ³⁻)	8.06	^a Montgomery (1985); ^b Wilkinson et al. (1987)
Borate	B(OH) ₄ ⁻	1	tetrahedral	0.229 (B(OH) ₄ ⁻)	4.37	^a Ferreira et al. (2006); ^b David (2003)
Chromate ^d	CrO ₄ ²⁻	2	tetrahedral	0.240 (CrO ₄ ²⁻)	8.33	^a Faust and Aly (1999); ^b Wilkinson et al. (1987)
Molybdate	MoO ₄ ²⁻	2	tetrahedral	0.246 (MoO ₄ ²⁻)	8.13	^a Lazaridis et al. (2003); ^b Wilkinson et al. (1987)
Selenate	SeO ₄ ²⁻	2	tetrahedral	0.243 (SeO ₄ ²⁻)	8.23	^a Montgomery (1985); ^b Stephan et al. (2004)
Vanadate ^e	HVO ₄ ²⁻	2	tetrahedral	0.260 (VO ₄ ³⁻)	7.69	^a Peacock and Sherman (2004); ^b Jenkins and Thakur (1979)
<u>Oxyhalide</u>						
Bromate	BrO ₃ ⁻	1	trigonal pyramid	0.214 (BrO ₃ ⁻)	4.67	^b David (2003)
Chlorate	ClO ₃ ⁻	1	trigonal pyramid	0.208 (ClO ₃ ⁻)	4.81	^b David (2003)
Iodate	IO ₃ ⁻	1	trigonal pyramid	0.218 (IO ₃ ⁻)	4.59	^b David (2003)
Perchlorate	ClO ₄ ⁻	1	tetrahedral	0.240 (ClO ₄ ⁻)	4.17	^b Moyer and Bonnesen (1997)

Figure 4.4 depicts that FCHT-LDH attained considerably higher removal efficiency than IE-LDH for all the oxyanions and oxyhalides, primarily owing to its lower carbonate content, larger surface area, porous nature, and nanocrystalline property. The highly porous nanocrystalline FCHT-LDH with large surface area has allowed for an enhanced surface chemical reactivity and imparted a very large area of contact between anions and FCHT-LDH particles, resulting in its good sorption ability. Almost 100% of divalent arsenate, chromate, molybdate, selenate, and vanadate were successfully sorbed by FCHT-LDH whereas monovalent borate and oxyhalides (i.e. bromate, chlorate, iodate, and perchlorate) sorbed by FCHT-LDH were 55% and < 20%, respectively. Apparently, the divalent anions were more favorably sorbed by FCHT-LDH compared to the monovalent anions.

Figure 4.4 Sorption efficiencies of FCHT-LDH and IE-LDH for various oxyanions and oxyhalides (pH = 9.5, time = 24 h, oxyanion or oxyhalide = 0.2 mM, dose = 1 g/L, background electrolyte = 0.01 M NaNO₃).

Based on the sorption results, the anions can be generally grouped into two classes as shown in Figure 4.5: (1) anions more favorably sorbed by FCHT-LDH which ionic potentials are higher than 7 nm^{-1} (oxyanions with $z = 2$) and (2) anions less favorably sorbed by FCHT-LDH which ionic potentials are lower than 5 nm^{-1} (oxyanions and oxyhalides with $z = 1$). The ionic potential (μ) is defined as z/r , where z is the ionic charge and r is the molecular radius (McBride, 1994). The ionic potential will greatly influence the degree to which water dipoles are attracted to the ion, and thus will also determine the mobility of the anion in aqueous solution. The tetrahedral oxyanions appeared to be more preferably sorbed by FCHT-LDH than the trigonal pyramid

oxyhalides. Tetrahedral coordinated anions have also been reported to show a higher degree of specificity for the surface of precipitated hydrous iron oxides than the trigonal planar anions in a previous study (Harrison and Berkheiser, 1982). The relatively low sorption efficiency of FCHT-LDH for borate was partially due to a transition in its coordination from tetrahedral B(OH)_4^- to trigonal HBO_3^{2-} during the incorporation of B(OH)_4^- into FCHT-LDH (at $\text{pH} > 9.2$) which would require elimination of an energy barrier (Zhang and Reardon, 2003).

Figure 4.5 The relationship between anion ionic potential and anion sorption efficiency by FCHT-LDH.

4.3.3 Sorption characteristics of bromate, chromate, and vanadate

The equilibrium sorption capacity of bromate on FCHT-LDH decreased with the increasing temperature from 25 °C to 55 °C (Figure 4.6). In contrast, the sorption capacities of both chromate and vanadate increased with temperature, attributable to increased diffusivity and activity of the oxyanions that facilitated their incorporation into FCHT-LDH. Overall, Langmuir isotherm fitted the equilibrium data of anions better than Freundlich isotherm, on the basis of the linear coefficient of determination (R^2) and nonlinear Chi-square (χ^2) statistical test (Table 4.3). The characteristics of a Langmuir isotherm can be described in terms of a dimensionless separation factor, R_L (Weber and Chakravorti, 1974), which explains the type of isotherm and is defined by:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4.1)$$

where K_L is the Langmuir sorption constant (L/cmol), C_0 is the initial concentration of anion (cmol/L), and if $R_L > 1 \Rightarrow$ unfavorable, $R_L = 1 \Rightarrow$ linear, $0 < R_L < 1 \Rightarrow$ favorable, and $R_L = 0 \Rightarrow$ irreversible. The values of R_L were found to be less than 1 for bromate, chromate, and vanadate sorption on FCHT-LDH, suggesting that the sorption process was favorable (Table 4.3). The values of heterogeneity factor ($1/n$) were found to be less than 1 for all the anions, confirming their favorable sorption on FCHT-LDH. Among the investigated anions, the sorption capacity for chromate on FCHT-LDH was the highest ($q_m = \sim 120$ cmol/kg), and followed by vanadate and bromate. The Freundlich constants related to the sorption capacity (K_F) for chromate and vanadate sorption were much larger than that of bromate. The higher sorption capacities of chromate and vanadate on FCHT-LDH were possibly due to their higher ionic potential and tetrahedral coordination compared to those of bromate.

Figure 4.6 Sorption isotherms of (a) bromate, (b) chromate, and (c) vanadate on FCHT-LDH at different temperatures (pH = 9.5, time = 24 h, dose = 0.4 g/L, background = 0.01 M NaNO_3) and the insets are the van't Hoff plots of $\ln K_c$ against reciprocal temperature.

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Table 4.3 Sorption isotherm and thermodynamic parameters for the sorption of bromate, chromate, and vanadate by FCHT-LDH

Anion	Temperature (°C)	Freundlich isotherm ^a				Langmuir isotherm ^b					Thermodynamics		
		K _F	n	R ²	χ^2	K _L	q _m	R _L ^c	R ²	χ^2	ΔG°	ΔH°	ΔS°
						(L/cmole)	(cmole/kg)				(kJ/mole)	(kJ/mole)	(J/mole.K)
Bromate	25	46	1.74	0.986	0.26	55	10	0.32	0.979	0.56	-4.65	-4.64	-0.028
	35	32	1.67	0.992	0.09	46	7	0.36	0.974	0.31	-4.57		
	45	29	1.71	0.979	0.17	48	7	0.35	0.953	0.31	-4.71		
	55	46	1.33	0.941	0.54	36	6	0.42	0.976	0.21	-4.60		
Chromate*	25	704	1.71	0.963	7.41	108	116	0.10	0.996	1.16	-5.60	3.00	29
	35	715	1.75	0.957	8.48	123	116	0.08	0.995	1.83	-5.89		
	45	640	1.89	0.927	14.48	142	118	0.07	0.984	7.34	-6.18		
	55	534	2.23	0.960	14.31	210	119	0.05	0.975	23.10	-6.47		
Vanadate*	25	290	2.36	0.913	15.83	408	61	0.02	0.960	8.36	-5.88	4.04	33
	35	323	2.41	0.922	13.35	480	69	0.02	0.954	19.77	-6.21		
	45	330	2.49	0.942	15.21	423	79	0.02	0.944	17.35	-6.54		
	55	299	2.95	0.920	20.77	1290	78	0.01	0.928	17.59	-6.88		

^aFreundlich isotherm: $q_e = K_F C_e^{1/n}$ where q_e is the amount of anion sorbed at equilibrium (cmol/kg), K_F is the Freundlich constant ((cmol/kg)/(cmol/L)^{1/n}), C_e is the concentration of anion at equilibrium (cmol/L), and $1/n$ is the heterogeneity factor; ^bLangmuir isotherm: $C_e/q_e = 1/K_L q_m + C_e/q_m$ where K_L is the Langmuir sorption constant (L/cmole) and q_m signifies sorption capacity (cmol/kg); ^c $R_L = 1/(1 + K_L C_0)$ where $C_0 = 0.039$ cmol/L for bromate, 0.096 cmol/L for chromate, and 0.098 cmol/L for vanadate. *Concurrent monitoring of the solution pH showed a slight pH increment of about 0.5 during chromate and vanadate sorption equilibrium.

The thermodynamic parameters for the sorption process, Gibbs free energy (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°), were determined using the following equations and van't Hoff plot.

$$\Delta G^\circ = -RT \ln K_c \quad (4.2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4.3)$$

where R is universal gas constant (8.314 J/mol.K), T is temperature (K), and K_c is the thermodynamic equilibrium constant that can be defined as follows:

$$K_c = \frac{a_s}{a_e} = \frac{v_s C_s}{v_e C_e} \quad (4.4)$$

where a_s is the activity of sorbed anion (bromate, chromate, or vanadate), a_e is the activity of the anion in solution at equilibrium, C_s is the surface concentration of anion (cmol/kg), C_e is the concentration of anion at equilibrium (cmol/L), v_s is the activity coefficient of the sorbed anion, and v_e is the activity coefficient of the anion in solution. As the ionic strength approaches zero, the activity coefficient approaches unity, and equation 4.4 can be simplified to:

$$\frac{C_s}{C_e} = \frac{a_s}{a_e} = K_c \quad (4.5)$$

K_c values were then obtained by plotting $\ln (C_s/C_e)$ vs C_s and extrapolating C_s to zero (Biggar and Cheung, 1973; Khan and Singh, 1987). The values of ΔH° and ΔS° were derived respectively from the slope and intercept of the van't Hoff plot.

The negative values of ΔG° for all the anions indicated the spontaneous nature of their sorption on FCHT-LDH (Table 4.3). Higher negative ΔG° values of chromate and vanadate showed that their sorption on FCHT-LDH were more energetically favorable than that of bromate. The positive values of ΔH° and ΔS° indicated the endothermic nature of chromate and vanadate sorption on FCHT-LDH and suggested the increased randomness at the solid/aqueous interface during the sorption process. In the contrary,

bromate sorption on FCHT-LDH was an exothermic process. The kinetic curves showed that anion sorption on FCHT-LDH was a rapid process with equilibrium generally attained within 4 h (Figure 4.7). This type of fast sorption process involving LDHs has been reported to be due to ion exchange reactions (Hermosín et al., 1996). Bromate sorption on FCHT-LDH was considerably faster than those of chromate and vanadate, indicating that molecular property of an anion had a significant effect on its sorption rate on FCHT-LDH and also on its equilibrium sorption capacity.

Figure 4.7 Kinetics of bromate, chromate, and vanadate sorption by FCHT-LDH.

Figure 4.8 illustrates the effects of pH and ionic strength on bromate, chromate, and vanadate sorption on FCHT-LDH. At the ionic strength of 0.005 M, more than 90% of the chromate was sorbed by FCHT-LDH in the pH range of 4.4-10.2, and the sorption decreased drastically at higher pH. Vanadate sorption was more than 95% at pH 5-7, but decreased significantly at pH > 7, which coincided approximately with the second pK_a (7.3) of H_3VO_4 (Richens, 1997). The sorption of bromate was about 19% at pH 4.5 and reduced gradually to 14% as the pH increased to 11. The insensitivity of bromate sorption to pH change was probably due to the presence of single negatively charged bromate species at pH ranging from 4.5 to 11 ($HBrO_3 \leftrightarrow BrO_3^- + H^+$; $pK_{a1} = 1.87$) (Kamble and Nandibewoor, 1996). The lower sorption of chromate or vanadate at high pH values was owing to an increased Donnan exclusion between the more negatively charged chromate or vanadate species and negatively charged surface sites of FCHT-LDH. The competition between carbonate (from atmospheric CO_2) or hydroxide ion (from NaOH) and chromate or vanadate for the sorption sites on

FCHT-LDH might also partially contribute to the lower anion sorption at high pH. The sorption of chromate decreased more gradually with increasing pH compared to vanadate because chromate has comparatively less negatively charged species at the same pH value, and therefore they do not exhibit as much repulsion as vanadate with the FCHT-LDH. These results confirmed that both chromate and vanadate had stronger affinities for FCHT-LDH than bromate over a broad pH range.

Figure 4.8 Effects of pH and ionic strength on the sorption of bromate, chromate, and vanadate by FCHT-LDH (time = 24 h, oxyanion or oxyhalide = 0.4 mM, dose = 0.4 g/L).

4.3.4 Sorption mechanisms

The reduction of N in FCHT-LDH was more significant for the sorption of chromate and vanadate which have higher ionic potentials compared to that of the lower-ionic-potential bromate (Table 4.1). This result indicated the occurrence of ion exchange process between the guest anions and the interlayer nitrate in FCHT-LDH. The anion-loaded FCHT-LDHs showed the shift of (003) reflection peaks in the XRD patterns to a lower 2θ and slight increased interlayer spacing after the sorption process (Figure 4.1 and Table 4.1), further suggesting the exchange of anion with nitrate in the interlayer region. Marginal increase of interlayer spacing of LDHs after incorporation of chromate has also been reported by some researchers (El-Malki et al., 1989; Prasanna et al., 2006). The increment of interlayer spacing was larger for the FCHT-

LDHs loaded with higher concentration of anions, implying the expansion of interlayer region to accommodate more guest anions for the exchange process. The broad peak with lower intensity observed at 22.5° for chromate-loaded FCHT-LDHs was probably due to the slight structural disorder arising out of stacking faults.

The FTIR band of interlayer nitrate (1384 cm^{-1}) for all the anion-loaded FCHT-LDHs became weaker after the sorption process, while new bands corresponding to Br-O stretching vibration, Cr-O stretching vibration and V-O stretching vibration, appeared at 791 cm^{-1} , 883 cm^{-1} , and 824 cm^{-1} , respectively (Figure 4.2). It was also found that the FTIR band assigned to $\delta_{\text{H}_2\text{O}}$ water bending (1637 cm^{-1}) could almost not be observed after anion removal. All the results of CHNS/O, XRD, and FTIR have demonstrated that anion exchange played a significant role in the sorption mechanism of bromate, chromate, and vanadate onto FCHT-LDH.

The study of ionic strength effect on the sorption at the solid/aqueous interface and EM measurements can be used to indirectly distinguish between the formation of outer-sphere and inner-sphere complexes (Arai et al., 2001). Both bromate and chromate sorption appeared to be sensitive to the changes in ionic strength in the pH range of 4.5-11 (Figure 4.8). Vanadate sorption was virtually unaffected by the changes in ionic strength in the pH range of 5-7, but decreased slightly with increasing ionic strength at pH 7-11. These findings suggested that bromate and chromate might predominantly form outer-sphere complexes on FCHT-LDH at pH 4.5-11, while the formation of outer-sphere vanadate complexes on FCHT-LDH was predominant at pH 7-11. Vanadate sorption on FCHT-LDH was less influenced by ionic strength compared to bromate and chromate, probably due to the energetic sorption activity of vanadate that led to weaker competition between the electrolyte ion and vanadate for the available surface sites on FCHT-LDH. The formation of outer-sphere complexes on FCHT-LDH by these anions was probably resulted from the anion exchange process (an electrostatic Coulombic interaction).

