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ABSTRACT

The objectives of this thesis research were to (i) synthesize cost-effective layered double hydroxides (LDH) or anionic clays to remove arsenite and arsensate oxyanions from water and (ii) quantify oxyanion uptake by LDH and understand the mechanisms of uptake. Two types of LDH were synthesized: hydrotalcite and hydrocalumite by coprecipitation at room temperature or higher with different compositions of layers and interlayers.

Removal of 100% arsenate and 87.5% removal of arsenite with nitrate form of hydrotalcite and 99.9% of arsenate and 83.6% of arsenite with nitrate form of hydrocalumite were achieved. Chloride and carbonate forms of hydrotalcite and chloride form of hydrocalumite removed 50-90% of these oxyanions.

The uptake capacity of LDH synthesized by different methods was also compared. Layered double hydroxides synthesized by co-precipitation method had greater uptake capacity than those synthesized by hydrothermal method because of smaller crystal size in the former. Powder X-ray diffraction (XRD) patterns showed greater crystallinity of LDH synthesized by hydrothermal method than those synthesized by coprecipitation method. These results suggest that oxyanion uptake is less in the case of well crystallized hydrothermally synthesized LDH compared to that of the poorly crystallized materials because it is more difficult to break electrostatic bonds in the former than in the latter.

Higher oxyanion uptake was observed with calcined LDH than with commercially available un-calcined carbonate form of LDH. Calcination of LDH produced intermediate non-stoichiometric oxides, which undergo rehydration and regeneration of the structure with the incorporation of these oxyanions.
The mechanism of arsenate and arsenite uptake is by topotactic anion exchange for all forms of hydrotalcites while the mechanism of uptake of these ions in hydrocalumites appears to be initial anion exchange followed by dissolution-precipitation. The results of uptake were confirmed by XRD, Raman Spectroscopy, and Scanning Electron Microscopy. This study indicated that LDH are efficient and probably cost-effective materials for removal of arsenite and arsenate contaminants from water.
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CHAPTER 1
INTRODUCTION

Contamination of drinking water due to industrial pollution is a major concern in modern society. Contamination occurs from naturally-occurring minerals to man-made chemicals and by-products. While many contaminants are found at levels not enough to cause immediate discomfort or sickness, it is known that even low-level exposure to many common contaminants could, over time, cause severe illness including liver damage, cancer, and other serious ailments. There are many water contaminants that can enter in drinking water naturally or through human activities. In the US, some of the most common anionic water pollutants are derived from arsenic, phosphorous, chromium and fluorine. Arsenic and phosphorous are two inorganic contaminants which are of environmental concern because they can affect human beings and wild life depending upon their concentration in drinking water or irrigation water. These contaminants exist as oxyanions (arsenite, arsenate, and phosphate) in water.

Several materials such as orange waste, slag-iron oxide-titanium dioxide, and aluminum modified zeolites have been used for removal of anionic contaminants from water (Hichour et al., 2000. Ghimire et al., 2003; Zhang et al., 2006; Qiu et al., 2007; Blaney et al., 2007). Synthetic adsorbents, including activated carbon (Chuang et al., 2005) titania (Pena et al., 2005), activated alumina (Singh et al., 2004), iron oxides (Thirunavukkarasu et al., 2003) and lanthanum compounds (Wasay et al., 1996; Tokunaga et al., 1997; Jang et al., 2004) have been used to remove arsenic. Likewise fly ash (Ugurlu et al., 1998), blast furnace slag, zeolite and titanium dioxide (Ozacar 2003), activated alumina (Brattebo et al., 1986), and activated coir pith carbon (Namasivayam et al., 2004)
have been used to remove phosphate. Although these synthetic adsorbents generally showed much higher adsorption capacities than natural adsorbents, they are not very cost effective.

Another group of synthetic adsorbents, hydrotalcites, which are layered double hydroxides (LDH), hold a great potential for removal of contaminants and are cost effective. The LDH have been tested for arsenic removal from drinking water, but, only on a limited scale (Gillman, 2005). There is a need to study this important group of materials in a greater detail for removing contaminants from drinking water. Here we propose the use of LDH to remove these anionic contaminants from water.

Layered double hydroxides are a class of layered compounds, also called hydrotalcites or anionic clays, in which charge on the layer and intercalated ions is reverse of that found in smectite. The first hydrotalcite was discovered in Sweden around 1842. It occurs as foliated and contorted plates in nature and is a hydroxycarbonate of magnesium and aluminum (Cavani et al., 1991). The name LDH is derived from the early works of Feithnecht, who called these compounds “Doppelschichtstrukturen” with intercalated hydroxide layers. This hypothesis was refuted many years later on the basis of single crystal x-ray diffraction analysis (Allmann 1968; Taylor 1980), which showed that all the cations were placed in the same layer, with anions and water molecules located in the interlayer regions.

Layered double hydroxide structure is derived from mineral brucite, in which magnesium is octahedrally surrounded by hydroxyl ions and different octahedra share edges to form infinite sheets (Kovanda et al., 1999). When some divalent ions are substituted by trivalent cations, a positive charge is created on the layers, which is
compensated by anions and water molecules in the interlayers (Taylor 1973; Cavani et al., 1991; DeRoy et al., 1992; Rives and Ulibarri 1999). The octahedral units of divalent or trivalent ions form infinite sheets by their edge sharing. These sheets are stacked on top of each other and are held together mainly by electrostatic bonding. They have relatively weak interlayer bonding compared to cationic clays such as micas and, as a result, exhibit excellent ability to capture inorganic anionic contaminants (Houri et al., 1998; Roh et al., 2000; Tezuka et al., 2004). They have large surface area and anion exchange capacity comparable to anion exchange resins, and good thermal stability (Bish et al., 1980, Cavani et al., 1991; Vaccari, 1998; Das et al., 2004) and therefore, these materials need to be explored for arsenic removal from contaminated water.

The main objectives of this research were (a) to synthesize a variety of LDH with different composition of layers and interlayers, (b) to quantify the uptake of arsenite, and arsenate by these LDH, and (c) to understand the mechanisms of uptake of arsenite and arsenate anions. The six chapters of this thesis deal with different aspects as given below:

Chapter 2 includes the review of current literature on structure, anionic contaminant removal studies by LDH and current literature on chemistry and properties of oxyanions of arsenite and arsenate. Chapter 3 describes the materials and methods used to synthesize and characterize LDH in this study. Chapters 4 and 5 describe the results on uptake of arsenite and arsenate by LDH, respectively. Chapter 6 discusses the summary, overall conclusions, and future studies from this research.
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CHAPTER 2

LITERATURE REVIEW

This chapter reviews the structure, synthesis, characterization and applications of layered double hydroxides.

2.1 Structure of Layered Double Hydroxides

Layered double hydroxides, commonly known as hydrotalcite-like compounds or anionic clays, are homogeneous, basic, mixed metal hydroxides with lamellar structure. Their structure is derived from mineral brucite. Brucite structure has stacking of neutral layers of Mg(OH)$_2$ (Fig. 2.1a, 2.2) in which Mg(OH)$_6$ octahedra are connected via edge sharing into two dimensional sheets having layer thickness of 4.8Å. When some of the divalent ions are substituted by trivalent cations such as Al$^{3+}$ (Fig 2.1b), a positive charge is created in the layers (Hickey et al., 2000; Rajamathi et al., 2001). Various anions along with water molecules could be inserted between the metal hydroxide sheets to neutralize the positive charge (Carrado et al., 1988). The relative proportion of divalent and trivalent ions and interlayer anions could be varied to give rise to a variety of materials with general formula:

$$[\text{M (II)}]_{1-x} \text{M (III)}_x \text{(OH)}_2]^{x+} [\text{A}^{n-}_{x/n}].mS$$

Where M (II) may be (Mg$^{2+}$, Ca$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and so forth) MIII (Al$^{3+}$, Cr$^{3+}$, Fe$^{3+}$ and so forth) A$^{n-}$ is the inter layer anion (Cl$^-$, NO$_3^-$, ClO$_4^-$, CO$_3^{2-}$, SO$_4^{2-}$, organic anion and so forth); m is the number of moles of coordinated solvent (S) generally water per formula weight (Olanrewaju et al., 2000; Iyi et al., 2004; Aisawa et al., 2004 & 2005; Chang et al., 2005). The x is ratio of M(III) / M(II) + M(III) and its value ranges from 0.20-0.33 (Ingram et al., 1967; Allmann, 1968). The stability of structure is due to
hydrogen bonding between water molecules in the interlayers and electrostatic interaction between anions and the layer (Han et al., 1997; Puttaswamy et al., 1997).

The charge density and anion exchange capacity of the LDH may be controlled by varying the M(II) / M(III) ratio. The most common anion found in naturally occurring LDH is carbonate. The naturally occurring LDH, hydrotalcite, has a formula Mg₆Al₂(OH)₁₆CO₃.₄H₂O. Layered double hydroxides have been shown to have affinity for various anions in the following order (Miyata 1983): \( \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \Gamma \).

Fig 2.1  Two-dimensional representation of the structure of the hydroxide layers in: (a) brucite–Mg(OH)₂; (b) hydrotalcite–Mg₆Al₂(OH)₁₆(CO₃²⁻).₄H₂O (Hickey et al., 2000).
Fig 2.2 Three-dimensional representation of structure of brucite mineral (Rajamathi et al., 2001).

Fig 2.3 Three-dimensional representation of structure of hydrotalcite (Rajamathi et al., 2001).
Figures 2.3 and 2.4 schematically illustrate the LDH structure. In Fig. 2.4b, d001 (this is actually 003) shows the distance between two layers and it is different for different anions that occupy the interlayers. The detailed structure of LDH is shown in Figure 2.5.

Fig. 2.4 Schematic representation of the hydrotalcite crystal structure (Kovanda et al., 1999): (a) Brucite-like layers with isomorphous substitution of M(III) for M(II) in octahedral sites, (b) Interlayers composed of anions and water molecules neutralizing a net positive charge of hydroxide sheets.
2.2 Synthesis of LDH or Anionic Clays

Anionic clays can be easily synthesized by controlling some factors. Several methods have been used to synthesize anionic clays (Hickey, 2001) such as:

(1) Hydrolysis/precipitation reactions below 100°C

(2) Hydrothermal synthesis: (i) Hydrolysis/precipitation reactions above 100°C and (ii) Urea hydrolysis method

(3) Structural reconstruction method after calcination

(4) Anion exchange of a precursor LDH method

In all of these methods, it is difficult to avoid contamination from carbon dioxide because anionic clays have very high affinity for carbon dioxide and it is readily incorporated in the interlayers (Newman, 1998). The most common methods used for LDH synthesis are described below:
2.2.1 Hydrolysis / precipitation reactions below 100°C

In coprecipitation, a mixed solution of M$^{2+}$ and M$^{3+}$ salts containing the anion which needs to be incorporated in anionic clays is used as precursor. All cations precipitate simultaneously in a ratio fixed in the starting solution. Coprecipitation can occur either at low supersaturation or high supersaturation. The material formed at high saturation is relatively less crystalline than that synthesized at low supersaturation (Reichle, 1986).

The most important factor that needs to be controlled in coprecipitation procedure is pH of the solution. The pH of the solution should be from 10-12. If pH is above 12, dissolution of Al$^{3+}$ occurs; and if pH is lower than 10, a more complex pathway for the precipitation exists and thus the process is not always complete.

The M(II) / M(III) ratio also influences the crystallinity and purity of LDH. For an example, Kloprogge et al. (2005) studied the effect of ratio of divalent / trivalent metal ions on crystallinity of Zn / Cr hydrotalcite. They prepared 18 samples at varying ratios of Zn / Cr at two different pH values. Samples 1-9 were prepared at pH 10 and samples 10-18 were prepared at pH 4. They reported that at pH 4 and 10, pure highly crystalline hydrotalcite like phase resulted when ratio of divalent / trivalent cations was 3. At a ratio of 1, peaks were broad and less intense (Fig. 2.6). Thus the crystallinity of LDH varies with the type of M (II)/M(III) cations, their ratios, pH , temperature etc.
Fig 2.6 XRD patterns of samples 1–18 with variable metal ion ratios. Samples 1–9 were prepared at pH = 10 and samples 10–18 were prepared at pH = 4 (Kloprogge et al., 2005).
2.2.2 Hydrothermal synthesis

(i) Hydrolysis/precipitation reactions above 100°C

This method involves treating the precipitated samples at moderate temperatures above 100°C for few hours. This treatment results in increased crystallinity of the product formed. Kovanda et al., (2005) studied the effect of aging time and temperature on crystal size, crystallinity and surface area of synthetic hydrotalcites (Fig. 2.7). They found that hydrotalcite content increased with an increase in temperature and aging time. Scanning electron microscope images showed that with the increases in temperature, aggregates of small thin crystals were transformed into thin plates with a hexagonal morphology (Fig. 2.8).