Figure 4.9 shows that the isoelectric point (IEP) of FCHT-LDH was ~ 13.5 . Sorption of bromate resulted in insignificant EM change and IEP shift. Sorption of chromate and vanadate however resulted in lower EM between pH 7-13 but did not significantly shift the IEP. These EM measurements again implied that bromate predominantly

formed outer-sphere complexes on FCHT-LDH at pH 4.5-13.5. The relatively larger reduction in EM for chromate and vanadate sorption on FCHT-LDH (at pH > 7) can be explained by either the formation of outer-sphere complexes or the formation of both outer-sphere and inner-sphere complexes.

Figure 4.9 Zeta potentials of fresh FCHT-LDH and anion-loaded FCHT-LDHs as a function of pH (time = 4 h, dose = 0.4 g/L, background electrolyte = 0.01 M NaNO₃).

Among the regenerating solutions, the highest desorption rate could be attained by desorbing anion-loaded FCHT-LDHs in Na₂CO₃ (Figure 4.10). This was probably due to the orientation of carbonate with its planes parallel to the principal layers that is more preferred in LDH formation. The high bromate desorption rate (~100%) suggested that bromate sorption on FCHT-LDH was reversible and non-specific, mainly due to its low ionic potential and weaker affinity for FCHT-LDH. It could be therefore deduced that bromate sorbed on FCHT-LDH via predominant anion exchange mechanism and formed outer-sphere complexes and this hypothesis was validated by the study of ionic strength effect and the EM measurements. In contrast, a significant fraction of vanadate was not displaceable by Na₂CO₃. A small fraction of non-displaceable chromate was also observed. These results generally suggested the occurrence of specific adsorption of vanadate and chromate to the FCHT-LDH surface through ligand exchange mechanism which would subsequently form inner-sphere complexes of vanadate and chromate in addition to the predominant outer-sphere complexes formed by the anion exchange mechanism. The exchange of

chromate or vanadate with the OH ligands on the FCHT-LDH surface is possible since these ligands are hard bases which preferably react with hard acids like Al^{3+} center, based on Pearson's hard and soft acids and bases (HASB) theory. The singly coordinated OH groups at the edges of FCHT-LDH were believed to be primarily responsible for the ligand exchange mechanism whereas the less-reactive OH groups, i.e. doubly coordinated OH at the edges and triply coordinated OH on the planar surfaces might play a secondary role, based on the observations reported for mineral surfaces (Torrent et al., 1990; Sparks, 2003).

Figure 4.10 Desorption of bromate, chromate, and vanadate from FCHT-LDH with various regenerating solutions.

4.3.5 XPS and EXAFS studies

Additional spectral evidence and structural data were collected using XPS and EXAFS spectroscopies to provide more direct and unequivocal information on the formation of anion complexes on FCHT-LDH. The XPS spectra of Mg 2p of FCHT-LDH before and after bromate, chromate, and vanadate sorption showed insignificant change, indicating that Mg atoms might not take part in their sorption (Figure 4.11a). In comparison with Mg 2p, a noticeable increase of the Al 2p spectra intensity of FCHT-LDH was observed after chromate and vanadate sorption, showing their strong interaction with Al atoms (Figure 4.11b). Conversely, the Al 2p spectra showed almost no change following bromate sorption on FCHT-LDH. These results suggested

that Al atoms played a key role in chromate and vanadate sorption, but not in bromate sorption.

Figure 4.11 (a) Mg 2p, (b) Al 2p, (c) O 1s, and (d) N 1s XPS core-level spectra of fresh and anion-loaded FCHT-LDHs (a = fresh FCHT-LDH, b = bromate-loaded FCHT-LDH (20 mg/L), c = bromate-loaded FCHT-LDH (100 mg/L), d = chromate-loaded FCHT-LDH (20 mg/L), e = chromate-loaded FCHT-LDH (100 mg/L), f = vanadate-loaded FCHT-LDH (20 mg/L), and g = vanadate-loaded FCHT-LDH (100 mg/L)).

O 1s narrow scans showed that the O 1s spectra of FCHT-LDH and anion-loaded FCHT-LDHs were quite different (except for bromate-loaded FCHT-LDHs), demonstrating that the oxygen constituents of FCHT-LDH changed after chromate and vanadate sorption (Figure 4.11c). The disappearance of the peak at 406.5 eV (N 1s) following chromate and vanadate sorption implied the successful exchange of nitrate with chromate and vanadate (Figure 4.11d). On the other hand, the N 1s spectra of bromate-loaded FCHT-LDHs were almost unchanged after the sorption process, indicating weak surface interaction between bromate and FCHT-LDH. Based on the atomic ratios of fresh and anion-loaded FCHT-LDHs obtained from XPS analysis, the atomic ratio of N decreased to zero with the increase of the Cr atomic ratio from 0 to 1.1% for FCHT-LDH loaded with 100 mg/L chromate, and from 0 to

0.8% for FCHT-LDH loaded with 100 mg/L vanadate. Nonetheless, Br was not detected on the surface of FCHT-LDH after bromate sorption.

Figure 4.12 presents the valence band photoelectron spectra of FCHT-LDH before and after anion sorption. The spectra of bromate-loaded FCHT-LDH were similar to that of fresh FCHT-LDH. Chromate and vanadate sorption influenced the nature of the valence band spectrum more substantially than that of bromate. The valence bands of chromate-loaded and vanadate-loaded FCHT-LDHs were shifted by about 2 eV to less negative binding energy relative to FCHT-LDH, whereas the intensity of the peaks were considerably higher. This spectroscopic variation suggested the formation of inner-sphere chromate and vanadate complexes on FCHT-LDH (Ding et al., 2000).

Furthermore, the stoichiometric ratio of OH^- between the fresh FCHT-LDH and anion-loaded FCHT-LDH was 1.8:1 for chromate-loaded FCHT-LDH and 1.9:1 for vanadate-loaded FCHT-LDH (Table 4.4), which was close to the configuration of the bidentate surface complexes (Sparks, 2003). The insignificant change of the content of OH^- for bromate-loaded FCHT-LDH further reinforced the absence of the inner-sphere surface complex.

Figure 4.12 Valance band spectra of (a) FCHT-LDH, (b) bromate-loaded FCHT-LDH (100 mg/L), (c) chromate-loaded FCHT-LDH (100 mg/L), and (d) vanadate-loaded FCHT-LDH (100 mg/L).

Table 4.4 Binding energies and relative contents of O 1s peaks for fresh and anion-loaded FCHT-LDHs

Sample	Assignment ^a	Binding energy (eV)	Relative content (%)
FCHT-LDH (fresh)	O ²⁻	530.65	18.1
	OH ⁻	531.32	33.2
	H ₂ O	531.80	48.7
Bromate-loaded	O ²⁻	530.72	23.1
FCHT-LDH (100 mg/L)	OH ⁻	531.32	34.9
	H ₂ O	531.92	42.0
	O ²⁻	530.42	27.0
Chromate-loaded FCHT-LDH (100 mg/L)	OH ⁻	531.24	18.1
	H ₂ O	531.74	54.9
	O ²⁻	531.18	29.9
Vanadate-loaded FCHT-LDH (100 mg/L)	OH ⁻	531.60	17.7
	H ₂ O	532.10	52.4
	O ²⁻	531.18	29.9

^aSurface species: O²⁻ indicates oxygen bonded to metal; OH⁻ indicates hydroxyl bonded to metal; H₂O indicates surface and interlayer water; Note: All the peaks modeled as 70:30 Gaussian:Lorentzian.

For analysis of the XANES data, the absorption edge of chromate sorbed on FCHT-LDH appeared to be the same as reference Cr(VI) (K₂Cr₂O₇ and K₂CrO₄) (Figure 4.13a) whereas the absorption edge of vanadate sorbed on FCHT-LDH was located at energy value that was similar to that determined for V₂O₅ (Figure 4.13b). The energies of the absorption edge, determined from the related zero crossing of the derivative spectrum (points) for a series of Cr and V references with known oxidation states, are shown in Figures 4.13c and 4.13d, respectively. These results corroborated that chromate sorbed on FCHT-LDH in the form of Cr(VI) and vanadate sorbed in the form of V(V), showing no reduction of chromate or vanadate after their sorption.

Figure 4.13 (a) Cr K-edge XANES spectra of references Cr, Cr_2O_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, K_2CrO_4 , and chromate-loaded FCHT-LDH, (b) V K-edge XANES spectra of references V, V_2O_5 , and vanadate-loaded FCHT-LDH, and the oxidation states versus the energy shifts in absorption edge (maximum derivative) for (c) references of Cr and chromate-loaded FCHT-LDH and (d) references of V and vanadate-loaded FCHT-LDH.

EXAFS spectroscopy was employed to determine the local coordination environment of chromate and vanadate sorbed on FCHT-LDH. The first peaks in the Fourier transformed spectra in Figures 4.14a and 4.14b were resulted from the Cr-O and V-O shells, respectively. The average interatomic distance (R) was 1.66 Å for chromate-loaded FCHT-LDH and 1.72 Å for vanadate-loaded FCHT-LDH. The average coordination number (CN) of oxygen was about 4 for both chromate and vanadate samples, confirming the tetrahedral geometry of these oxyanions. The second peaks centered at 2.5~3.0 Å with the CN of about 1 were attributed to chromate and vanadate bonding with Al. The EXAFS features indicated that chromate and vanadate were possibly adsorbed on FCHT-LDH by forming inner-sphere bidentate surface complexes, which was consistent with previous EXAFS studies of the association of polyvalent oxyanions on similar mineral surfaces (Fendorf et al., 1997; Arai et al., 2001). The inner-sphere bidentate complexes involved ionic bonding, covalent bonding or some combinations of covalent and ionic bonding (Stumm, 1992). The exact bonding mechanism at different experimental conditions can be further determined by a combined and comprehensive XANES and EXAFS analyses (Elzinga and Sparks, 2002).

Figure 4.14 Fourier transformed EXAFS spectra for (a) chromate-loaded FCHT-LDH and (b) vanadate-loaded FCHT-LDH (solid lines and open circles represent fitted and experimental data, respectively).

Overall, bromate sorption on FCHT-LDH was likely occurred via predominant anion exchange mechanism with subsequent formation of outer-sphere complexes:

Conversely, two mechanisms have been found responsible for the sorption of chromate or vanadate on FCHT-LDH, i.e. primary anion exchange and secondary ligand exchange mechanisms, resulting in a mixture of outer-sphere and inner-sphere

complexes of chromate or vanadate. These postulated mechanisms and surface complexes are illustrated in Figure 4.15 and described in the following equations:

Figure 4.15 Hypothesized schematic diagram of anion sorption mechanisms on FCHT-LDH.

4.4 Conclusions

This study shows that nanocrystalline Mg/Al LDH with nitrate intercalation (FCHT-LDH) has excellent potential for use as a new sorbent for harmful anion removal from aqueous solution owing to its simple preparation method, high sorption capacity, and reusability. The sorption characteristics of oxyanions and oxyhalides on FCHT-LDH were dependent on their ionic potentials and molecular structures. FCHT-LDH exhibited a much higher sorption capacity for divalent oxyanions (e.g. chromate and vanadate) than monovalent oxyhalides (e.g. bromate), attributable to their higher ionic potential and tetrahedral coordination. Chromate and vanadate sorption on FCHT-LDH were endothermic, while bromate sorption was exothermic. Sorption of chromate and vanadate was more sensitive to changes in pH than bromate. The kinetic study showed that the sorption of bromate, chromate, and vanadate on FCHT-LDH was a rapid process with equilibrium generally attained within 4 h. Macroscopic and microscopic studies revealed that monovalent oxyhalide sorption on FCHT-LDH likely occurred via anion exchange mechanism with subsequent formation of outer-sphere surface complexes. On the other hand, polyvalent oxyanion sorption mechanisms on FCHT-LDH possibly involved both anion exchange and ligand exchange between the oxyanions and surface-coordinated OH ligands, resulting in the coexistence of outer-sphere and inner-sphere surface complexes. The chemical bond in the inner-sphere complexes can be ionic, covalent, or a combination of the two.

Chapter 5 Enhanced Arsenic Removal by Nanocrystalline LDH: Sorption, Mechanism, Regeneration, and Surface Analysis

5.1 Introduction

In Chapter 4, FCHT-LDH has shown great potential in removing polyvalent oxyanions with high ionic potential from the aqueous solution. These oxyanions include arsenate which exists as a polyvalent oxyanion at circumneutral to alkaline pH and its occurrence in the environment has raised substantial health and regulatory concerns as a result of its toxic and carcinogenic properties. Knowing the interactions between arsenate and metal (hydr)oxides like FCHT-LDH is important since it will enable the accurate description of arsenate mobility in the environment, prediction of the sorptive properties of this sorbent, prediction of the long-term fate of arsenate in the LDH/aqueous environment, and development of the molecular sorption models.

Most previous works have suggested that arsenic was removed by LDHs via anion exchange mechanism, but remained hypothetical at best (Lazaridis et al., 2002; Yang et al., 2005; Gillman, 2006). A limitation of these studies was that insufficient experiments were conducted to illustrate the ion exchange stoichiometry for LDH and to provide direct evidence of the occurrence of anion exchange mechanism. It was therefore rather difficult to quantitatively assess the impact of anion exchange property of LDH on arsenic removal. Wang et al. (2008a) indicated that arsenate sorption by Mg/Al LDH could occur through surface adsorption and interlayer anion exchange depending on the interlayer nitrate orientation. Nonetheless, the predominant mechanism was not clearly identified. Moreover, the quantification of the contributions of the different mechanisms (e.g. anion exchange and adsorption) to arsenate removal will greatly promote the thorough understanding of arsenic interaction with LDH. An EXAFS study performed by Liu et al. (2006) reported that arsenate was removed by chloride-Li/Al LDH by reacting with Li cations located in the octahedral holes within $\text{Al}(\text{OH})_3$ and Al in the edges of $\text{Al}(\text{OH})_3$ layers. They

showed arsenate adsorption on the surface of chloride-Li/Al LDH with the formation of inner-sphere bidentate complexes. Conversely, Wang et al. (2008a) suggested that arsenate was sorbed on Mg/Al LDH by forming outer-sphere complex. These limited but significant reports indicated that arsenate-LDH surface complex might vary with LDH with different structural aspects and revealed the need for more information of adsorbed complexes via other promising techniques such as XPS which has been used to study the effect of surface properties on arsenate adsorption (Zhang et al., 2005; Deng et al., 2008).

This part of study aimed to (1) assess arsenate binding by FCHT-LDH through anion exchange mechanism using stoichiometric calculations, nitrate displacement investigation, and analyses of XPS, XRD, FTIR, CHNS/O, and EDX, (2) unravel the predominant nature of the interaction between the LDH and arsenate and subsequently quantify the contributions of the different mechanisms to arsenate removal using sorption/desorption experiments, and (3) understand the possible dominant arsenate-LDH surface complex based on the XPS analysis. Other ancillary objectives included investigation of the thermodynamics of arsenate sorption by the LDH and examination of the reusability of the regenerated LDH for subsequent cycles of arsenate sorption.

5.2 Experimental section

Arsenate sorption experiments were mainly carried out with FCHT-LDH in the batch system. IE-LDH was used for comparison. The chemicals used, the material synthesis method, the procedures of the characterization techniques as well as some other experimental procedures have been presented in Chapter 3. Several analytical techniques such as XPS, XRD, FTIR, CHNS/O, and EDX were used to characterize the LDH samples before use, after use, and after regeneration.

Batch experiments were performed to investigate the displacement of interlayer nitrate by arsenate as a function of arsenate loading and reaction time. In addition, the sorption isotherms, effect of temperature, kinetics, and effect of pH were also

examined according to the procedures mentioned in Section 3.3.3. Several cycles of arsenate sorption-desorption were performed in the regeneration study.

5.3 Results and discussion

5.3.1 Characterizations

The $\text{Mg}^{2+}/\text{Al}^{3+}$ molar ratio and C and N content of the fresh FCHT-LDH and IE-LDH have been discussed in Section 4.3.1. The specific surface area, based on BET method, of FCHT-LDH was $127 \text{ m}^2/\text{g}$ whereas the pore volume, based on BJH method, was $0.31 \text{ cm}^3/\text{g}$ (Table 5.1), and they were higher than those of IE-LDH by 2-8 times. The pore size of both FCHT-LDH and IE-LDH fell in the meso size range (2-50 nm). The PCS analysis demonstrated that FCHT-LDH had a narrow particle size distribution with an equivalent hydrodynamic diameter of 122 nm and all particles fell within 38-396 nm.

Table 5.1 Chemical composition, textural properties, and lattice parameters of the fresh and arsenate-loaded FCHT-LDHs

Sample	Chemical composition				Textural property				Lattice parameter		
	$\text{Mg}^{2+}/\text{Al}^{3+}$ molar ratio	C (wt %)	N (wt %)	As (mass %)	S^a (m^2/g)	V^b (cm^3/g)	D^c (nm)	Particle size [average size] (nm)	a^d (Å)	c^e (Å)	Crystal size ^f (nm)
IE-LDH	3.1/1	9.2	1.4	n/a	56	0.04	3.0	22-564 [200]	3.04	22.67	21.5
FCHT-LDH	2.0/1	0.7	3.3	0	127	0.31	8.0	38-396 [122]	3.04	23.53	5.9
FCHT-LDH (As(V)- loaded)	n/a	0.7	0.5	14 ^g	n/a	n/a	n/a	n/a	3.04	23.90	9.1

^aBET surface area; ^bBJH pore volume; ^cBJH pore size; ^d $a = 2 \times d(110)$; ^e $c = 3 \times d(003)$; ^fAverage value calculated from fwhm of peak (003) and (006); ^gValue determined from SEM-EDX analysis; *n/a denotes “data not available”.

Figure 5.1 depicts the HRTEM image of the fresh FCHT-LDH. The elliptic regions show the randomly oriented LDH crystallites consisting of nanocrystalline grains which ranged from 5.3 nm to 5.8 nm. The identified interplanar distance (0.26 nm)

was close to that of (009) plane. The selected area diffraction (SAED) patterns confirmed the presence of LDH (as identified by the diffraction rings corresponding to (003) and (006) planes).

Figure 5.1 HRTEM image of FCNT-LDH with the elliptic regions highlighting the diffraction pattern of a number of randomly oriented crystal grains (the inset on the top left is its SAED pattern whereas the inset on the bottom left is the identified interplanar distance (0.26 nm) that is close to that of (009)).

5.3.2 Interaction of Arsenate with FCNT-LDH

Figure 5.2a shows that the amount of sorbed arsenate increased linearly with arsenate loading up to 114 cmol/kg, which corresponded to the anion exchange capacity estimated from the FCNT-LDH stoichiometry ($\text{Mg}_2\text{Al}(\text{OH})_6(\text{NO}_3)_{0.82}(\text{CO}_3)_{0.09} \cdot n\text{H}_2\text{O}$) and the anion exchange stoichiometry (equation 5.1), assuming that interlayer carbonate was not exchangeable (Jobbagy and Regazzoni, 2005).

Figure 5.2 (a) Arsenate sorbed as a function of the arsenate loading (no background electrolyte added) and (b) arsenate remained in solution and nitrate displaced as a function of reaction time (number in bracket indicates the molar ratio of nitrate displaced to arsenate sorbed).

To assess the extent of arsenate binding by anion exchange, the equilibrium exchange constant, K_{ex} was determined. This parameter is useful for determining the state of ionic equilibrium at different ion concentrations. K_{ex} was calculated by referring to the methods of Vanselow (Vanselow, 1932) and Gaines and Thomas (Gaines and Thomas, 1953). According to these methods, K_{eq} (apparent equilibrium exchange constant) is written as:

$$K_{\text{eq}} = \frac{\gamma_{\text{As(V)}} C_{\text{As(V)}} (N_{\text{NO}_3^-})^2}{(\gamma_{\text{NO}_3^-})^2 C_{\text{NO}_3^-} (N_{\text{As(V)}})} \quad (5.2)$$

where $\gamma_{\text{As(V)}}$ and $\gamma_{\text{NO}_3^-}$ are the solution-phase activity coefficients of the two anions calculated using the extended Debye-Hückel equation (Stumm and Morgan, 1996), $C_{\text{As(V)}}$ and $C_{\text{NO}_3^-}$ are the equilibrium concentrations (M) of arsenate and nitrate, respectively, and N_{NO_3} and $N_{\text{As(V)}}$ are the LDH-phase activity in terms of mole fraction ($N_{\text{NO}_3^-} = \{\text{NO}_3^-\} / (\{\text{NO}_3^-\} + \{\text{As(V)}\})$ and $N_{\text{As(V)}} = \{\text{As(V)}\} / (\{\text{As(V)}\} + \{\text{NO}_3^-\})$ where braces indicate the LDH phase composition in mol/kg). K_{ex} was then computed from equation 3.4.

All the parameters obtained in the computation process of K_{ex} are shown in Table 5.2. The calculated value of K_{ex} was 30.6. The value obtained was within the range reported by Miyata (1983) ($K_{\text{ex}} = 24.5\text{-}69.2$) in similar heterovalent exchange system (e.g. SO_4^{2-} exchanged for NO_3^-) but smaller than the one demonstrated by Israëli et al. (2000) for a homovalent exchange system (e.g. OH^- exchanged for Cl^-). The obtained K_{ex} confirmed the stoichiometric and reversible electrostatic interaction between the arsenate in the solution and the nitrate in the interlayer region of FCHT-LDH.

Figure 5.2b shows that nitrate was released steadily from FCHT-LDH with simultaneous arsenate sorption. A molar ratio ranging from 2-3 for the displacement of nitrate by arsenate on FCHT-LDH throughout the reaction time supported the occurrence of anion exchange process. The slight difference between the obtained molar ratio and the stoichiometry ratio of 2 was possibly due to the leaching of residual nitrate (from the precursor used) remained in the FCHT-LDH product.

Table 5.2 Summary of parameters used for the computation of equilibrium exchange constant (K_{ex})

Test	Solution phase concentration (M)	LDH phase concentration (mol/kg)		Mole fractions		K_{eq}	$\ln K_{eq}$	$(LDH)_{As(V)}$	
	As(V)	Nitrate	As(V)	Nitrate	$N_{As(V)}$	N_{NO_3}			
1	0	1.05×10^{-4}	0.00	2.55	0.000	1.000	–	6.42 ^a	0.000
2	1.07×10^{-6}	3.40×10^{-4}	0.04	1.70	0.022	0.978	412	6.02	0.011
3	1.46×10^{-6}	3.51×10^{-4}	0.15	1.67	0.083	0.917	125	4.83	0.043
4	2.58×10^{-6}	3.84×10^{-4}	0.31	1.59	0.163	0.837	78.6	4.36	0.089
5	2.89×10^{-6}	3.95×10^{-4}	0.46	1.56	0.226	0.774	51.3	3.94	0.127
6	4.84×10^{-6}	4.78×10^{-4}	0.78	1.35	0.365	0.635	24.5	3.20	0.223
7	3.21×10^{-5}	6.89×10^{-4}	1.06	0.83	0.562	0.438	24.4	3.19	0.391
8	1.44×10^{-4}	8.37×10^{-4}	1.15	0.46	0.717	0.283	24.3	3.19	0.558
9	2.69×10^{-4}	8.81×10^{-4}	1.18	0.35	0.773	0.227	24.1	3.18	0.631
10	2.69×10^{-4}	0	1.19	0.00	1.000	0.000	–	3.13 ^a	1.000

^aExtrapolated $\ln K_{eq}$ values.

According to Figure 5.3 and Table 5.1, the (003) reflection peak moved to a lower 2θ after FCHT-LDH reacted with arsenate, indicating the exchange of arsenate (molecular diameter ~ 0.5 nm) for nitrate (molecular diameter ~ 0.4 nm). The decrease of the intensity of (003) reflection peak also suggested that arsenate entered the interlayer of FCHT-LDH. Decrement of N with simultaneous increment of As in the exhausted FCHT-LDH was observed in the XPS, CHNS/O and EDX analyses (Tables 5.1 and 5.3). These results corroborated that anion exchange was one of the important mechanisms for the arsenate removal by FCHT-LDH and subsequently arsenate might bind on the internal surfaces by forming outer-sphere complex (Wang et al., 2008a). After FCHT-LDH reacted with arsenate, the FTIR band assigned to interlayer nitrate (1384 cm^{-1}) became weaker, while a new band, corresponding to As-O stretching vibration, was detected at 830 cm^{-1} , further suggesting the exchange of nitrate with arsenate (Figure 5.4).

Figure 5.3 XRD patterns of the fresh FCHT-LDH, arsenate-loaded FCHT-LDH, and FCHT-LDH after regeneration for 4 cycles (peaks are labeled with indices of reflection plane).

Table 5.3 Atomic ratios of fresh and arsenate-loaded FCHT-LDHs obtained from XPS analysis

Types of FCHT-LDH	Atomic ratio %					
	Mg	Al	N	O	As	Total
FCHT-LDH	21.3	9.7	2.9	66.2	0.0	100
FCHT-LDH-50 cmol As(V)/kg	20.6	10.6	0.0	68.0	0.8	100
FCHT-LDH-334 cmol As(V)/kg	19.8	10.3	0.0	67.1	2.9	100

Figure 5.4 FTIR spectra of the fresh FCHT-LDH and arsenate-loaded FCHT-LDH.

The concurrent monitoring of the solution pH showed a discernible pH increment of ca. 0.4-0.6 during arsenate sorption equalization, implying the occurrence of ligand exchange of the surface OH groups with arsenate under this experimental condition. The exchange of arsenate with OH^- was possible since both ligands are hard bases which preferentially react with hard acids such as Al^{3+} center, according to HASB theory. The peak shift to 3599 cm^{-1} from 3480 cm^{-1} after arsenate sorption also suggested the possible involvement of OH group in the sorption process. Therefore, it could be deduced that while anion exchange was the predominant mechanism for arsenate sorption by FCHT-LDH, and ligand exchange might occur concurrently as the secondary sorption mechanism. These mechanisms are further discussed in the subsequent sections.

5.3.3 Sorption isotherms, thermodynamics, and kinetics

On the basis of R^2 and χ^2 , Langmuir isotherm was found more suitable than Freundlich isotherm for describing the arsenate sorption on FCHT-LDH as well as on IE-LDH (Freundlich isotherm for IE-LDH: $R^2 = 0.989$ and $\chi^2 = 0.19$) (Figure 5.5). The sorption maxima for arsenate on FCHT-LDH was 114 cmol/kg or 85 mg/g and it was much higher than those of the IE-LDH as well as most conventional sorbents (Goh et al., 2008).

Figure 5.5 Sorption isotherms of arsenate on FCHT-LDH.

Figure 5.6 depicts the equilibrium sorption isotherms of arsenate at 25, 35, 45, and 55 °C. The equilibrium sorption capacity increased with increasing temperature, suggesting that the interaction between arsenate and FCHT-LDH was endothermic in nature. The negative ΔG° value (-6.43 kJ/mol) indicated that the arsenate removal by FCHT-LDH was a spontaneous process, implying that the exchange force was strong enough to break the potential and drive the reaction to displace nitrate with arsenate in the FCHT-LDH. The positive value of ΔH° (3.73 kJ/mol) confirmed the endothermic nature of anion exchange process. The positive value of ΔS° (0.03 kJ/mol.K) revealed the increased randomness at the solid/solution interface for the anion exchange between arsenate and interlayer nitrate.

Figure 5.6 Sorption isotherms of arsenate on FCHT-LDH at different temperatures (pH = 9.5, time = 24 h, dose = 0.4 g/L, background = 0.01 M NaNO₃) and the inset is the van't Hoff plot of $\ln K_c$ against reciprocal temperature. Experimental data are reported as points and model (Langmuir Isotherm) by curves.

Four kinetic models were used to fit the experimental data, including the commonly used pseudo-first order and pseudo-second order models, modified multiplex model (Lv et al., 2007), and Elovich model. The modified multiplex and Elovich models have been explained in Section 3.5. Elovich was considered the most suitable in describing the sorption kinetics of arsenate on FCHT-LDH in terms of the statistical parameters ($R^2 > 0.990$, $\chi^2 < 0.95$ and $\Delta q < 5$) (Table 5.4) and the fits of experimental data to Elovich model by non-linear and linear regressions are shown in Figures 5.7a and 5.7b, and Figure 5.7c, respectively. Elovich equation which considers the

heterogeneous sorptive sites (Cheung et al., 2001) also matched the sorption properties of FCHT-LDH since it was postulated that there were interlayer and external surface sites of FCHT-LDH for the arsenate sorption.

Among the FCHT-LDHs, FCHT-LDH intercalated with nitrate showed tremendous arsenate sorption performance and greatest sorption rate compared to that of FCHT-LDH with interlayer carbonate and phosphate, indicating that interlayer anions with lower valence were more readily exchanged with arsenate than the higher-valence interlayer anions (Figure 5.7a). The activation energy (E_a) is usually less than 30 kJ/mol for anion exchange-controlled processes (Ho et al., 2000). The E_a value calculated from the gradient ($-E_a/R$) of $\ln k_2$ vs $1/T$ using the data for arsenate sorption at 5-65 °C in this study was 24.7 kJ/mol (Figure 5.7b), suggesting the predominantly anion exchange process for the arsenate sorption by the FCHT-LDH.

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Table 5.4 Experimental conditions for all kinetic experiments (above) and kinetic and statistical parameters of the four kinetic models (below)

Exp. No.	Types of LDH	Dosage (g/L)	Interlayer anions	Temp. (°C)	$q_{e, \text{exp}}$ (cmol/kg)
1	FCHT-LDH	0.4	NO_3^-	25	53.6
2	FCHT-LDH	0.4	CO_3^{2-}	25	6.6
3	FCHT-LDH	0.4	PO_4^{3-}	25	5.0
4	FCHT-LDH	0.4	NO_3^-	5	50.0
5	FCHT-LDH	0.4	NO_3^-	45	53.7
6	FCHT-LDH	0.4	NO_3^-	65	53.7

Exp. No.	Pseudo-first order model					Pseudo-second order model					Modified multiplex model					Elovich model					
	$q_{e, \text{ cal}}$	$k_1 \times 10^{-2}$	R^2	χ^2	Δq	$q_{e, \text{ cal}}$	$k_2 \times 10^{-3}$	R^2	χ^2	Δq	$q_{e, \text{ cal}}$	k_{m1}	$k_{m2} \times 10^{-3}$	R^2	χ^2	Δq	α	β	R^2	χ^2	Δq
	(cmol/kg)	(min ⁻¹)			(%)	(cmol/kg)	(kg/cmol·min)			(%)	(cmol/kg)	(min ⁻¹)	(kg/cmol·min)			(%)					(%)
1	53.6	3.53	0.927	450.22	46.8	54.1	11.8	0.998	0.40	3.1	53.1	3.62×10 ⁻⁶	13.8	0.995	0.227	2.2	1.28×10 ⁴	0.23	0.992	0.944	4.7
2	6.6	2.94	0.899	61.89	48.3	6.6	48.2	0.973	0.89	11.5	6.2	1.67×10 ⁻¹⁰	108	0.976	0.170	5.5	4.37×10 ²	1.77	0.998	0.025	2.1
3	4.8	3.34	0.922	40.54	46.2	4.8	83.6	0.975	0.45	9.9	4.6	2.27×10 ⁻⁵	147	0.962	0.196	6.9	2.92×10 ²	2.37	0.996	0.036	2.7
4	49.2	3.26	0.890	915.76	45.8	50.3	7.01	0.991	1.69	6.8	49.2	4.57×10 ⁻⁷	7.65	0.981	1.469	6.3	3.52×10 ²	0.18	0.994	0.664	4.0
5	53.7	3.81	0.797	541.17	47.0	54.1	24.6	0.998	0.30	2.5	53.8	1.13×10 ⁻⁵	22.2	0.996	0.229	2.2	1.78×10 ⁶	0.33	0.992	0.874	4.2
6	53.7	4.00	0.762	587.78	46.9	53.8	45.5	0.998	0.25	2.3	53.8	1.34×10 ⁻²	31.2	1.000	0.014	0.5	6.77×10 ⁸	0.44	0.994	0.664	3.6

Figure 5.7 Time-dependent sorption of arsenate on (a) FCHT-LDH with different interlayer anions (non-linear regression with Elovich model) and (b,c) FCHT-LDH at different temperatures (non-linear and linear regressions with Elovich model and the inset in (b) is the Arrhenius plot). Experimental data are reported as points and Elovich model by solid lines.