Fig 2.7 Powder X-ray diffraction patterns of hydrotalcite samples depending on temperature and time of hydrothermal treatment (Kovanda et al., 2005).
Fig 2.8 SEM images of hydrotalcite samples hydrothermally treated at 160 °C and 180 °C for various times (Kovanda et al., 2005).
(ii) Urea hydrolysis method

This method can be used both below and above 100°C and applies to the first two methods described above. In this method, solid urea is dissolved into metal salt solution. Compounds formed by this method have been found to have a well defined hexagonal shape with carbonate as the interlayer anion. Rao et al. (2004) synthesized Mg-Al hydrotalcites hydrothermally using the urea hydrolysis method. For the first time, they claimed to have successfully synthesized hydrotalcite with Mg / Al ratio of 1, which could not be achieved by using coprecipitation method where Mg / Al ratio is in the range of 2-4.

Ogawa et al. (2002) used the urea hydrolysis method to synthesize hydrotalcite and studied the effect of temperature and concentration of reactants on the particle size. Their results showed that particle size was controlled in the range of 2-20 µm by the reaction temperature and concentration of reactants. The morphology of hydrotalcite was retained even after thermal decomposition had occurred. Similarly, Oh et al. (2002) observed that as the aging time increased and metal concentration decreased, crystallinity of hydrotalcite increased (Fig. 2.9). Because the decomposition rate of urea in aqueous solution depends on temperature, the particle size distribution was controlled by altering reaction temperature.
Fig. 2.9 Scanning electron microscope images of LDH synthesized by the urea method at 90°C with (a) aging times 6, 30, 45, and 69 h, and (b) the concentration of metal ions, 0.87, 0.67, 0.44, and 0.06 M (scale bar = 2.5 μm) (Oh et al., 2002).
2.2.3 Structural reconstruction method after calcination

Calcination involves heating of anionic clays at 450-500°C which results in removal of interlayer water, interlayer anions and hydroxyl groups with all carbonate lost as CO₂ (Reichle, 1985). The remaining residue is a poorly crystalline mixed metal oxide. After calcination the surface area has been reported to increase from 120 to 200 m²/g (Reichle, 1986). Calcined anionic clays have the ability to regenerate their structure when exposed to water and anions (Marchi and Apestegui’a, 1998; Rocha et al., 1999; Erickson et al., 2005). The anions incorporated need not be the same as that of original LDH. This is an excellent method to obtain various inorganic and organic anionic forms of LDH as well as pillared structure (Vaccari, 1999). Amino acids (Aisawa et al., 2004) and surfactants (You et al., 2002) can also be incorporated through rehydration process.

The conversion of mixed metal oxides into LDH is known as regeneration, reconstruction, rehydration or structural memory effect. This method is suitable for intercalation of large guest anions. It avoids the competition between inorganic anions arising from metal salts. Reconstruction time depends upon the calcination temperature. When sample has been calcined at or below 550 °C the reconstruction is completed after rehydration for 24h, but it requires 3 days to reconstruct if calcination is done at 750 °C and partial reconstruction is observed after calcination at 1000 °C. Reconstruction requires nitrogen atmosphere for incorporation of non-carbonated anion because carbonate LDH forms preferentially in presence of atmospheric carbon dioxide (He et al., 2005).
2.2.4 Anion exchange of a precursor LDH method

This method has considerable usefulness when co-precipitation method is not suitable, such as when divalent or trivalent metal cations and anions are unstable in basic solution, or when direct reaction between the metal ions and the guest anions is more favorable. Thermodynamically, ion exchange in LDH depends upon the electrostatic interaction between the positively charged sheets and the exchanging anions, and to lesser extent, on free energy involved in the changes of hydration (Israëli et al., 2000; Desrosiers et al., 2003). Layered double hydroxides with easily exchangeable ions such as Cl$^-$ or NO$_3^-$ can be used to prepare SO$_4^{2-}$, CO$_3^{2-}$ or PO$_4^{3-}$ forms of LDH.

Fig 2.10 Schematic of ion exchange (He et al., 2005)

2.3 Characterization of anionic clays

Anionic clays can be characterized by several analytical techniques. Most frequently used techniques include powder X-ray diffraction, Raman spectroscopy, infrared spectroscopy (IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Other techniques that are used for characterization of anionic clays include nuclear magnetic resonance (NMR), UV/VIS spectroscopy and neutron scattering.
2.3.1 X-ray diffraction

X-ray patterns generated by Powdered X-ray diffraction (PXRD) are normally obtained using randomly orientated powder samples. Layered double hydroxides have a characteristic XRD pattern as shown in fig 2.11. They have sharp peaks at low 2θ angles and relatively weak non basal reflections at higher 2θ values.

![X-ray diffraction pattern](image)

**Fig 2.11 x-ray diffraction patterns of original HTCl hydrotalcite (Ulibarri et al., 2001)**

The d-spacing can be calculated by using Bragg’s equation:

\[ d = \frac{\lambda}{2\sin\theta} \]

where \( d \) is the distance between planes of atoms; \( \theta \) is diffraction angle; \( \lambda \) is wave length.

The (003) d-spacing depends upon size and orientation of the charge balancing ion. The (003) d-spacing of the sample shown in Fig. 2.11 is 7.9Å

2.3.2 FTIR Spectroscopy

Infrared spectroscopy is another useful tool for characterization of LDH. It involves the stretching vibrations of octahedral structural hydroxyl groups and interlayer
anions. This technique can be used to find the interlayer anion, type of bond formed by the anion and their orientation (Dousova et al., 2003).

2.3.3 Raman spectroscopy

Raman spectroscopy is much like IR spectroscopy. Infrared bands arise from change in dipole moment of molecules while Raman bands arise from change in polarizability. Raman spectroscopy can be used to identify the presence of exchanged anions in the interlayers.

2.4 Applications of Layered Double Hydroxides

Layered double hydroxides have anionic exchange capacity and the ability to capture organic and inorganic anions makes them unique inorganic materials (Feng et al., 2005). High uptake levels of anionic species are due to their large surface area and high anion exchange capacities (Bish et al., 1980) and flexible interlayer space that can accommodate a variety of contaminants from soil water and sediments.

2.4.1 Adsorption of inorganic anions

Ay et al., (2007) studied boron removal by carbonate free nitrate form of hydrotalcite. The results indicated that more than 95% of borate was removed by the carbonate free nitrate form of hydrotalcite. Adsorption of boron was diffusion controlled and there was no effect of calcination on boron removal. The adsorption capacities of uncalcined and calcined samples were nearly the same. Ferreira et al., (2006) also studied the boron removal by two types of hydrotalcites. They found that with nitrate form of Mg-Al hydrotalcites, the borate removal occurred by both ion exchange and surface
adsorption and with carbonate form of Mg-Fe hydrotalcites it occurred by surface adsorption due to presence of carbonate ion in the interlayer that can hardly be exchanged by other anions. The study showed that Mg-Al hydrotalcites were effective in removal of borate from drinking water to the limit recommended by World Health Organization.