5.3.4 pH effect

The pH influence on arsenate sorption on FCHT-LDH is illustrated in Figure 5.8, along with the results of a similar study performed on arsenite. The results showed that arsenate sorption decreased gradually with increasing pH in the range of pH 5.3 to 9.5. For the arsenate loading of 115 cmol/kg, more than 80% of arsenate (equivalent to ~92 cmol/kg) was removed by FCHT-LDH in this pH range. The arsenate sorption however decreased remarkably at pH > 9.5. The decrease of arsenate sorption with increasing pH was due to the decreasing Coulombic attraction resulting from the decreasing positive charge of FCHT-LDH as well as increasing competition from OH⁻ ions. This sorption characteristic was different from that of arsenite. Arsenite removal increased from 12% to 52% when the pH was increased from 5.3 to 10.1. The maximum sorption was observed at pH value slightly higher than the first dissociation constant of H₃AsO₃ (pK_{a1} = 9.2). The higher sorption of arsenate than arsenite by FCHT-LDH was due to the presence of monovalent H₂AsO₄⁻ and divalent HAsO₄²⁻ which were more favorable for the anion exchange process compared to the uncharged H₃AsO₃ and monovalent H₂AsO₃⁻.

Figure 5.8 Sorption results for the reaction of arsenate and arsenite with FCHT-LDH as a function of pH.

5.3.5 Regeneration

Highest arsenate desorption rate (~76%) was achieved by desorbing arsenate-loaded FCHT-LDH in Na_2CO_3 with Mg and Al dissolutions of less than 0.1% of their initial masses (Table 5.5). Both desorption and regeneration rates decreased gradually with number of cycle (Figure 5.9). Dissolution of Mg was relatively high in the initial cycles but progressively reduced to 0.13% in the forth cycle whereas dissolution of Al remained constant at $< 0.1\%$ in each cycle. These results showed satisfactory chemical stability of the FCHT-LDH over several sorption-desorption repetition. The XRD reflection peaks corresponding to (003) and (006) planes observed in the regenerated FCHT-LDH indicated no significant decline in the crystallinity of the FCHT-LDH (Figure 5.3).

It is worth noting that ~24% of arsenate was not displaceable by Na_2CO_3 (a hysteretic sorption/desorption characteristic), indicating the irreversible and specific adsorption of this arsenate fraction to the FCHT-LDH surface. They were likely adsorbed on FCHT-LDH through ligand exchange process which subsequently formed inner-sphere surface complex. This hypothesis was confirmed by the observed pH increase of ca. 0.4-0.6 unit during the arsenate sorption equalization that corresponding to the release of about $0.5\text{--}1.0 \times 10^{-4} \text{ M OH}^-$ into the solution for a system with an initial arsenate concentration of $2 \times 10^{-4} \text{ M}$ at pH 9.5 (with ~100% sorption). This amount of released OH^- equaled to an upper-bound value of 25% of total sorbed arsenate which could have exchanged with surface OH^- through ligand exchange process.

Table 5.5 Arsenate desorption from FCHT-LDH with various regenerating solutions

Regenerating solution	Desorption		
	Desorption rate (%)	Dissolution of Mg (%)	Dissolution of Al (%)
0.05 M NaOH	63.9 ± 0.6	0.04 ± 0.01	0.06 ± 0.01
0.1 M NaOH	68.3 ± 1.8	0.01 ± 0.00	0.10 ± 0.01
1 M NaNO_3	37.0 ± 1.6	0.70 ± 0.02	0.01 ± 0.00
1 M $\text{Mg}(\text{NO}_3)_2$	46.2 ± 1.6	n/a	0.09 ± 0.00
1 M NaNO_3 + 0.1 M NaOH	58.5 ± 2.1	0.00 ± 0.00	0.16 ± 0.01
0.1 M Na_2CO_3	76.0 ± 0.5	0.08 ± 0.02	0.03 ± 0.01

Figure 5.9 Reusability and chemical stability of FCHT-LDH with recycle times (Regeneration method: 0.1 M Na_2CO_3 followed by calcination; Desorption rate = $A_{\text{des}}/A_0 \times 100$, Regeneration rate = $A_{\text{reg}}/A_0 \times 100$, where A_0 = initial arsenate sorbed, A_{des} = desorbed amount of arsenate, A_{reg} = sorbed amount of arsenate by regenerated FCHT-LDH).

5.3.6 Surface analysis

XPS analysis showed insignificant change of the Mg 2p spectra of FCHT-LDH before and after arsenate sorption, suggesting that Mg atoms might not participate in arsenate sorption (Figure 5.10a). The remarkable increase of As 3d spectra after arsenate sorption, particularly at higher arsenate loading, signified the successful arsenate binding to FCHT-LDH. The binding energy value of Al in FCHT-LDH (74.4 eV) indicated that the Al phase of FCHT-LDH can be assigned to Al-OH (Figure 5.10b). Compared to Mg 2p, a significant increase of the Al 2p spectra intensity of FCHT-LDH and a spectra shift to 74.2 eV (assigned to Al-O) were observed following arsenate sorption, showing the strong interaction between arsenate and Al atoms. Thus Al atoms likely played a pivotal role in arsenate sorption. The O 1s spectra of FCHT-LDH and FCHT-LDH loaded with arsenate were slightly different, implying the alteration of oxygen constituents of FCHT-LDH after arsenate sorption (Figure 5.10c). On the other hand, the peak at 406.5 eV (N 1s) disappeared after arsenate sorption, demonstrating the successful exchange of nitrate with arsenate (Figure 5.10d).

Figure 5.10 XPS spectra of (a) Mg 2p and As 3d, (b) Al 2p, (c) O 1s, and (d) N 1s for fresh and arsenate-loaded FCHT-LDHs.

Three possible inner-sphere arsenate complexes can be postulated to form at the Al^{3+} center in the FCHT-LDH resulting from arsenate interaction with aluminol functional group, namely monodentate mononuclear complex, bidentate mononuclear complex, and bidentate binuclear complex (Arai et al., 2001). The hypothetical depictions and the stoichiometry of the formations of these complexes are:

Monodentate mononuclear complex:

Bidentate mononuclear complex:

Bidentate binuclear complex:

According to the configurations of these complexes, the stoichiometric ratio of surface hydroxyl between the fresh sorbent and the sorbent sorbed with arsenate was 1:2 for a monodentate surface complex and 2:1 for a bidentate complex. Table 5.6 depicts the ratio of OH^- to total oxygen atoms in FCHT-LDH increased from 33.2% to 56.1% for FCHT-LDH-50 cmol As(V)/kg and from 33.2% to 59.1% for FCHT-LDH-334 cmol As(V)/kg, equivalent to a ratio of OH^- of 1:1.7 and 1:1.8, respectively, which was in good agreement with the monodentate mononuclear complex. Therefore, it was hypothesized that monodentate mononuclear complex was dominant on FCHT-LDH after arsenate sorption. The slight difference in the inner-sphere surface complex postulated in this study and the previous study in Chapter 4 might be attributable to the different surface loadings of oxyanion applied which have resulted in different surface coverage of oxyanion on the LDH and subsequently distinct forms of surface complexes. It was also possible that the different surface structures were a consequence of oxyanion protonation at different oxyanion surface loadings.

Table 5.6 O 1s peak parameters for fresh and arsenate-loaded FCHT-LDHs

Types of FCHT-LDH	Species ^a	Binding energy	fwhm	Percent ^b
		(eV)	(eV)	(%)
FCHT-LDH	O ²⁻	530.65	1.6	18.1
	OH ⁻	531.32	1.6	33.2
	H ₂ O	531.80	1.6	48.7
FCHT-LDH-50 cmol As(V)/kg	O ²⁻	530.52	1.7	25.7
	OH ⁻	531.42	1.7	56.1
	H ₂ O	531.80	1.7	18.2
FCHT-LDH-334 cmol As(V)/kg	O ²⁻	530.39	1.5	25.7
	OH ⁻	531.50	1.5	59.1
	H ₂ O	532.36	1.5	15.2

^aO²⁻: oxygen bonded to metal, OH⁻: hydroxyl bonded to metal, H₂O: surface and/or interlayer water; ^bPercentage of the atomic concentration of each species to the total oxygen atom

5.4 Conclusions and environmental implications

In summary, this study has demonstrated that hydrothermal treatment can be employed to synthesize FCHT-LDH which exhibits enhanced arsenate removal and the removal reaction can be satisfactorily modeled with Elovich kinetics. Arsenite was not as effectively removed by FCHT-LDH most probably due to the presence of uncharged and single negatively charged arsenite species that were not favorable for the sorption process. Enhanced arsenate removal by FCHT-LDH was likely occurred through two mechanisms: (1) primary anion exchange mechanism with possible formation of outer-sphere complex and (2) secondary ligand exchange mechanism with formation of inner-sphere complex. The predominance of anion exchange mechanism in arsenate sorption by FCHT-LDH was evidenced by the nitrate-arsenate molar displacement ratio, increased interlayer spacing, weakened FTIR band of interlayer nitrate with simultaneous appearance of As-O band, and decreased nitrogen content in the interlayer region. On the other hand, slight pH increase during arsenate sorption equalization and the presence of ca. 25% irreversibly sorbed arsenate signified the occurrence of ligand exchange process as the secondary sorption

mechanism. This specific sorption process that possibly involved formation of inner-sphere arsenate complexes with a monodentate mononuclear configuration at the aluminum center, rendered the FCHT-LDH a high affinity for arsenate over nitrate but induced hysteretic sorption/desorption characteristic that limited its regenerated sorption capacity.

Despite the promising performances of the FCHT-LDH in the sorption of polyvalent oxyanions such as arsenate, the chemical stability and durability of this material are crucial for its application in water treatment. Therefore more future research should be devoted to rigorously examining the solubility of FCHT-LDH under various environmental conditions and further enhancing its crystallinity through novel synthesis in order to ensure sorbent stability and good sorption ability for prolonged application.

Chapter 6 Effect of Aqueous Matrix on Oxyanion Sorption by Nanocrystalline LDH

6.1 Introduction

As presented in Chapters 4 and 5, FCHT-LDH is potentially a good sorption media for oxyanion removal considering its high removal efficiency, reusability, and the availability of its precursor materials. It has been shown that the removal mechanisms might involve both anion exchange and surface adsorption. However, several types of co-solutes with different physicochemical properties are often present in groundwater and surface water and may influence oxyanion sorption reactions by competing for available binding sites on the surface of the sorbent or altering the electronic charge on the solid surface (Jain and Loeppert, 2000). Successful application of LDH technology for removing oxyanions in groundwater remediation or effluent treatment requires a good understanding of the possible interference of aqueous matrix species with the LDH particles and the sorption reaction.

To date, a number of studies have reported the effects of co-existing anions such as chloride, nitrate, carbonate, sulfate, phosphate, etc. on oxyanion sorption by LDHs (You et al., 2001a; You et al., 2001b; Yang et al., 2005; Wang et al., 2009b). They generally suggested that the co-existence of a competing anion with a higher ionic charge density has a greater negative impact upon the sorption of the target oxyanion for removal by LDHs. Nonetheless, there has been no comprehensive and systematic study on the influences of co-existing anions as functions of solution pH, relative anion concentration, and reaction time on the sorption of oxyanions, particularly arsenate, by LDHs. Furthermore, the competitive effects of the co-existing anions on various oxyanions having different molecular properties have not been directly compared. Most of the previous studies are based on the conventional coprecipitated LDH, the interaction between the co-existing anions and FCHT-LDH can be different from those reported for the coprecipitated LDH system since FCHT-LDH has a much larger specific surface area, better porosity characteristic, and nanocrystalline property.

Silica is commonly present in natural water due to the weathering of minerals and are constantly dissolving and precipitating over a large part of the earth's surface (Meng et al., 2000), but no information is available in the literature on the influence of silica on oxyanion removal by LDHs. While there are several studies on the effects of anions on oxyanion sorption by LDHs, comparatively little effort has been directed towards investigating the effect of NOM on the removal of oxyanions by LDHs. NOM is ubiquitous in soil and natural waters and has a high tendency to be adsorbed onto mineral surfaces (Saito et al., 2004) which could subsequently modify the properties of mineral surfaces and block the adsorption sites (Rao et al., 2009). It has been reported that NOM inhibited arsenic adsorption onto iron oxide surfaces by competing for adsorption sites and reducing the available adsorption sites (Grafe et al., 2001; Redman et al., 2002; Giasuddin et al., 2007). The studies examining the effects of silica and NOM on oxyanion removal by LDHs are therefore needed given the varying composition of natural waters. Indeed the knowledge of their effects on the sorption reaction is vital for the development of an effective oxyanion treatment system.

In this part of study, the effects of co-existing species commonly found in the contaminated groundwater, surface water, and industrial effluents (i.e. nitrate, silica, sulfate, carbonate, phosphate, and NOM) on arsenate removal by FCHT-LDH were investigated over a wide pH range and at different concentrations and reaction times. The competitive effects of the common anions on various oxyanions having different molecular properties were also evaluated.

6.2 Experimental section

The chemicals used, material synthesis method and characterizations, sorption experiments, and analyses have been described in Chapter 3. Batch experiments were carried out to investigate the effects of co-existing species on the sorption of oxyanions by FCHT-LDH. Influence of each matrix species was studied in a single

species system with the concentrations ranging from 0.4 to 100 mM in an enclosed container.

In the first part of this study, the effects of common anions (i.e. nitrate, silica, sulfate, carbonate, and phosphate) with different concentrations on the sorption of various oxyanions including arsenate, bromate, chromate, and vanadate by FCHT-LDH were examined. In the second part, the effects of anions and NOM on arsenate sorption were investigated as functions of reaction time, concentration, and pH. The experimental procedures were similar to those described in Section 3.3.4. The concentrations of arsenate, chromate, and vanadate were determined by ICP-OES whereas the concentrations of bromate were measured by IC. The reacted FCHT-LDH samples were also characterized by XRD and FTIR.

6.3 Results and discussion

6.3.1 Characterizations

The fresh FCHT-LDH was found to have a specific surface area of 127 m²/g, a pore volume of 0.31 cm³/g, and a pore size of 8 nm, as measured by the QuantaChrome Autosorb-1 analyzer. The XRD patterns of the fresh and reacted FCHT-LDH under different conditions are depicted in Figure 6.1. Three major peaks at lower 2 θ values, i.e. 11.5°, 22.9°, and 34.7°, that are associated with the respective (003), (006), and (009) planes of characteristic LDH compounds were observed for all the FCHT-LDH samples. After reaction in all but the carbonate solution, the intensity of LDH reflections decreased. After reaction in the carbonate solution, the carbonate intercalated into the interlayer region of FCHT-LDH, resembling that of the fresh FCHT-LDH. This could be due to the formation of prismatic interlayer sites that strongly accommodated carbonate ions with their planes parallel to the layers.

Figure 6.1 XRD patterns of fresh FCHT-LDH and FCHT-LDH after reaction in ultrapure water, anion, and NOM solutions.