Lazaaridis et al., (2003) studied the sorptive removal of chromium (VI) from aqueous solution by calcined Mg-Al-CO$_3$ hydrotalcite. Uptake of Cr (VI) increased at increased agitation speed, low solution pH and high initial chromium concentration and low sorbent concentration. Similarly, Frost et al., (2006) investigated the removal of nitrate ion by calcined form of Zn-Al hydrotalcite having carbonate in the interlayers. The results showed that nitrate ion was removed within 30 min. Raman spectroscopy also proved the presence of nitrate in the interlayers.

In another study, Nava et al., (2003) observed the removal of fluoride ions by thermally treated hydrotalcite at different pH levels. The distribution coefficient indicated that the best condition for removal of fluoride ion was at pH 5. More than 80% of fluoride ions were removed by calcined hydrotalcites within one hour. Likewise, Ookubo et al., (1998) studied the ion exchange of chloride form of hydrotalcite with phosphate. They studied the effect of aging time and pH on phosphate uptake. The results showed that phosphate uptake was increased with increased aging time; and maximum phosphate uptake occurred at pH 7. The isotherm for phosphate uptake followed Langmuir-type equation. Das et al., (2006) also studied the removal of phosphate by calcined Mg-Al layer double hydroxides. They found that molar ratio of adsorbent cations affect the adsorption capacity. The results showed that Mg:Al 2:1 showed higher adsorption of phosphate than any other calcined LDH due to higher Al$^{3+}$ content in it. The effect of
competitive ions on adsorption of phosphate was also studied and it was found that LDH had more affinity for highly charged ions than monovalent ions. Dousova et al., (2003) found 70% removal of As (V) from aqueous solution by calcined Mg-Al LDHs at neutral pH utilizing memory effect.

Toraishi et al., (2002) studied the removal of IO$_3^-$ by hydrotalcites. It was found that when IO$_3^-$ was exchanged with nitrate anion, the d-spacing decreased because IO$_3^-$ was adsorbed horizontally in the interlayers. There was also effect on crystallinity due to different orientations of NO$_3^-$ and IO$_3^-$. The results showed that IO$_3^-$ was adsorbed on external surface of carbonated form of hydrotalcites and exchanged for interlayer NO$_3^-$ for nitrate form of hydrotalcites.

You et al., (2001) studied the adsorption behavior of selenite (SeO$_3^{2-}$) on Mg / Al and Zn / Al LDH. The SeO$_3^{2-}$ adsorption was rapid and dependent upon initial concentration and pH. The results showed that the maximum adsorption was higher on Mg-Al LDH than on Zn-Al LDH and decreased with increase in molar ratio of Mg/Al. Competing ions also affected the adsorption of SeO$_3^{2-}$ and the competition for various anions increased in the order HPO$_4^{2-}$ > SO$_4^{2-}$ > CO$_3^{2-}$ > NO$_3^-$.  

2.4.2 Adsorption of Organic anions

Layer double hydroxides also have the ability to entrap organic contaminants via ion exchange and reconstruction. Ulibarri et al., (2001) reported the removal of two anionic organic contaminants of 2,4,6 trinitrophenol (TNP) and dodecyl benzene sulfonate (DBS) by calcined and un-calcined hydrotalcites. The results showed that the uncalcined chloride form of hydrotalcite was more effective in uptake of these organic contaminants than carbonate form. This study also showed that after calcination at 500
°C, the carbonate form removed TNP and DBS more effectively as compared to the chloride form. Siverio et al., (2008) studied the removal of phenylalanine (amino acid) by carbonate form of LDH and investigated the effect of temperature and ionic strength on adsorption. The results showed that phenylalanine was efficiently removed by LDH even at higher amino acid concentration, and adsorption decreased with increase in temperature and ionic strength.

L- Ascorbic acid (vitamin C) is essential for our body. It is sensitive to oxidation in the presence of oxygen. Choy et al., (2004) studied the intercalation of the anionic vitamin derivative such as ascorbic acid succinate and tocopherol in LDH. The results showed that vitamins were stabilized in the interlayer space of LDH without any changes in its chemical and functional integrity. Layered double hydroxides proved to be excellent host lattice for safe storage and effective delivery of biological compounds.

Pesticides are one group of organic contaminants that are widely used in agriculture and leached from soil into water. You et al., (2002) studied the adsorption of dicamba, a pesticide, by calcined and un-calcined carbonate form of LDH. The results showed that dicamba was adsorbed on calcined hydrotalcite but not on the un-calcined hydrotalcite. Desorption of adsorbed decamba could take place depending on the type of competing anion in the aqueous solution.

Aisawa et al., (2005) investigated the intercalation of nucleotides by nitrate form of Zn-Al and Mg-Al LDH by ion exchange. The results indicated that equilibrium reached after 2 days and the amount of nucleotide intercalated decreased with increase in number of phosphate groups. The x-ray diffraction pattern clearly showed the expansion of 003 peak to 13.8-16Å and proved exchange of nitrate ion with nucleotides adenosine
monophosphate (AMP), adenosine diphosphate (ADP), and adenosine triphosphate (ATP).

Orthman et al., (2003) studied the removal of colored substances from industrial effluent streams using LDH. Ninety-nine percent of the acid blue 29 dye was either adsorbed or entered the interlayer region within one hour. Likewise, Seida et al., (2000) were able to remove humic substances from aqueous system by un-calcined and calcined iron containing LDH. The removal of humic substances occurred by anion exchange and adsorption. Due to the ability of LDH to buffer pH, they could produce hydroxyl ions through dissolution which enhanced the removal process.

2.5 Hydrocalumite: Structure and exchange of anions

Hydrocalumite is also an anionic clay like hydrotalcite. Mg with Al is known as hydrotalcite and Ca with Al is known as hydrocalumite. Hydrocalumite–like anionic clays are less broad in composition in LDH family. The structure of hydrocalumite is composed of portlandite –like principal layers in which one third of Ca$^{2+}$ sites are occupied by Al$^{3+}$ (Taylor 1973). When some calcium ions are substituted by aluminum, a positive charge is generated in the octahedral layers, and anions along with water molecules are incorporated to balance these positive charges (Constantino et al. 1995). Ca$^{2+}$ and Al$^{3+}$ ions are seven- and six-coordinated in hydrocalumite, respectively. The seventh coordination in Ca- polyhedron is water molecule in the interlayer. The general formula of this type of anionic clays:

\[ [\text{Ca}_2\text{M}^{3+} (\text{OH})_6]^+ [\text{A}^{n-}_{1/n} \cdot m \text{H}_2\text{O}]^- \]
Ca$^{2+}$ can be replaced by Cd$^{2+}$ and Al$^{3+}$ can be replaced by Cr$^{3+}$, Ga$^{3+}$ and Fe$^{3+}$ but few studies have been done on these types of phases (Ecker et al., 1994 and Auer et al., 1994). Most common divalent and trivalent ions are Ca$^{2+}$ and Al$^{3+}$, respectively.

Fig 2.12 Schematic representation of the structure of hydrocalumite (Zhang et al., 2003) consisting of portlandite-like layers intercalated by hydrated anions, modified from Constantino and Pinnavaia (1995).

The common name of Ca layered double hydroxide is Friedel salt and it has composition of 3CaO·Al$_2$O$_3$·CaCl$_2$·10H$_2$O. Renaudin et al., (2000) studied the structure of Ca$_4$Al$_2$(OH)$_{12}$(NO$_3$)$_2·4$H$_2$O and found that at 70 °C its structure looked like pillared layer structure with composition Ca$_4$Al$_2$(OH)$_{12}$(NO$_3$)$_2·2$H$_2$O because adjacent main layers were connected by nitrate groups. The remaining two water molecules were free and not connected to the main layers (Fig. 2.13). Villie et al., (2003) studied the dehydration and decomposition of chloride intercalated Friedel salts. They found that main layers were bridged by chloride anion in the interlayer forming a pillar structure (Fig 2.14), and that it became amorphous at 400 °C.
Figure 2.15 includes the SEM pictures showing the effect of aging on the crystal size of hydrocalumite formed by coprecipitation. Crystal size increased with time (Zhang et al., 2003).

\[ \text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2\cdot2\text{H}_2\text{O} \]

Fig 2.13 Projection on (010) of (a) dihydrated and (b) tetra hydrated binitroaluminate (Renuadin et al., 2000).
Fig. 2.14 Crystal structure of dehydrated Friedel's salt at 116°C (Renuadin et al., 2003).
Fig 2.15 Micrographs of the solid recovered from the coprecipitation experiments: (A) hexagonal platy crystals of hydrocalumite after 7 d of reaction; (B) well-formed hexagonal plates of hydrocalumite after 30 d of reaction (Zhang et al., 2003).

2.5.1 Exchange of anions

Compared to hydrotalcite, only a limited number of studies have focused on uptake of anions by hydrocalumite. Segni et al. (2006) studied the uptake of oxoanions of Cr, V and Si by chloride and nitrate intercalated hydrocalumite. The incorporation of $\text{V}_2\text{O}_7^{4-}$, $\text{SiO}_3^{2-}$ occurred via the exchange of nitrate and chloride ion, respectively. The incorporation of $\text{CrO}_4^{2-}$ took place through coprecipitation and anion exchange.

Zhang et al. (2003) examined the removal of oxoanions of B, Cr, Mo and Se by hydrocalumite and ettringite at high pH. The results indicated that hydrocalumite was capable of reducing the concentration of borate, chromate, molybdate and selenate to levels below drinking water standards.

Millangi et al., (2000) studied the selective intercalation of 1, 4 benzenedicarboxylate in hydrocalumite from a solution containing equimolar ratio of 1,2
and 1,4 benzenedicarboxylate. The intercalation proceeded by exchange of nitrate ion of hydrocalumite by both 1,2 and 1,4 benzenedicarboxylate, followed by replacement of 1,2 benzenedicarboxylate by the 1,4 benzenedicarboxylate. Thus hydrocalumite provided low temperature means of separating and purifying these two isomers.

2.6 Literature review on chemistry and properties of arsenite and arsenate

Arsenic is a non-metal and ranks 20th in natural abundance, 14th in sea water, and 12th in human body (Mandal et. al., 2002). It is commonly recognized as a toxic and carcinogenic metal compound (Bates et al., 1992; Smith et al., 1992). A long-term exposure to arsenic can cause cancer of skin, kidney, bladder and lung as well as neurological and cardiovascular problems (WHO 1981; Kiping et al., 1997; Jain et al., 2000; Mandal et al., 2002).

Arsenic can exist in four oxidation states: +5, +3, 0 and -3. In natural water the most common forms are inorganic oxyanions of trivalent arsenite and pentavalent arsenate (Brandhuber and Amy, 1998). Soluble pentavalent or arsenate species are $\text{AsO}_4^{3-}$, $\text{HAsO}_4^{2-}$, $\text{H}_2\text{AsO}_4^-$ and $\text{H}_3\text{AsO}_4$. The soluble trivalent or arsenite species include $\text{AsO}_3^{3-}$, $\text{HAsO}_3^-$ and $\text{H}_2\text{AsO}_3^-$ (Sorg and Logsdon, 1978). Organic species of arsenic in water are less significant than inorganic species (Anderson et al., 1991; Sadiq, 1997).

Arsenic speciation is controlled by two factors: redox potential and pH (Smedley et al., 2002; Fig. 2.16 and 2.17). Trivalent arsenic is 60 times more toxic than pentavalent arsenic (Jain et al., 2000). Under oxidizing conditions, arsenic (V) species dominate with $\text{H}_2\text{AsO}_4^-$ dominating at a pH less than 6.9, while $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$ species dominating
at higher pH (Table 2.1). By contrast, under reducing environment, As (III) species dominate; at pH less than 9.2, uncharged H$_3$AsO$_3$ species dominate (Wang et al., 2006). Fig 2.18 describes the structural difference between arsenite and arsenate species.

Fig. 2.16 Eh-pH diagram of aqueous As species in the system As–O$_2$–H$_2$O at 25°C and 1bar total pressure (Smedley et al., 2002).
Fig. 2.17 Arsenite (As(III)) and arsenate (As (V)) species predominance in water as a function of pH (Smedley et al. 2002).
Table 2.1.  $pK_a$ values of inorganic arsenic species (Cherry et al., 1979).