The FTIR spectra of the fresh FCHT-LDH and reacted FCHT-LDH (Figure 6.2) show that the spectrum is broadly divided into three noticeable adsorption regions: (1) $4000\text{--}2000\text{ cm}^{-1}$, (2) $2000\text{--}1200\text{ cm}^{-1}$, and (3) $1200\text{--}400\text{ cm}^{-1}$. The fairly broad band between 3400 and 3500 cm^{-1} in each spectrum could be due to OH stretching vibration of hydrogen-bonded groups in the brucite-like sheets and water in the interlayer space. In the second region, the peak at 1636 cm^{-1} in each of the spectra refers to the water bending vibration of the interlayer water whereas the strong peak at 1384 cm^{-1} is due to the nitrate intercalated in the interlayer space. The peaks at 1390 and 1559 cm^{-1} in the spectrum of the reacted sample in the presence of NOM correspond to the symmetric and asymmetric vibrations of carboxylate in humic acid (Rao et al., 2009) and the disappearance of the nitrate peak could be ascribed to the coverage of NOM on FCHT-LDH due to adsorption. The band observed at 1363 cm^{-1} in the spectrum of the reacted sample in the presence of carbonate could be assigned to C-O bending vibration of CO_3^{2-} (You et al., 2002), thereby suggesting the intercalation of carbonate into FCHT-LDH. The spectral features at 1115 cm^{-1} and 1067 cm^{-1} in the third region could be attributed to the sorbed sulfate and phosphate for the reacted sample after reaction in sulfate solution and phosphate solution, respectively (Nakamoto, 1997). The bands recorded at 795 , 668 , 556 , and 447 cm^{-1} are due to the M-O vibrations and M-O-H bending. Though rather weak, arsenic peaks seemed to appear at $820\text{--}830\text{ cm}^{-1}$ which corresponding to As-O stretching

vibration (Goldberg and Johnston, 2001) after FCHT-LDH reacted with arsenate in ultrapure water and nitrate solution.

Figure 6.2 FTIR spectra of fresh FCHT-LDH and FCHT-LDH after reaction in ultrapure water, anion, and NOM solutions.

6.3.2 Effects of common anions

6.3.2.1 Investigation on the sorption of oxyanions and oxyhalides having different molecular properties

Figure 6.3 shows that the sorption of oxyanions on FCHT-LDH was affected by both the type and concentration of the common anions that co-existed in the aqueous solutions. Increasing the concentration of the co-existing anions generally resulted in the decrease of oxyanion sorption on FCHT-LDH regardless of the type of the anions, indicating that the co-existing anions competed with the oxyanions for the same positively charged sites on FCHT-LDH and their sorption mechanisms were identical. On the other hand, the type of co-existing anions can determine the extent of selectivity of LDH toward oxyanions (Wang et al., 2009b). With an initial arsenate concentration of 0.4 mM and LDH dosage of 0.4 g/L, about 83% of arsenate was sorbed by FCHT-LDH in the absence of co-existing anions (Figure 6.3a). The sorption of arsenate on FCHT-LDH declined marginally to 80, and 78% when the nitrate/arsenate molar ratio was increased to 10 and 100, respectively, showing that the effect of nitrate on arsenate sorption was not significant.

Figure 6.3 Influences of anions on the sorption of (a) arsenate, (b) bromate, (c) chromate, and (d) vanadate by FCHT-LDH (pH = 8-11.5, time = 24 h, dose = 0.4 g/L, oxyanion concentration = 0.4 mM).

In the contrary, a more significant adverse effect on arsenate sorption could be induced by silica, sulfate, carbonate, and phosphate. Based on the detrimental effects on arsenate sorption, the co-existing anions can be ranked in the order of: nitrate < silica $\leq$ sulfate < carbonate < phosphate. The similar order was also generally valid for the cases of bromate, chromate, and vanadate sorption by FCHT-LDH (Figures 6.3b-d). On the other hand, based on their abilities to outcompete co-existing anions for LDH sorption sites, the oxyanions followed the order of: bromate < arsenate $\approx$ chromate $\leq$ vanadate. This generally suggested that the adverse effects of co-existing anions were more profound on the sorption of monovalent oxyanion (i.e. bromate with $\mu = 4.7 \text{ nm}^{-1}$) than the sorption of polyvalent oxyanion (i.e. vanadate, arsenate, and chromate with $\mu > 7.6 \text{ nm}^{-1}$).

Previous macroscopic and microscopic studies showed that monovalent oxyanion with $\mu < 5 \text{ nm}^{-1}$ formed outer-sphere complexes on FCHT-LDH and had a lower degree of specific sorption by FCHT-LDH than the polyvalent oxyanion with $\mu > 7 \text{ nm}^{-1}$ which formed both outer-sphere and inner-sphere complexes with FCHT-LDH.

Therefore, bromate sorption on the FCHT-LDH was subjected to the greater adverse impact of sorption competition with co-existing anions (generally possessed $\mu > 4.7 \text{ nm}^{-1}$) compared to the sorption of arsenate, chromate, and vanadate.

6.3.2.2 Investigation on the sorption of arsenate as functions of time, anion concentration, and pH

Figure 6.4 illustrates the time-dependent arsenate sorption on FCHT-LDH in the presence of various anions of different concentrations (at anion/arsenate molar ratio of 1 and 10). The experimental results were best fitted with the Elovich model on the basis of the statistical parameters ($R^2 > 0.97$, $\chi^2 < 2.8$, $\Delta q < 35$) among the examined kinetic models. The kinetic data are presented in Table 6.1, along with the observed initial and final pH values and precursor metals released from FCHT-LDH after 24 h reaction.

Figure 6.4 Influences of anions of different concentrations on arsenate sorption by FCHT-LDH as a function of reaction time (dose = 0.4 g/L, arsenate concentration = 0.4 mM). Experimental data are reported as points and Elovich model by curves.

Chapter 6

Table 6.1 Kinetic and statistical parameters of three kinetic models for arsenate removal in various matrix solutions and the corresponding pH changes and metals released

Competing ions	Pseudo-first order					Pseudo-second order					Elovich					pH		Metals released ^a	
	$q_e, \text{ cal}$	$k_1 \times 10^{-2}$	R^2	χ^2	Δq	$q_e, \text{ cal}$	$k_2 \times 10^{-3}$	R^2	χ^2	Δq	α	β	R^2	χ^2	Δq	Initial	Final	Mg	Al
	(cmol/kg)	(min ⁻¹)			(%)	(cmol/kg)	(kg/cmol·min)			(%)					(%)			(wt%)	
Ultrapure Water (control)	86.8	1.38	0.603	8913	68.4	87.0	10.75	0.970	2.01	13.3	56.9	0.16	0.984	1.93	6.9	9.5	9.9	0.09	0.04
4 mM Nitrate	79.1	1.53	0.723	7464	66.8	79.4	9.51	0.955	3.29	17.0	51.6	0.18	0.986	1.47	6.3	9.4	9.8	0.08	0.04
0.4 mM Silica	73.3	0.77	0.424	15995	75.8	71.4	16.61	0.969	1.11	12.2	51.5	0.23	0.984	1.34	6.5	10.1	10.4	0.03	0.06
4 mM Silica	51.4	1.11	0.657	7387	70.5	51.5	17.84	0.951	0.99	16.0	37.0	0.32	0.990	0.71	4.5	11.0	11.5	0.02	0.05
0.4 mM Sulfate	72.6	1.12	0.664	8917	70.0	73.0	11.04	0.960	1.59	16.1	48.7	0.20	0.989	1.17	5.0	10.0	10.4	0.06	0.06
4 mM Sulfate	45.6	0.56	0.546	16467	78.4	45.2	8.07	0.827	15.06	29.8	32.7	0.47	0.999	0.09	1.4	10.3	10.8	0.07	0.04
0.4 mM Carbonate	45.6	1.43	0.784	6110	67.8	45.7	9.07	0.955	0.70	13.4	35.1	0.48	0.990	0.52	4.4	10.5	10.8	0.03	0.04
4 mM Carbonate	15.8	0.61	0.776	2904	75.4	15.8	7.13	0.864	10.70	34.5	8.8	0.87	0.992	0.26	4.0	10.9	11.3	0.02	0.05
0.4 mM Phosphate	49.1	0.88	0.604	14584	74.2	49.0	7.74	0.876	2.55	19.1	41.3	0.71	0.999	0.05	1.5	9.1	9.4	0.18	0.11
4 mM Phosphate	4.0	0.59	0.583	43	67.5	4.0	5.12	0.987	0.26	11.6	0.6	1.58	0.959	0.84	35.0	7.2	7.6	2.45	0.44
10 mg/L NOM	76.8	1.11	0.759	4480	67.7	77.5	5.07	0.979	1.81	18.8	35.4	0.12	0.985	2.79	6.8	9.6	9.7	0.10	0.09
100 mg/L NOM	11.6	0.38	0.681	113	62.4	11.6	5.15	0.969	2.85	31.6	1.0	0.55	0.988	0.49	33.7	9.2	9.4	0.36	0.26

^aMg and Al released from the LDH samples after reaction for 24 h.

Note: pK_a for nitrate: $\text{HNO}_3 \xrightarrow{pK_{a1}=1.4} \text{NO}_3^-$; pK_a for silica: $\text{H}_2\text{SiO}_3 \xrightarrow{pK_{a1}=6.9} \text{HSiO}_3^- \xrightarrow{pK_{a2}=9.5} \text{SiO}_3^{2-}$; pK_a for sulfate: $\text{H}_2\text{SO}_4 \xrightarrow{pK_{a1}=-3.0} \text{HSO}_4^- \xrightarrow{pK_{a2}=1.9} \text{SO}_4^{2-}$; pK_a for carbonate: $\text{H}_2\text{CO}_3 \xrightarrow{pK_{a1}=6.3} \text{HCO}_3^- \xrightarrow{pK_{a2}=10.3} \text{CO}_3^{2-}$; pK_a for phosphate: $\text{H}_3\text{PO}_4 \xrightarrow{pK_{a1}=1.7} \text{H}_2\text{PO}_4^- \xrightarrow{pK_{a2}=6.5} \text{HPO}_4^{2-} \xrightarrow{pK_{a3}=12.1} \text{PO}_4^{3-}$; ionic potential for nitrate = 5.00 nm⁻¹; ionic potential for silica = 4.90 nm⁻¹; ionic potential for sulfate = 8.70 nm⁻¹; ionic potential for bicarbonate = 6.13 nm⁻¹; ionic potential for carbonate = 10.81 nm⁻¹; ionic potential for phosphate = 8.40 nm⁻¹.

The Elovich equation can be expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (6.1)$$

where q_t is the amount of sorbate per unit mass of sorbent at time t (cmol/kg), α is the initial sorption rate (cmol/kg·min), and β is related to the extent of surface coverage (kg/cmol). Integration of equation 6.1 with boundary condition $q = q_t$ at sorption time t and $q = 0$ at $t = 0$ yields

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t + t_0) \quad (6.2)$$

where $t_0 = 1/\alpha\beta$. The value of the constant β can be obtained from the slope of the straight line plot of q_t versus $\ln(t+t_0)$ and the constant α can be calculated from the t_0 and β values (Aharoni and Tompkins, 1970). The Elovich equation, which accounts for the characteristics of heterogeneous sorptive sites (Cheung et al., 2001), is appropriate for FCHT-LDH since there were external surface sorption sites as well as the interlayer ion exchange sites for the target oxyanions that resulted in heterogeneous sorption process.

Since the presence of nitrate is common in many groundwater resources and polluted runoffs and it may compete with arsenate for available sorption sites on FCHT-LDH, the influence of nitrate on arsenate removal was examined at different reaction times and pH conditions. It was found that the decrease of arsenate removal by FCHT-LDH was marginal (< 8%) when 4 mM nitrate (10 times higher than arsenate concentration) was spiked as a co-existing anion (Figure 6.4), relative to the ultrapure water. Yang et al. (2005) also reported that nitrate had almost no effect on the sorption of arsenate on the calcined LDH up to a concentration of 1000 ppm. Furthermore, the presence of nitrate only slightly affected the sorption rate of arsenate (indicated by α value in the best-fitted Elovich model in Table 6.1). Figure 6.5 shows the effects of anions on arsenate sorption by FCHT-LDH at pH 4, 7, and 10. Arsenate removal decreased slightly with increasing pH in the presence of nitrate. At pH 4, 7, and 10, nitrate had only minor effect on arsenate removal by showing a reduction of 2.9%, 2.8%, and 2.0%, respectively. The insignificant effect of nitrate on arsenate sorption by FCHT-LDH could be ascribed to the fact that nitrate is a nonspecific anion in solid-liquid interfacial reactions (Davis and Burgoa, 1995). It generally has a lower ionic potential

than arsenate, resulting in its weaker competition ability with arsenate for binding sites on FCHT-LDH.

Figure 6.5 Influences of anions on arsenate sorption by FCHT-LDH as a function of pH (time = 4 h, dose = 0.4 g/L, arsenate concentration = 0.4 mM).

Silica and sulfate are omnipresent in groundwaters, surface waters, and seawaters. Figure 6.4 reveals that both silica and sulfate had modest adverse effect on arsenate removal by FCHT-LDH, relative to nitrate. The amount of arsenate sorbed at equilibrium (~3 h) reduced notably from 71.3 to 51.2 cmol/kg when the silica concentration increased from 0.4 to 4 mM (equivalent to the increment of silica/arsenate molar ratio from 1 to 10). Likewise, arsenate sorption dropped from 72.5 to 43.1 cmol/kg with increasing sulfate concentration from 0.4 to 4 mM (Table 6.1). It was also reported that the sorption of arsenate on iron and aluminium oxides at pH 6 decreased significantly with increasing silica concentration from 5 to 10 mg/L (Jeong et al., 2007) whereas reduction in arsenate sorption on calcined LDH increased from 20% to 45% with increasing sulfate concentration from 500 to 1000 mg/L (Yang et al., 2005). The α values for arsenate sorption in 0.4 mM silica and sulfate solutions were only slightly smaller than that in ultrapure water but decreased by about 40% in 4 mM silica and sulfate solutions, implying that arsenate sorption rate on FCHT-LDH was only retarded by the overwhelming presence of silica and sulfate (Table 6.1).

The effects of silica and sulfate on arsenate removal by FCHT-LDH appeared to be more pH-dependent than that of nitrate (Figure 6.5). The presence of silica decreased

arsenate removal by 3.7%, 8.0%, and 6.2% whereas the presence of sulfate decreased arsenate removal by 2.9%, 6.3%, and 6.9% at pH 4, 7, and 10, respectively. The enhanced detrimental effect of silica on arsenate removal at higher pH, particularly at $\text{pH} \geq 7$ has also been reported for sorbents such as iron oxide hybrid media, amorphous ferric hydroxide, and activated alumina by other researchers (Meng et al., 2000; Smith and Edwards, 2005; Möller and Sylvester, 2008). The effect of silica on arsenate removal by FCHT-LDH became more significant with increasing pH, probably due to the change in speciation of silicic acid with pH. Silica exists as neutral molecules (H_2SiO_3) at pH below 7 and they generally have weak affinity for sorbent surface, and thus have smaller effect on arsenate sorption. At pH 7 and above, silica dissociates (HSiO_3^- and SiO_3^{2-}) and it has a greater affinity for sorbent surface, contributing to a stronger competition with arsenate. On the other hand, SO_4^{2-} is the prevalent sulfate species at pH 4, 7, and 10, and the decrease in arsenate removal with increasing pH could be ascribed to the competition of arsenate with sulfate and hydroxide ions. Examinations of the FCHT-LDH reacted in silica solution however did not show noticeable presence of any silicon compound, suggesting marginal sorption of silica on FCHT-LDH upon its competition with arsenate (Figure 6.2). In contrast, the FTIR spectral feature corresponding to the sorbed sulfate on the surface sites can be observed for the reacted FCHT-LDH in the sulfate solution. The sorption of sulfate on FCHT-LDH was more evident compared to that of silica revealed that the former caused a slightly larger competition effect on arsenate sorption than the latter. In summary, the results obtained suggested that both silica and sulfate could compete with arsenate, especially at $\text{pH} \geq 7$ over which arsenate has weak affinity with increasing pH.

The carbonate solution chemistry may affect the arsenic geochemistry. Some previous studies have demonstrated that the release of arsenic into groundwaters and subsurface systems was positively related to the carbonate concentration in the leaching solution (Kim et al., 2000; Katsoyiannis and Zouboulis, 2002; Anawar et al., 2004). In the present study, the presence of carbonate caused a sizeable reduction in the sorption equilibrium and sorption rate for arsenate removal by FCHT-LDH (Figure 6.4 and Table 6.1). Nonetheless, at pH 4, arsenate removal was not notably reduced by the presence of 0.4 mM carbonate (carbonate/arsenate molar ratio = 1) (Figure 6.5). At pH 7 and 10, carbonate caused significant reduction in arsenate

removal, i.e. 10.7% and 31.4%, respectively, mainly owing to the prevalence of monovalent HCO_3^- and divalent CO_3^{2-} compared to the uncharged H_2CO_3 at pH 4. The evidence of carbonate intercalation into FCHT-LDH is shown in the XRD pattern and the FTIR spectrum of the reacted LDH samples in carbonate solution (Figures 6.1 and 6.2). Compared to silica and sulfate, the presence of carbonate resulted in a larger detrimental effect on arsenate removal due to the relatively strong electronic forces of carbonate attraction to the host lattice of LDH and the orientation of carbonate with its planes parallel to the principal layers that is more preferred in the interlayer site formation. In short, at higher carbonate concentration and at alkaline condition, carbonate outcompeted arsenate in the sorption process and subsequently reduced the amount of binding sites available for arsenate.

Phosphate is believed to be competing with arsenate for sorption sites on FCHT-LDH mainly due to their similarities in molecular structure and deprotonation constants. Several researchers have reported that phosphate reduced the amount of arsenic sorbed on the iron oxide surface through competition (Jain and Loeppert, 2000; Zhao and Robert, 2001; Violante and Pigna, 2002). In the present study, remarkable sorption equilibrium and kinetic suppression were observed for arsenate removal by FCHT-LDH in the presence of phosphate (Figure 6.4 and Table 6.1). Phosphate decreased arsenate removal to a greater degree at 4 mM phosphate ([phosphate]:[arsenate] = 10:1) than at 0.4 mM phosphate ([phosphate]:[arsenate] = 1:1) at each time interval.

The decrease in arsenate removal in the phosphate solution was highly dependent on pH values (Figure 6.5). At pH 4, 7, and 10, arsenate removal was reduced by 6.7%, 24.5%, and 38.2%, respectively, by the presence of 0.4 mM phosphate. The reduction in arsenate sorption in the presence of phosphate with increasing pH can be correlated to the decreasing sorption capacity and the competition between arsenate and phosphate for binding sites (Hering et al., 1996; Jain and Loeppert, 2000) as well as the change of phosphate speciation with pH. The characteristic peak for P-O vibration evidenced in the FTIR spectrum of the reacted FCHT-LDH was probably corresponded to the phosphate intercalated into the interlayer surface sites and also those sorbed on the external surface sites (Figure 6.2). Phosphate has also been reported to form inner-sphere complexes upon specific adsorption on various mineral

surfaces (Hingston, 1981; Sposito, 1989; McBride, 1994). Based on these results, it could be deduced that the great decrease in arsenate sorption caused by the presence of phosphate under neutral and alkaline conditions was primarily associated with the competition between phosphate and arsenate for the same group of sorption sites on LDH due to their comparable chemistry.

In summary, the effects of competitive anions on arsenate sorption by FCHT-LDH increased in the order: nitrate < silica $\leq$ sulfate < carbonate < phosphate. These anions can be generally categorized into two groups based on their molecular properties and their competitive effects on arsenate sorption reaction: (1) anions with ionic potential $\leq 5 \text{ nm}^{-1}$, such as nitrate ($\mu = 5 \text{ nm}^{-1}$) and silica ($\mu = 4.9 \text{ nm}^{-1}$) that have negligible and moderate competitive effects on arsenate sorption and (2) anions with ionic potential $> 5 \text{ nm}^{-1}$, such as sulfate ($\mu = 8.7 \text{ nm}^{-1}$), carbonate ($\mu = 6.1 \text{ nm}^{-1}$), and phosphate ($\mu = 8.4 \text{ nm}^{-1}$) that have moderate to significant competitive effects on arsenate sorption. Relative to cases of reaction in the ultrapure water and nitrate solution, there seemed to be weaker peak associated with As-O stretching vibration at $820\text{-}830 \text{ cm}^{-1}$ of the FTIR spectra for the LDH reacted in silica, sulfate, carbonate, and phosphate solutions, indicating lesser arsenate sorbed on the surface of FCHT-LDH particles. The pH of the aqueous solutions increased slightly after 24 h reaction in all cases (Table 6.1). The pH increase was expected because sorption of oxyanions would release OH groups from LDH as a result of the ligand exchange mechanism.

6.3.3 Effect of NOM

NOM is a potentially important compound affecting arsenic geochemistry. Humic acid and fulvic acid generally represent about 60% of the NOM in aquatic systems (Stevenson, 1994) and they may interfere strongly with arsenic sorption under some circumstances. Humic acid consists of a large number of functional moieties including carboxylic, phenolic, and alcoholic groups that interact with surface groups and ions in solution. Since NOM is not only reactive toward arsenic but also ubiquitous in natural waters, its potential influences on arsenic sorption and mobility cannot be ignored. Figure 6.6 presents the time-dependent sorption results of arsenate on FCHT-LDH in the presence of NOM. The arsenate sorption equilibrium on FCHT-LDH without NOM was 103.1 cmol/kg at 3 h, but was reduced by 24% in the presence of

10 mg/L NOM. Higher concentration of NOM was observed to result in greater drop in arsenate removal (89%). The sorption rate of arsenate on FCHT-LDH was also declined tremendously in the presence of NOM (Table 6.1).

Figure 6.6 Influence of NOM on arsenate sorption by FCHT-LDH as a function of reaction time (dose = 0.4 g/L, arsenate concentration = 0.4 mM). Experimental data are reported as points and Elovich model by curves.

As shown in Figure 6.7, the removal percentage of arsenate by FCHT-LDH was slightly affected by the presence of 10 mg/L NOM at pH 4-10. However, the presence of 100 mg/L NOM dramatically decreased the arsenate removal, particularly over the pH range of 7-10. The decrease in arsenate removal by FCHT-LDH caused by the presence of NOM was mainly owing to the large NOM molecules (typically 1-1000 nm diameter for humic acid) that occupied a large proportion of sorption sites on the FCHT-LDH, which caused steric congestion and formed physical barrier to obstruct the mass transfer of arsenate to the FCHT-LDH surface. The disappearance of the FTIR peak for intercalated nitrate with concurrent emergence of new peaks correspond to carboxylate in humic acid confirmed the coverage of NOM on FCHT-LDH due to adsorption (Figure 6.2). On the other hand, competition between NOM (e.g. deprotonated anionic fulvate) and arsenate for sorption sites on FCHT-LDH might also contribute to the decrease of arsenate removal. It has also been reported that NOM can coagulate or precipitate with sorbent and subsequently diminish the number of available sorption sites (Giasuddin et al., 2007). In the present study, formation of LDH-NOM precipitate was observed during the experiment investigating

on arsenate removal by FCHT-LDH in the presence of 100 mg/L NOM at pH 7-10. Apparently, the NOM precipitation at alkaline condition might trap and settle out the LDH particles from the aqueous solution. This resulted in the drastic reduction in arsenate sorption (Figure 6.7).

Figure 6.7 Influence of NOM on arsenate sorption by FCHT-LDH as a function of pH (time = 4 h, dose = 0.4 g/L, arsenate concentration = 0.4 mM).

6.3.4 Stability of FCHT-LDH in aqueous matrix

The releases of Mg and Al from FCHT-LDH increased with increasing acidity, attaining a maximum of 4.3% Mg released for arsenate sorption at pH 4 in the presence of sulfate while 1.3% Al released at pH 4 in the presence of carbonate (Table 6.2 and Figure 6.8). At the neutral and alkaline conditions, the Mg released was found in the range of 0.1-1.3% whereas the Al released was lower than 0.2%. Nevertheless, our previous study revealed that if the FCHT-LDH was regenerated and reused in the subsequent cycles, it would become rather stable with negligible further releases of Mg and Al. Thus, the Mg and Al releases from the freshly synthesized FCHT-LDH could be attributed to the dissolution of the small fraction of poorly crystalline FCHT-LDH or the residual Mg or Al precursor salts that still remained in the synthesized FCHT-LDH. Overall, it can be generally concluded that the presence of different electrolyte solutions and NOM did not appear to affect the mineral stability of the FCHT-LDH, as can be inferred from Table 6.2 and Fig. 6.8.

Table 6.2 The amount of Mg and Al released from FCHT-LDH at different pH in the presence of anions

Competing ions	Mg released (wt%)			Al released (wt%)		
	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10
Ultrapure Water (control)	2.88 ± 0.25	1.17 ± 0.08	0.07 ± 0.00	0.76 ± 0.06	0.05 ± 0.00	0.08 ± 0.01
4 mM Nitrate	2.81 ± 0.24	1.27 ± 0.02	0.07 ± 0.00	0.78 ± 0.04	0.04 ± 0.00	0.09 ± 0.01
0.4 mM Silica	2.35 ± 0.16	1.20 ± 0.05	0.10 ± 0.00	0.46 ± 0.03	0.04 ± 0.00	0.05 ± 0.00
0.4 mM Sulfate	4.25 ± 0.29	0.88 ± 0.05	0.10 ± 0.00	0.90 ± 0.04	0.04 ± 0.00	0.10 ± 0.00
0.4 mM Carbonate	3.02 ± 0.17	0.94 ± 0.03	0.06 ± 0.00	1.33 ± 0.05	0.04 ± 0.00	0.06 ± 0.01
0.4 mM Phosphate	2.69 ± 0.17	1.07 ± 0.07	0.18 ± 0.00	0.11 ± 0.01	0.04 ± 0.00	0.10 ± 0.00

Figure 6.8 The amount of Mg and Al released from FCHT-LDH at different pH in the presence of NOM.

6.4 Conclusions and environmental implications

This study presents a detailed investigation of the effects of NOM and common anions including nitrate, silica, sulfate, carbonate and phosphate on oxyanion removal using FCHT-LDH in the single-species system. Among the investigated oxyanions, the adverse effects of co-existing anions were more profound on the monovalent oxyhalide with lower ionic potential (e.g. bromate) than the polyvalent oxyanion with higher ionic potential (eg. arsenate, chromate, and vanadate), mainly correlated to their respective removal mechanisms and surface complexes formed on the FCHT-LDH surface.

In general, based on their sorption competitiveness with the oxyanions, the common anions can be ranked in the order of nitrate < silica $\leq$ sulfate < carbonate < phosphate, while the affinities of the oxyanions for the FCHT-LDH in the presence of common anions followed the order of bromate < arsenate $\approx$ chromate $\leq$ vanadate. This indicates that the oxyanions with lower ionic potentials tend to be less preferably sorbed by the FCHT-LDH. The competition of the common anions for common sorption sites on the FCHT-LDH is predominantly occurred through ion exchange mechanism, the extent of which can be predicted by the ionic potentials of the competing anions. NOM can induce sorption inhibition of the oxyanions through obstruction of the FCHT-LDH surface, direct competition for sorption sites, and settle out LDH from aqueous solution at alkaline condition. The common anions and NOM do not appear to affect the mineral stability of the FCHT-LDH.

It was found that harmful co-existing anions such as sulfate, phosphate, etc. were also favorably removed by FCHT-LDH. This can be advantageous in that the FCHT-LDH could treat a mixed contaminant plume of arsenate and other harmful co-existing anions. However, it should be cautioned that excess anions will significantly reduce the effectiveness of FCHT-LDH for arsenate remediation. In this case, an excess amount of FCHT-LDH may be needed for remediation of arsenate in aqueous system containing large amounts of co-existing anions. For successful field applications of long term in-situ and ex-situ water treatment using FCHT-LDH, a more detailed study of surface reactions of FCHT-LDH with oxyanions in the presence of co-existing

species using advanced analytical techniques such as in-situ ATR-FTIR and XPS should be undertaken. On the other hand, cations such as calcium, magnesium, sodium etc. are ubiquitously present in natural water bodies and they may have great impacts on the sorption of oxyanions. An understanding of the effects of cations on oxyanion sorption by FCHT-LDH is therefore needed to fully assess the potential utility of FCHT-LDH for oxyanion treatment.

Chapter 7 Preparation, Characterization, and Sorption Performance of LDHs Obtained by Various Synthetic Routes

7.1 Introduction

Previous studies have shown that LDHs prepared using the alternative synthetic routes such as fast coprecipitation with hydrothermal treatment method (FCHT) and sol-gel method (SG) could exhibit more stable and homogeneous particles, larger surface area, and more uniform pore size distribution (Aramendia et al., 2002; Xu et al., 2006; Valente et al., 2007) compared to those obtained by conventional routes. These unique properties may partly contribute to the better oxyanion removal efficiency attained by FCHT-LDH as reported in the previous chapters. However, a comparison of the main chemical–physical features and sorption abilities of LDHs prepared by a range of conventional synthetic methods and alternative synthetic methods is scarcely available in the literature. This information is essential in order to understand how the characteristics and sorption performances of LDHs are influenced by the synthesis process.

Though nanosized FCHT-LDH has shown promising performance in oxyanion removal, their separation and recovery remain as a main obstacle from an engineering application point of view. In particular, they are rather small to be separated, can cause problems like high pressure drops, and cannot be easily recovered for repeated application. Micron-sized solid spherical materials have been produced by some researchers (Li et al., 2003b; Wang et al., 2008b) and they are potentially good candidate for easy separation and recovery in system like fluidized bed as they can easily settle in aqueous suspensions by gravity. To date, no work has been performed on fabricating and controlling macroscopic form of LDHs for oxyanion sorption. A simple and easily controlled synthetic method is therefore needed for the preparation of micron-sized LDH particles amenable to scale up for its commercial applications.

Spray drying is a simple and low-cost process for the preparation of microspherical particles that can readily be scaled up (Iskandar et al., 2003; Okuyama et al., 2006; Wang et al., 2009a) and has been successfully used in industries like pharmaceutical and food processing (Okuyama et al., 2006). Spherical particles produced by spray drying are generally of practical importance as they have better rheological properties than the irregular particles (Luo and Nieh, 1995). Recently, Wang et al. (2008b) has prepared micron-sized LDH spheres by spray drying a precursor slurry synthesized by a method involving separate nucleation and aging steps. However, research work on the different operating parameters influencing the characteristics of spray-dried LDH microspheres appears to be unavailable in the literature. These parameters can significantly influence their sorptive properties.

The purposes of this study were to (1) compare the characteristics of arsenate sorption by the LDHs prepared using the alternative routes and the conventional routes, (2) develop LDH microspheres by combining fast coprecipitation, hydrothermal, and spray drying methods and understand the effects of various spray drying process parameters on the characteristics of microspheres, and (3) evaluate the sorption capacity and recovery of LDH microspheres via batch techniques.

7.2 Experimental section

The chemicals used, the conventional LDH synthetic routes (IE-LDH for LDH prepared by ion exchange method, COP-LDH for LDH prepared by coprecipitation method, and CAL-LDH for LDH prepared by calcination method), the alternative LDH synthetic routes (FCHT-LDH for LDH prepared by fast coprecipitation with hydrothermal treatment method, SGRF-LDH for LDH prepared by sol-gel with reflux method, and SGST-LDH for LDH prepared by sol-gel with solvothermal method), the spray drying method, the procedures of the characterization techniques, sorption experiments, and analyses have been presented in Chapter 3. Analytical techniques such as CHNS/O, N₂ adsorption-desorption, XRD, and FTIR were used to characterize the LDH samples prepared by the alternative routes and the conventional

routes whereas SEM, particle size analysis, XRD, N₂ adsorption-desorption analysis, and FESEM were used to characterize the LDH microspheres.