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
<th>$pK_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III): Arsenites</td>
<td>9.2</td>
<td>12.1</td>
<td>13.4</td>
</tr>
<tr>
<td>As(V): Arsenates</td>
<td>2.2</td>
<td>6.96</td>
<td>11.2</td>
</tr>
</tbody>
</table>
The occurrence of arsenic pollution is associated with natural conditions or the industrial practices of mankind. The most abundant mineral sources of As are arsenian pyrite and arsenopyrite (Cullen et al., 1989). Weathering of these minerals in oxidizing environments solubilizes arsenic as As (III) and ultimately as As (V). An anthropogenic source of arsenic pollution is discharge from various industries such as smelting, petroleum refining, pesticides, herbicides, glass and ceramic manufacturing. These sources of pollution introduce significant quantities of arsenic not only in waterways but also in soil and ground water (Huang et al., 1984).

Many countries like USA, China, Chile, Bangladesh, Taiwan Mexico Newzeland, Japan, India, and Argentina are affected by arsenic contamination (Borgono et al., 1971; Kaneko et al., 1976; Cebrian et al., 1983; Das et al., 1983; Meranger et al., 1984; Chanda et al., 1994; Chen et al., 1994; Dhar et al., 1997; Burkel et al.1999; Chowdhury et al., 1999; Koch et al., 1999; Karim et al., 2000; Nickson et al., 2000; Chakraborti et al., 2002; Hossain et al., 2006; Mondal et al., 2006) with arsenic concentration in excess of 10 ppb in potable water which is maximum level recommended by World Health Organization.

2.6.1 Materials used to remove arsenic

Wasay et al., (1996) studied the removal of arsenite and arsenate from synthetic wastewaters by basic yttrium carbonate. They removed greater than 99% of arsenite and arsenate by adsorption on yttrium carbonate. The adsorption capacity increased with increase in temperature.

Zhang et al., (2006) studied the removal of arsenite from water using slag-iron oxide-TiO2 adsorbent. He developed this adsorbent which could oxidize arsenite as well
as remove the generated arsenate from aqueous sample. The optimum pH for oxidation and adsorption was found to be around 3 for this adsorbent.

Qui et al., (2007) reported the removal of arsenate by using cancrinite-type zeolite (ZFA) synthesized from fly ash. They found that ZFA had higher adsorption capacity than activated carbon, silica gel, zeolite NaY and zeolite 5. Shevada et al., (2004) found zeolites NH4+/Y (NY6), were effective in removal of arsenic from water over wide initial pH range of 2-12.

Several other materials like activated carbon (Chuang et al., 2005), iron containing granular activate carbon (Gu et al., 2005), hematite and feldspar (Singh et al., 1996), titania (Pena et al., 2005), activated alumina (Singh et al., 2004), iron oxides (Thirunavukkarasu et al., 2003), zero valent iron (Bang et al., 2005), goethite (Manning et al., 1998), and lanthanum compounds (Wasay et al., 1996; Tokunaga et al., 1997; Jang et al., 2004) have been used to remove arsenic.

Hydrotalcites have been reported to remove arsenic from drinking water, but only investigated on a limited scale by Gillman (2005). There is a need to study this important group of materials in a greater detail for removing arsenite and arsenate from contaminated water because these materials may be cost-effective compared to other explored materials. Here we propose to synthesize and use hydrotalcite and hydrocalumite with different composition of layers and interlayers to remove As contaminants and to understand the mechanism of As oxyanion uptake.
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Renuaudin, G., Rapin, J.P., Humbert, B., and Fran-cois, M. (2000). Thermal behavior of the nitrated AFm phase \( \text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_4\text{H}_2\text{O} \) and structure determination of the intermedium hydrate \( \text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2\text{H}_2\text{O} \). Cement and Concrete Research 30, 307-314.


CHAPTER 3

EXPERIMENTAL SYNTHESIS OF LAYERED DOUBLE HYDROXIDES

Layered double hydroxides can be synthesized by various techniques. Different methods may be adopted as a function of composition required, such as coprecipitation, hydrothermal method, urea hydrolysis method etc. (as described in chapter 2). Some new field-assisted methods such as microwave irradiation method (Fetter et al., 1997; Komarneni et al., 1992), ultrasound method (Kooli et al., 1997; Seida et al., 2002) and electrochemical preparation (Silva et al., 2003) have also been developed. The methods used in this study to synthesize LDH and their characterization are described in this chapter.

3.1 Materials

Aluminum chloride, magnesium chloride, aluminum nitrate, magnesium nitrate, calcium chloride, calcium nitrate, urea, sodium hydroxide, sodium carbonate, ammonium hydroxide were obtained from Aldrich Company for synthesis of LDH with varying composition. One commercially available carbonate form of hydrotalcite was obtained from Alcoa Company located in Pittsburgh, PA.

3.2 Methods

Several types of LDH were synthesized (Table 3.1). Hydrotalcites having Mg-Al in the layers (Mg $^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2), and chloride, carbonate, or nitrate in the interlayers and hydrocalumite with Ca-Al (Ca$^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2) in the layers and chloride and nitrate in the interlayers were prepared by coprecipitaion. One LDH with carbonate in the interlayers and Mg$^{2+}$/Al$^{3+}$ molar ratio 3 has been synthesized by urea method.
Table 3.1 List of Synthesized LDH with different composition of layers and interlayers.

<table>
<thead>
<tr>
<th>LDH</th>
<th>Base</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al 4:1-Cl-</td>
<td>NaOH</td>
<td>RT</td>
</tr>
<tr>
<td>Mg-Al 3:1-Cl</td>
<td>NaOH</td>
<td>RT</td>
</tr>
<tr>
<td>Mg-Al 2:1-Cl</td>
<td>NaOH</td>
<td>RT</td>
</tr>
<tr>
<td>Mg-Al 4:1-NO₃⁻</td>
<td>NH₄OH</td>
<td>RT</td>
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<tr>
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<td>NH₄OH</td>
<td>RT</td>
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</tr>
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<td>Na₂CO₃+NaOH</td>
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<td>Na₂CO₃+NaOH</td>
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</tr>
<tr>
<td>Ca-Al 4:1-NO₃⁻</td>
<td>NaOH</td>
<td>RT</td>
</tr>
<tr>
<td>Ca-Al 3:1-NO₃⁻</td>
<td>NaOH</td>
<td>RT</td>
</tr>
<tr>
<td>Ca-Al 2:1-NO₃⁻</td>
<td>NaOH</td>
<td>RT</td>
</tr>
</tbody>
</table>
3.2.1 Synthesis by Coprecipitation

3.2.1.1 Hydrotalcites (Mg-Al LDHs)

3.2.1.1a Chloride form of Mg-Al LDH.

The chloride form of Mg-Al LDH was synthesized by following the method of Fetter (1997). A mixed solution of MgCl$_2$.6H$_2$O (1.2 M) and AlCl$_3$.6H$_2$O (0.4M) salts with Mg/Al ratio of 3, was made in 50 ml of deionized water. This mixed solution containing Mg$^{2+}$ and Al$^{3+}$ ions was added drop wise in 50 ml of 6M base solution of sodium hydroxide under vigorous stirring conditions maintaining a pH greater than 10. The addition was completed in 3-4 hrs. The resulting slurry was aged for 24 hrs at room temperature. The product was centrifuged, washed with deionized water 3-4 times and then dried by freeze drying. LDH with Mg/Al stochiometric ratios of 4 and 2 have been prepared by the same method as above.

3.2.1.1b Carbonate form of Mg-Al LDH

Carbonate form of Mg-Al LDH was synthesized by method of Yamaoka (1989). A 50 ml aqueous solution containing 0.3 M Mg (NO$_3$)$_2$.6H$_2$O and 0.1 M Al (NO$_3$)$_3$.6H$_2$O with Mg/Al ratio 3 was added drop wise into a 50 ml mixed solution of (NaOH (1.7 M) + Na$_2$CO$_3$ (0.8 M) with vigorous stirring conditions maintaining a pH of greater than 10 at room temperature. After complete addition, the slurry formed was aged at 60°C for 24 hrs. The product was centrifuged washed with distilled water 3-4 times and dried by freeze drying. The same procedure was followed to synthesize LDH with Mg/Al stochiometric ratios of 4 and 2.
3.2.1.1c Nitrate form of Mg-Al LDH

The nitrate form of Mg-Al LDH was synthesized by following the method of (Olanrewaju et al., 1997). A 10 ml aqueous solution of Mg (NO$_3$)$_2$. 6H$_2$O and Al (NO$_3$)$_3$. 6H$_2$O having Mg/Al ratio 3 was added drop wise in 90 ml of aqueous ammonium hydroxide solution under vigorous stirring conditions. The addition was completed in 2-3 hrs. The obtained slurry was aged for 24 hrs at room temperature. The product was centrifuged, washed with distilled water 3-4 times and dried by freeze drying. In a similar way LDH with Mg/Al stoichiometric ratios of 4 and 2 were synthesized.

3.2.1.2 Hydrocalumites (Ca-Al LDHs)

3.2.1.2 a Chloride form of Ca-Al LDH

The chloride form of Mg-Al LDH was synthesized by following the method of Fetter (1997). CaCl$_2$. 6H$_2$O (0.9 M) and AlCl$_3$. 6H$_2$O (0.3M) in a Ca/Al molar ratio of 3 were dissolved in 50 ml of deionized water. This mixed solution containing Ca$^{2+}$ and Al$^{3+}$ was slowly added drop by drop to 50 ml of 2M of NaOH aqueous solution under vigorous stirring conditions maintaining a pH greater than 10. The addition was completed in 3-4 hrs. The resulting slurry was aged for 24 hrs at room temperature. The product was centrifuged, washed with deionized water 3-4 times and then dried by freeze drying. LDH with Ca/Al stoichiometric ratios of 4 and 2 have been prepared by same method as above.

3.2.1.2 b Nitrate form of Ca-Al LDH

The nitrate form of Ca-Al LDH was synthesized by following the method of Fetter (1997). A 50 ml aqueous solution containing 1.2 M of Ca (NO$_3$)$_2$.6H$_2$O and 0.4 M
Al(NO₃)₃·6H₂O having a Ca/Al ratio of 3 was added drop wise to a base solution of NaOH (2M) with vigorous stirring conditions maintaining a pH of greater than 10 at room temperature. After complete addition, the slurry formed was aged for 24 hrs at room temperature. The product was centrifuged, washed 3-4 times with deionized water and dried by freeze drying. The same procedure was followed to synthesize LDH with Ca/Al stochiometric ratios of 4 and 2.

3.2.2 Synthesis by Urea method

3.2.2.1 Carbonate containing Mg-Al LDH

The Mg: Al 3:1 was synthesized by the method of Ogawa (2002). An aqueous stock solution of urea, magnesium chloride and aluminum chloride were mixed together at Mg/Al/urea molar ratio of 3:1:10 with magnetic stirring at room temperature. The concentrations of components in starting solution were 0.3, 0.1 and 1M for MgCl₂, AlCl₃ and urea, respectively. Then homogeneous solution was transferred into Teflon–lined autoclave and heated at 150°C for 24 hrs. After cooling at room temperature, the solid precipitate was collected by centrifugation and washed with distilled water 3-4 times. The pH of the solution changed from 3.4 at the beginning to 8.4 at the end of the reaction.

3.2.2.2 Calcined carbonate form of Mg-Al 3:1 LDH

Commercially available carbonate form of Mg-Al was calcined by heating it at 500°C for 4-5 hrs to form mixed oxides. By calcination carbonate interlayer anion can be removed as CO₂ and the LDH transforms to reactive mixed oxides.
3.3 Characterization of the synthesized LDH

3.3.1 X-ray Diffraction

The X-ray powder diffraction pattern of synthesized LDH were taken with a Scintag diffractometer operated at 35 kV voltage and 30 mA current using CuKα radiation. A step scan of 5° /min was used in the continuous method in a range of 5-40°. LDH materials before and after arsenite and arsenate treatment were loaded into the cavity of a zero background slide and hence semi quantitative comparisons of their peak intensities can be made.

3.3.2 Scanning Electron Microscopy

Some of the samples were characterized by scanning electron microscope (SEM) to determine the particle size and morphology. Scanning electron microscopy was done using a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with very thin carbon using a carbon coater. An accelerating voltage of 5 KV was used for observation with the microscope.