To investigate the influences of the different process parameters on the formation and performance of LDH microspheres, the parameters were varied in the following ranges: inlet air temperature from 110 to 190 °C, compressed air flow rate from 5 to 30 L/min, and suspension feed concentration from 0.4 to 3.2 wt%. In addition, the effect of the ionic type of surfactant (nonionic F127, anionic SDS, and cationic CTAB) on the preparation of LDH microspheres was also examined.

Sorption of arsenate by the LDH samples was performed in the batch system as described in Section 3.3.5. SEM-EDX analysis was carried out to characterize the LDH microspheres before use, after use, and after regeneration. Prior to the analysis, a cross section of LDH microspheres was prepared by embedding the microspheres into epoxy resin, which was then solidified by heating on a laboratory hot plate and subsequently ground carefully using a Gatan disc grinder in order to obtain the cross-sectional view. During the grinding, the specimen disc was held parallel to the polishing surface to produce uniformly thin specimens.

7.3 Results and discussion

7.3.1 Characterizations of the LDHs prepared by conventional and alternative synthetic routes

The molar ratios of Mg/Al in the synthesized LDHs were generally in good agreement with the ratios determined in the starting materials (Table 7.1). The CHNS/O analyses indicated the presence of N and C in most LDHs, implying the co-existence of both nitrate and carbonate with different proportions in the interlayer spaces (except for SG-LDHs). The pore sizes of all the LDHs fell 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.

Table 7.1 Composition, structural properties, and lattice parameters of the LDHs prepared by conventional and alternative synthetic routes

Types of LDH	Composition			Structural property			Lattice parameter		
	Mg ²⁺ /Al ³⁺ molar ratio	C (wt %)	N (wt %)	S ^a (m ² /g)	V ^b (cm ³ /g)	D ^c (nm)	a ^d (Å)	c ^e (Å)	Crystal size ^f (nm)
IE-LDH	3.1/1	9.2	1.4	56	0.04	3.0	3.04	22.67	21.5
COP-LDH	2.1/1	1.8	7.5	22	0.01	1.4	3.04	22.91	12.1
CAL-LDH	2.4/1	1.2	5.7	90	0.06	1.4	3.08 ^g	23.60 ^g	9.7 ^g
FCHT-LDH	2.0/1	0.7	3.3	127	0.31	8.0	3.04	23.53	5.9
SGRF-LDH	2.1/1	1.0	0	75 ^h	0.05 ^h	1.4 ^h	3.05	23.22	7.6
SGST-LDH	2.5/1	0.9	0	161 ^h	0.13 ^h	1.4 ^h	3.05	23.23	5.9

^aBET surface area; ^bBJH pore volume; ^cBJH pore size; ^da = 2 × d(110); ^ec = 3 × d(003); ^fAverage value calculated from fwhm of peak (003) and (006) using Scherrer Equation; ^gRehydrated LDH; ^hCalcined sample; *n/a denotes “data not available”.

The XRD patterns of all the LDHs are illustrated in Figure 7.1. A single phase corresponding to LDH compounds can be identified for all the LDHs. For CAL-LDH, the periclase (ICSD 9863) was the main mixed oxides derived upon calcination, with characteristic peaks at ~43° and ~62° attributed to (200) and (220) crystal planes. 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. 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 7.2). The FTIR spectra of COP-LDH, CAL-LDH, and FCHT-LDH showed a peak at ~1384 cm⁻¹ whereas the spectra of IE-LDH exhibited a slightly strong peak at 1360 cm⁻¹, showing the presence of nitrate and carbonate, respectively, and these findings were consistent with the results of CHNS/O analysis. TEM images (Figures 4.3 and 7.3) 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 (40-100 nm).

Figure 7.1 XRD patterns of the LDHs prepared by conventional and alternative synthetic routes.

Figure 7.2 FTIR spectra of the LDHs prepared by conventional and alternative synthetic routes.

Figure 7.3 TEM image of SGST-LDH particles in a cluster.

7.3.2 Arsenate sorption performance: conventional routes versus alternative routes

The sorption isotherms of arsenate on various LDHs were examined. Langmuir isotherm was found suitable for describing the sorption of arsenate on all the LDHs (Figure 7.4a). The arsenate 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 of LDHs prepared by the conventional routes. The higher arsenate sorption capacity on FCHT-LDH and SGST-LDH could be due to their low carbonate content, larger surface area, and better porosity characteristic. 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. 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 7.4b). These observations implied that FCHT-LDH and SG-LDHs might have multiple sites for retention of arsenate including external, edge, and internal surface sites, resulting in their slower sorption reactions.

Figure 7.4 (a) Sorption isotherms and (b) time-dependent sorption of arsenate on various LDHs.

7.3.3 Effects of various process parameters on the formation of LDH microspheres

7.3.3.1 Effect of inlet air temperature

Table 7.2 lists the process parameters of the spray drying experiment along with the mean sizes of LDH microspheres obtained by varying the parameters. The results did not show a significant relationship between the inlet air temperature and the size of the LDH microspheres (Table 7.2 and Figure 7.5). At lower inlet air temperature, the morphology of the microspheres was more stable for the production of spherical particles (Figures 7.5a-c). However, at higher inlet air temperature, it was observed

that the microspheres showed a more unstable shape, i.e. doughnut-shape and convex-shape (Figure 7.5d). This was probably due to the predominance of thermal effects at a higher temperature which have led to the occurrence of surface tension gradient and subsequently the formation of more unstable microspheres (Iskandar et al., 2003).

Table 7.2 Process parameters of the spray drying method and mean sizes of the LDH microspheres

Samples	Inlet air temp. (°C)	Outlet air temp. (°C)	Compressed air flow rate (L/min)	Suspension feed concentration (wt %)	Liquid feed rate (mL/min)	Compressed air pressure (bar)	Mean size (µm)
LDHM1	110	60±3	17.5	2.8	10	0.5	10.3
LDHM2	150	77±3	17.5	2.8	10	0.5	20.1
LDHM3	190	91±3	17.5	2.8	10	0.5	14.2
LDHM4	150	77±3	5	2.8	10	0.5	16.5
LDHM5	150	77±3	30	2.8	10	0.5	10.3
LDHM6	150	77±3	17.5	0.4	10	0.5	4.5
LDHM7	150	77±3	17.5	1.2	10	0.5	7.0
LDHM8	150	77±3	17.5	2.0	10	0.5	8.9
LDHM9	150	77±3	17.5	3.2	10	0.5	23.2
LDHM10 ^a	150	77±3	17.5	2.8	10	0.5	37.5
LDHM11 ^b	150	77±3	17.5	2.8	10	0.5	31.3
LDHM12 ^c	150	77±3	17.5	2.8	10	0.5	15.8

^aLDH suspension feed added with nonionic surfactant (F127); ^bLDH suspension feed added with anionic surfactant (SDS); ^cLDH suspension feed added with cationic surfactant (CTAB).

Figure 7.5 SEM images of the LDH microspheres prepared at different inlet air temperatures: (a) 110 °C (sample LDHM1), (b) and (c) 150 °C (sample LDHM2) at different magnification, and (d) 190 °C (sample LDHM3).

7.3.3.2 Effect of compressed air flow rate

From the viewpoint of hydrodynamics, the effect of compressed air flow rate is regarded as one of the principal parameters that control the structure and morphology of the microspheres produced by spray drying. The effect of compressed air flow rate on the morphology of LDH microspheres is depicted in Figure 7.6. The results showed that lower compressed air flow rate, i.e. 5 L/min and 17.5 L/min did not cause substantial destabilization of the shape of the LDH microspheres. However, at a higher flow rate such as 30 L/min, a significant reduction of the residence time of the droplet in the spray dryer due to an increase in droplet velocity has resulted in the production of more unstable LDH microspheres. On the other hand, the particle size of the LDH microspheres was observed to decrease slightly with the increase of compressed air flow rate (Table 7.2). Wang et al. (2009a) has also reported similar observation for their hydroxyapatite microspheres obtained at different compressed air flow rates.

Figure 7.6 SEM images of the LDH microspheres prepared at different compressed air flow rates: (a) 5 L/min (sample LDHM4) and (b) 30 L/min (sample LDHM5).

7.3.3.3 Effect of suspension feed concentration

To explore the influence of varying LDH nanoparticle concentration in the suspension feed on the formation of LDH microspheres, five types of suspension feed concentrations ranging from 0.4 to 3.2 wt% were used and the SEM images of the products are presented in Figure 7.7. At low nanoparticle concentration, i.e. 0.4 wt%, the LDH nanoparticles were unable to assemble to form stable microspheres (Figure 7.7a) because the amount of nanoparticle was too small to increase the stiffness of the droplets as well as the internal surface energy inside the droplets for the formation of spherical morphology during spray drying. When the suspension feed concentration increased to 1.2 wt%, a small quantity of stable microspheres was observed (Figure 7.7b). Further increase in the concentration of nanoparticles in the suspension feed to 2.0 wt%, 2.8 wt%, and 3.2 wt% resulted in the formation of more stable LDH microspheres as demonstrated in Figure 7.7c, 7.5b, and 7.7d, respectively. The change in microspherical size was also observed besides the change in shape and structure. The average particle size of LDH microspheres increased about 5 times with the increase of suspension feed concentration from 0.4 to 3.2 wt%.

Figure 7.7 SEM images of the LDH microspheres prepared using different suspension feed concentrations: (a) 0.4 wt% (LDHM6), (b) 1.2 wt% (LDHM7), (c) 2.0 wt% (LDHM8), and 3.2 wt% (LDHM9).

7.3.3.4 Effect of surfactant

The morphology of LDH microspheres can be controlled by adding surfactants to vary the interfacial forces. In order to investigate the effect of the ionic type of surfactant on the formation of the LDH microspheres, the microspheres were prepared using 0.1 wt% pluronic F127 (nonionic), SDS (anionic), and CTAB (cationic). Figure 7.8 shows that the LDH microspheres exhibited an unstable shape when a surfactant was added to the LDH nanoparticle suspension, regardless of the ionic type of the surfactant. The addition of surfactant into the suspension feed could have resulted in the reduction of the interfacial force of the droplets and subsequently produced less stable droplets during the spray drying process. Inter-agglomeration of microspheres were observed for the suspension feed added with nonionic F127 and anionic SDS (Figures 7.8a and 7.8b), resulting in larger particle sizes than that produced from the suspension without surfactant addition (Table 7.2). In contrast, the relatively smaller particle size of microspheres produced by suspension added with cationic CTAB was

possibly due to the electrostatic repulsion as LDH nanoparticles have net positive charge.

Figure 7.8 SEM images of the LDH microspheres prepared using different surfactants: (a) 0.1 wt% nonionic surfactant pluronic F127, (b) 0.1 wt% anionic surfactant SDS, and (c) 0.1 wt% cationic surfactant CTAB.

It could be deduced from the abovementioned findings that the inlet air temperature, the compressed air flow rate, the suspension feed concentration, and the addition of surfactant were crucial parameters that would affect the morphology and particle size of the prepared microspheres. Spherical microspheres can be generally produced under conditions of low inlet air temperature, low compressed air flow rate, and high suspension feed concentration whereas doughnut-shaped and convex-shaped microspheres can be obtained under conditions of high inlet air temperature, high compressed air flow rate, low suspension feed concentration, and by addition of surfactant. It was also found that the spray drying method permitted the increase of particle size by decreasing the compressed air flow rate, increasing suspension feed concentration, and adding nonionic or anionic surfactant. In short, it should be

possible to prepare LDH microspheres with desired properties by carefully selecting and evaluating the spray drying process parameters.

7.3.4 Characterizations of LDH microspheres and evaluation of their arsenate sorption abilities

In order to demonstrate the ability in removing oxyanions from water, four types of LDH microspheres were prepared using 1.2 wt% suspension feed concentration (or LDHM7), 2.8 wt% suspension feed concentration (or LDHM2) with and without subsequent calcination, and 2.8 wt% suspension feed concentration with addition of nonionic surfactant F127 (or LDHM10) and subsequent calcination, and they were characterized and investigated for their arsenate sorption performance.

Figures 7.9a and 7.9b display the FESEM images of LDH microspheres prepared using 2.8 wt% suspension feed concentration with and without addition of F127, respectively. It could be seen that the surface of LDH microsphere composed of well dispersed LDH nanoparticles upon F127 addition (Figure 7.9b). However, without addition of F127 into the suspension feed, the LDH nanoparticles seemed to be closely agglomerated together (Figure 7.9a).

Figure 7.9 Surface morphologies of the LDH microspheres prepared using (a) 2.8 wt% suspension feed concentration and (b) 2.8 wt% suspension feed concentration with addition of nonionic F127.

The textural properties of the microspheres were analyzed by N_2 adsorption-desorption analysis and the results were summarized in Table 7.3. Aggregating LDH

nanoparticles to microspheres using spray drying method has resulted in the reduction of specific surface area, pore volume, and pore size. The surface area and porosity of the LDH microspheres further decreased with increasing suspension feed concentration. This could be due to the fact that the droplets with high suspension concentration contain less moisture that likely take up those sites belong to LDH nanoparticles at low concentration. Upon vapor evaporation due to drying, less interstitial spaces remained and resulted in smaller surface area and porosity. On the other hand, the surface area and pore volume of LDH microspheres increased about two-fold after the calcination process. With the addition of nonionic surfactant F127 into the suspension feed and subsequent calcination, the surface area, pore volume, and pore size of the LDH microspheres further increased to 136 m²/g, 0.58 cm³/g, and 9.6 nm, respectively, which were close to those of FCHT-LDH obtained without spray drying. These results indicated that the presence of dissolved F127 in the suspension feed might have formed shell-like layer surrounding LDH nanoparticles to prevent the aggregation of nanoparticles, thus contributing to the production of LDH microspheres with larger surface area and better porosity characteristic than those of LDH microspheres prepared without adding F127. It can also be seen in Figure 7.9b that the interconnected nanoparticles formed the walls of the microspheres and generated macropores in the range of 40-150 nm, resulting in the LDH microspheres with the multi-scale meso/macro porosities.

Table 7.3 Textural properties of the LDH microspheres

Types of LDHs	S ^a (m ² /g)	V ^b (cm ³ /g)	D ^c (nm)
LDH nanoparticles (FCHT-LDH) ^d	127	0.31	8.0
LDH microspheres (1.2 wt%) ^d	56	0.21	7.8
LDH microspheres (2.8 wt%) ^d	40	0.18	6.5
LDH microspheres (2.8 wt%) ^e	88	0.37	8.6
LDH microspheres (2.8 wt% with F127) ^e	136	0.58	9.6

^aBET surface area; ^bBJH pore volume; ^cBJH pore size; ^dAs-synthesized sample; ^eCalcined sample (500 °C).

The phase compositions and crystal structures of the as-synthesized LDH microspheres prepared using 1.2 and 2.8 wt% suspension feed concentrations were

similar to those of FCHT-LDH (Figure 7.10). Only the diffraction pattern of LDH was observed for these microspheres and no additional diffraction peaks of other impurities were detected. Upon calcination of LDH microspheres (2.8 wt% with F127) at 500 °C, the XRD peaks for the LDH phase were almost lost and replaced by the poorly crystalline periclase phase. When the calcined LDH microspheres (2.8 wt% with F127) were dispersed in water, reconstruction of the LDH structure was observed as shown by the reappearance of characteristic reflections of LDH phase.

Figure 7.10 XRD patterns of the LDH microspheres.

The experimental data for arsenate sorption isotherms on various LDH microspheres are shown in Figure 7.11. Arsenate sorption on both as-synthesized and calcined LDH microspheres was appropriately described by Langmuir isotherm with values of R^2 generally higher than 0.9 for all the sorption systems. The arsenate sorption capacities of most of the investigated LDH microspheres, namely LDH microspheres (1.2 wt%), LDH microspheres (2.8 wt%), and calcined LDH microspheres (2.8 wt%) were lower than that of FCHT-LDH, probably due to their smaller surface area, pore size, and pore volume. However, the sorption capacity for arsenate on calcined LDH microspheres (2.8 wt% with F127) was 143 cmol/kg and it was slightly higher than that of FCHT-LDH. The higher arsenate sorption capacity of these LDH microspheres was mainly attributed to their larger surface area and multi-scale meso/macro porosity. The interlayer expansion resulted from the intercalation of F127 might also partially lead to the higher arsenate sorption capacity on calcined LDH microspheres (2.8 wt%

with F127) and further diffraction analysis would be required to validate this hypothesis.

Figure 7.11 Sorption isotherms of arsenate on various LDH microspheres (pH = 9.5, time = 24 h, dose = 0.4 g/L, background = 0.01 M NaNO₃).

Figure 7.12 shows the sorption of arsenate on various LDH microspheres as a function of reaction time. At an initial arsenate concentration of 0.2 mM, LDH microspheres (2.8 wt%) exhibited the lowest equilibrium sorption capacity among the LDH microspheres and this result was consistent with those observed in the sorption isotherm study. The sorption kinetics of arsenate on all the LDH microspheres were well described by Elovich model. The α values of LDH microspheres (1.2 wt%) ($\alpha = 6.4 \times 10^4$), LDH microspheres (2.8 wt%) ($\alpha = 5.8 \times 10^4$), and calcined LDH microspheres (2.8 wt%) ($\alpha = 3.2 \times 10^4$) were close to that of FCHT-LDH ($\alpha = 1.3 \times 10^4$), indicating that these LDH microspheres have comparable arsenate sorption rate with FCHT-LDH. On the other hand, the α value of calcined LDH microspheres (2.8 wt% with F127) was about two orders of magnitude smaller than that of FCHT-LDH, showing the significant effect of F127 addition in the preparation of LDH microspheres on the sorption rate. Furthermore, the LDH microspheres were found to be easily recovered by gravity for reuse. An approximate settling velocity of 0.5 mm/s for the LDH microspheres were observed, which was about 30 times faster than those obtained for FCHT-LDH (1 mm/min), implying the efficient separation of the LDH microspheres from the treated water after the reaction.

Figure 7.12 Time-dependent sorption of arsenate on various LDH microspheres (pH = 9.5, dose = 0.4 g/L, arsenate concentration = 0.2 mM, background = 0.01 M NaNO₃).

7.3.5 SEM-EDX analysis

SEM-EDX techniques were employed to investigate the sorption reactions at different periods of exposure of the LDH microspheres to the arsenate solution. Though the EDX method is not purely a surface technique since X-rays are generated from a region of a few micrometers in depth by the electron beam, this method however is representative of the reacted surface region. The cross-sectional SEM images in Figures 7.13a, 7.13b, 7.14a, 7.14b, 7.15a, 7.15b, and 7.16a show that the LDH microspheres were generally spherical. The qualitative EDX spectra for the fresh, reacted, and regenerated LDH microspheres demonstrated that Mg, Al, and O were the main constituents (Figures 7.13f, 7.14g, 7.15g, and 7.16f). However, no signal of N can be observed in all the spectra probably as a result of its low concentration in the sample. The presence of C was due to the epoxy resin used for embedding the microspheres whereas the Pt was due to the sputter coater used for reducing surface charging during SEM analysis, and their existence were considered negligible. The quantitative peak area analysis of the EDX results showed that the Mg/Al mass ratio was 1.8 for the fresh LDH microsphere (Figure 7.13f), similar to the molar ratios of Mg/Al reported in Chapters 4 and 5. The Mg/Al ratios for the reacted and regenerated LDH microspheres ranged from 1.6 to 1.7, indicating insignificant reduction in the crystallinity of LDH microspheres after reaction.

EDX dot mapping can provide an indication of the abundance of elements analyzed on a sample. The bright dots represent the elements spread over the surface of a sample. A relatively higher density of dots for Mg and O than Al was observed on the EDX maps of fresh, reacted, and regenerated LDH microspheres (Figures 7.13c-e, Figures 7.14c-e, Figures 7.15c-e, and Figures 7.16b-d). The quantitative EDX analysis also showed the larger amount of Mg and O compared to Al on all the LDH microspheres (Figures 7.13f, 7.14g, 7.15g, and 7.16f), confirming that Mg and O were more abundant and spread evenly throughout the microsphere.

Figure 7.14f depicts the distribution of the sorbed arsenate from the surface to the core of the LDH microsphere after 1 h. Arsenate has not been entirely diffused to the interior of the microsphere after reaction for 1 h and the mass percentage of the arsenate was about 5.8% (Figure 7.14g). These findings generally agreed with the time-dependent sorption results which indicated that the reaction required more than 1 h to reach sorption equilibrium (Figure 7.12). The internal surface of the LDH microsphere was fully covered with arsenate after reaction for 24 h and the mass percentage of arsenate increased to 9.3% (Figures 7.15f and 7.15g). It is also worth noting that the regenerated LDH microsphere was able to perform as good as the fresh LDH microsphere, with the percentage of arsenate sorbed only slightly lower than that of the fresh LDH microsphere reacted for 24 in arsenate solution (Figures 7.16e and 7.16f).

By micro-observation and micro-analysis within the cross section of the LDH microspheres, SEM-EDX results in this study therefore provided the direct evidence for the sorption of arsenate on the internal surface of the LDH microspheres. It was believed that the mesopore/macropore domain in the internal sites of the microspheres, having an accessible diffusion pathway for the arsenate, were responsible for the arsenate removal in the internal surface.

Figure 7.13 (a-b) Cross-sectional SEM images, (c-e) EDX maps, and (f) EDX spectrum of the fresh LDH microsphere.

Figure 7.14 (a-b) Cross-sectional SEM images, (c-f) EDX maps, and (g) EDX spectrum of the LDH microsphere after reaction for 1 h in arsenate solution.

Figure 7.15 (a-b) Cross-sectional SEM images, (c-f) EDX maps, and (g) EDX spectrum of the LDH microspheres after reaction for 24 h in arsenate solution.

Figure 7.16 (a) Cross-sectional SEM image, (b-e) EDX maps, and (f) EDX spectrum of the regenerated LDH microsphere after reaction for 24 h in arsenate solution.

7.4 Conclusions

In summary, LDHs prepared by the alternative synthetic routes can generally remove arsenate more effectively than those prepared by the conventional synthetic routes. The higher arsenate sorption capacity on the LDHs prepared by the alternative routes,

particularly FCHT-LDH and SGST-LDH could be due to their low carbonate content, larger surface area, better porosity characteristic, and nanocrystalline property. The time-dependent sorption results suggested that LDHs prepared by the alternative routes might have multiple sites for retention of arsenate, resulting in their slower sorption reactions compared to those of LDHs prepared by the conventional routes.

Solid LDH microspheres consisting of nanoparticles of 40-100 nm in diameter were successfully fabricated via a simple fast coprecipitation-hydrothermal-spray drying process. The inlet air temperature, compressed air flow rate, suspension feed concentration, and addition of surfactant were found to be the important parameters that would affect the morphology and particle size of the prepared microspheres. Among the investigated LDH microspheres, the calcined LDH microspheres prepared using suspension feed added with nonionic surfactant showed the highest arsenate sorption capacity, mainly due to their larger surface area and multi-scale meso/macroporous structure. In addition, they were also easily recovered by gravity for reuse. Nonetheless, a relatively slow sorption rate was observed for this type of LDH microspheres. The SEM-EDX analysis revealed the occurrence of arsenate sorption in the internal surface sites of the LDH microspheres which have an accessible diffusion pathway, no significant reduction in the crystallinity of the LDH microspheres after sorption reaction, and good sorption ability of the regenerated LDH microspheres. However, the efficiency of LDH microspheres in column system is yet to be investigated. This column study is required in the future work since it mimics actual field application and can predict the column breakthrough or the shape of the sorption wavefront, which determines the operational life span of the column and regeneration time.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

In this study, a simple and efficient method known as fast coprecipitation with subsequent hydrothermal treatment has been employed to prepare nanocrystalline Mg/Al layered double hydroxide with nitrate intercalation (FCHT-LDH) for oxyanion removal. The synthesized FCHT-LDH possessed crystalline layered structure with a rhombohedral symmetry and mesoporous characteristic with a large surface area. Well-formed and overlapping plate-like particles with a uniform size of 40-100 nm and comprising nanocrystalline grains were observed. A series of comparative studies were also performed using LDHs prepared by other synthetic routes.

Batch studies showed that FCHT-LDH had a much higher sorption capacity for divalent oxyanions than monovalent oxyhalides, mainly due to their higher ionic potential and tetrahedral coordination. Sorption of divalent oxyanions such as chromate and vanadate on FCHT-LDH was found to be endothermic, while sorption of monovalent oxyhalide like bromate was exothermic. Sorption of chromate and vanadate was more sensitive to changes in pH compared to bromate. The kinetic study showed that the sorption reactions of bromate, chromate, and vanadate on FCHT-LDH were fast with equilibrium completed within the first few hours. Both macroscopic and microscopic studies proposed that monovalent oxyhalide sorption on FCHT-LDH mainly occurred via anion exchange mechanism with subsequent formation of outer-sphere surface complexes whereas polyvalent oxyanion sorption mechanisms on FCHT-LDH probably involved both anion exchange and ligand exchange reactions, contributing to the formation of a mixture of outer-sphere and inner-sphere surface complexes.

The hydrothermal treatment method during the synthesis process of FCHT-LDH was shown to play an important role for enhanced arsenate removal. The arsenate removal reaction by FCHT-LDH can be adequately described by Elovich model. Arsenite was not effectively removed by FCHT-LDH due to the presence of uncharged and single

negatively charged arsenite species which were unfavorable for the sorption reaction. Enhanced arsenate removal by FCHT-LDH was likely occurred through primary anion exchange and secondary ligand exchange mechanisms. The predominance of anion exchange mechanism was evidenced by the nitrate-arsenate molar displacement ratio, increased interlayer spacing, weakened FTIR band of interlayer nitrate, and decreased nitrogen content in the interlayer region. Slight pH increase during arsenate sorption equalization and the presence of irreversibly sorbed arsenate indicated the occurrence of ligand exchange process as the secondary mechanism. This specific sorption process possibly resulted in the formation of inner-sphere arsenate complexes with a monodentate mononuclear configuration at the aluminum center.

A number of matrix species commonly present in natural waters such as nitrate, silica, sulfate, carbonate, phosphate, and NOM have shown great impacts on the sorption of oxyanions. It was found that the effects of co-existing anions were more profound on the monovalent oxyhalide with lower ionic potential than the polyvalent oxyanion with higher ionic potential. The co-existing anions can be ranked according to their influences on arsenate removal by FCHT-LDH as follows: nitrate < silica $\leq$ sulfate < carbonate < phosphate. The anions can be grouped into two groups based on their molecular properties and competitive effects on arsenate removal by FCHT-LDH: (1) anions such as nitrate and silica with ionic potential $\leq 5 \text{ nm}^{-1}$ that have negligible and moderate competitive effects on arsenate sorption and (2) anions such as sulfate, carbonate, and phosphate with ionic potential $> 5 \text{ nm}^{-1}$ that have moderate to significant competitive effects on arsenate sorption. High NOM concentration can inhibit arsenate sorption on FCHT-LDH by (1) obstructing FCHT-LDH surface, (2) competing with arsenate for sorption sites, and (3) settling out FCHT-LDH. The presence of anions and NOM did not significantly affect the stability of FCHT-LDH.

LDHs prepared by the alternative synthetic routes generally achieved higher arsenate removal efficiencies than those prepared by the conventional synthetic routes. The higher arsenate sorption capacity on the LDHs prepared by the alternative routes could be due to their lower carbonate content, larger surface area, better porosity characteristic, and nanocrystalline property. LDH microspheres were successfully fabricated via a simple fast coprecipitation-hydrothermal-spray drying process. The inlet air temperature, compressed air flow rate, suspension feed concentration, and

addition of surfactant were the important parameters that would affect the morphology and particle size of the prepared microspheres. The calcined LDH microspheres prepared using suspension feed added with nonionic surfactant showed the highest arsenate sorption capacity among the investigated microspheres, easy recovery by gravity, but a relatively slow sorption rate. The SEM-EDX analysis revealed the occurrence of arsenate sorption in the internal surface sites of the LDH microspheres and demonstrated the mineral stability and reusability of the microspheres.

8.2 Recommendations

Nanocrystalline Mg/Al LDH produced in this study exhibited excellent affinity for polyvalent oxyanions, but comparatively less affinity for monovalent oxyhalides. The nanocrystalline LDH can be potentially used for removing trace arsenate, chromate, molybdate, selenate, vanadate, etc. from the surface waters and groundwaters, and for polishing advanced treated wastewaters. However, there are 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 deionized water prior to usage may help to improve its stability. If the precursor metals in the brucite-like sheets of LDH are to be released into the solution, it would be important to ensure that they exist below the levels harmful to the environment, or otherwise the LDH should be free of toxic metals. Therefore more deliberate and rigorous studies should be performed to examine the solubility of the LDH under various environmental conditions and further enhancing its crystallinity through novel synthesis in order to ensure sorbent stability and meanwhile preserve good sorption ability for prolonged application.

LDH has a special affinity for carbonate ions and could incorporate carbonate from CO_2 present in the ambient. Indeed the carbonate-containing LDHs are also the most stable in comparison to LDHs intercalated with other anions. Therefore carbonate-containing LDHs are generally not effective in scavenging anionic contaminants. An improved synthesis method for LDH should be explored such that it ensures rigorous

exclusion of CO₂ during the exchange reactions, thus allowing the effective and widespread use of LDHs in the ambient.

Besides the LDH microspheres prepared in this study, another possible method to fabricate LDH into granular/microspheric form is to disperse the LDH particles within a macroporous polymeric host material to form a mixed matrix LDH granule (Figure 8.1). One such hybrid sorbent, produced by dispersing hydrated ferric oxide (HFO) nanoparticles inside a polymeric ion exchanger, still showed promising results in anion removal (DeMarco et al., 2003; Blaney et al., 2007). While the LDH granules retain their intrinsic sorption/desorption properties, the robust polymeric support may offer adequate mechanical strength and favorable hydraulic properties in the flow-through systems. Further development in this synthesis method should be explored.

Figure 8.1 Schematic representation of a mixed matrix LDH granule.

For the regenerated LDHs, a significant decrease in its sorption capacity within four cycles has been observed in the present study. Moreover, the need for calcination stage between each sorption-regeneration cycle may make the process less attractive. Further study is therefore necessary to fine-tune the regeneration method in order to enhance the regeneration capacity with minimal energy or chemical consumption. An in-depth investigation on the regeneration mechanism would also help to clarify how LDH regains sorption ability and why some oxyanions are irreversibly attached. Upon exhaustion of the sorption capacity, the spent LDH media can be added as filler in the concrete products for its beneficial end-of-life use. In this context, the leaching properties of the stabilized/solidified concrete matrix and the optimum percentage of this additive should be carefully assessed.

At most contaminated sites or in most polluted waters, there is co-existence of various potentially harmful anionic solutes including monoatomic anions, oxyanions,

dissolved organic matter, etc. However, complex systems comprising multi-species solutes, simulating the natural conditions, have rarely been studied. The understanding of the sorption performance of LDHs in the multi-species system is needed since this information is useful for assessing the viability of using LDHs for water and wastewater treatment. Future research should aim to fill this knowledge gap.

To the best knowledge of the author, as yet almost no sorption system has reported on the incorporation of ion exchange model (Stanton and Maatman, 1963) and surface complexation models such as constant capacitance model (Stumm et al., 1980), diffuse layer model, and triple layer model (Davis et al., 1978) for describing the equilibrium sorption on LDHs. One of the advantages of these models over the sorption isotherm equations is their ability to provide a molecular description sorption using an equilibrium approach with a theoretical basis. Therefore the integration of these models into the LDH sorption system for predicting the chemical reactions should be considered in the future work.

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