3.3.3 Raman Spectroscopy

Some samples were characterized by Raman spectroscopy for identifying the presence of arsenite and arsenate in the treated samples of LDH. Samples were pressed to form pellets and spectra were collected by RS 2000 Raman spectrophotometer.
References


Chapter 4

UPTAKE OF ARSENITE BY SYNTHETIC HYDROTALCITE-TYPE AND HYDROCALUMITE-TYPE LAYERED DOUBLE HYDROXIDES

Abstract

Two types of layered double hydroxides (LDHs), hydrotalcite and hydrocalumite with different composition of layers and interlayers have been used to remove arsenite from solutions. This study showed the effect of different variables such as M(II)/M(III) ratio and interlayer anions on the uptake of arsenite. The kinetic study showed that anion exchange process was very fast and apparently attained a steady-state in the range of 8-16 hrs. Arsenite removal was found to be 87.5% and 83.6% with the nitrate forms of hydrotalcite and hydrocalumite, respectively. Layered double hydroxides synthesized at room temperature showed higher uptake than those synthesized by hydrothermal method due to small crystal size of the former. Calcined LDH showed higher uptake than commercially available uncalcined carbonate form of hydrotalcite. The uptake process was confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

4.1 Introduction

Arsenic is a metalloid i.e., it has characteristics of both metals and nonmetals. It enters into water through natural deposits in the earth and anthropogenically from arsenic based insecticides, pesticides, wood preservatives etc. It exists commonly in four oxidation states 3-, 0, 3+, 5+. The soluble trivalent or arsenite species include AsO$_3^{3-}$, HAsO$_3^{2-}$, H$_2$AsO$_4^-$, and H$_3$AsO$_3$ (Sorg and Logsdon, 1978). Arsenite species mostly dominate in reducing environment. The speciation of arsenic is controlled by two factors: redox potential and pH (Smedley et al., 2002).
Several materials such as activated carbon (Chuang et al., 2005), iron containing granular activated carbon (Gu et al., 2005), hematite and feldspar (Singh et al., 1996), titania (Pena et al., 2005), activated alumina (Singh et al., 2004), iron oxides (Thirunavukkarasu et al., 2003), zero valent iron (Bang et al., 2005), goethite (Manning et al., 1998), and lanthanum compounds (Wasay et al., 1996; Tokunaga et al., 1997; Jang et al., 2004) have been used to remove arsenic.

Hydrotalcites have been reported to remove arsenic from drinking water, but only investigated on a limited scale by Gillman (2005). There is a need to study this important group of materials in a greater detail for removing arsenite and arsenate from contaminated water as these materials may be cost-effective compared to other explored materials. The purpose of the present study was to synthesize and use hydrotalcite and hydrocalumite with different composition of layers and interlayers to remove arsenite, and to understand the mechanism of arsenite uptake.

Layered double hydroxides are a class of layered compounds, also called hydrotalcites or anionic clays, in which charge on the layer and intercalated ions is reverse of that found in cationic clays such as smectite. Layered double hydroxide structure is derived from mineral brucite, in which magnesium is octahedrally surrounded by hydroxyl ions, and different octahedra share edges to form infinite sheets (Kovanda et al., 1999). When some divalent ions are substituted by trivalent cations, a positive charge is created on the layers, which is compensated by anions and water molecules in the interlayers (Taylor 1973; Cavani et al., 1991; DeRoy et al., 1992; Rives and Ulibarri 1999). The octahedral units of divalent or trivalent ions form infinite sheets by their edge sharing. These sheets are stacked on top of each other and are held together mainly by
electrostatic bonding. They have relatively weak interlayer bonding compared to cationic clays such as micas and, as a result, exhibit excellent ability to capture inorganic anionic contaminants (Houri et al., 1998; Roh et al., 2000; Tezuka et al., 2004). They have large surface area and anion exchange capacity comparable to anion exchange resins, and good thermal stability (Bish et al., 1980, Cavani et al., 1991, Vaccari, 1998, and Das et al., 2004).

4.2 Materials and methods

4.2.1 Synthesis of layered double Hydroxides

Hydrotalcites having Mg-Al in the layers (Mg$^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2) and chloride, carbonate or nitrate in the interlayers and hydrocalumite with Ca-Al (Ca$^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2) in the layers and chloride or nitrate in the interlayers were prepared by coprecipitation. One LDH with carbonate in the interlayers and Mg$^{2+}$/Al$^{3+}$ molar ratio 3 was synthesized by urea method as described in chapter 3.

4.2.2 Uptake of arsenite ($\text{AsO}_2^-$) by layered double hydroxides

The arsenite uptake experiments were carried out in triplicate by batch equilibration technique. The first set of uptake experiments was conducted with chloride intercalated hydrotalcite and hydrocalumite.

Fifty milligrams of each LDH, was weighed into centrifuge tubes and then mixed with 25 ml of sodium arsenite solution at a concentration of 1mM or 2 mM. The pH of the solution was 9.3. The suspensions were shaken for 4h, 8h, and 16h on a shaker. The tubes were then centrifuged, to separate solid and solution phases and arsenite concentration was determined in the supernatants by atomic absorption spectroscopy (AAS). The solid phases were analyzed by XRD.
A second set of uptake experiments was conducted with nitrate and carbonate forms of hydrotalcite, and nitrate form of hydrocalumite using the same procedure as for the first set of experiments except that the shaking was done for a time period of 16h only because a steady-state has been achieved by this equilibration time.

4.2.3 Characterization of the synthesized product

4.2.3.1 X-ray Diffraction

X-ray powder diffraction patterns of the synthesized LDH were taken with a Scintag diffractometer operated at 35 KV voltage and 30 mA current using CuKα radiation. A step scan of 5°/min was used in the continuous method in a range of 5-40° 2θ.

4.2.3.2 Scanning Electron Microscopy

Some of the samples were characterized by scanning electron microscope (SEM) to determine the particle size and morphology. Scanning electron microscopy was done using a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with very thin carbon using a carbon coater. An accelerating voltage of 5 KV was used for observation with the microscope.
4.3 Results and discussion

4.3.1 Powder X-ray diffraction results

Figures 4.1-4.5 show the XRD patterns of various Mg-Al LDH and Ca-Al LDH with different composition of layers and interlayers. The XRD patterns for all synthesized samples were characteristics of LDH materials with sharp or broad peaks at lower 2θ values, and less intense peaks at higher 2θ. Slight shifts were observed in major peaks towards higher 2θ with lowering molar ratio of Mg/Al and Ca/Al (Figs 4.2, 4.3 and 4.5) which also indicates higher charge density, and decreased interlayer distance and unit cell parameters except in the case of nitrate forms of LDH (Figs 4.1 and 4.4). This decrease in interlayer distance could be due to an increase in the electrostatic interaction between positive layers and negative interlayers. In the case of nitrate forms of LDH, the (003) increased because of repulsion of large anions in the interlayers (Figs. 4.1 and 4.4). A small amount of calcite impurity was detected at ~ 3.03Å in the case of Ca-Al-NO₃ samples (Fig.4.4).

The XRD patterns of the uncalcined and calcined LDH are shown in Fig 4.6. The XRD pattern of calcined LDH (Fig 4.6) clearly showed that the layer structure was completely destroyed.

The type of anion present in the interlayer of hydrotalcite and hydrocalumite directly affected the thickness of layer which can be seen by change of 003 and 006 reflections in the XRD spectra. Temperature of synthesis also affected the thickness of the layer. The LDH synthesized by urea method at 150° C had lower d₀₀₃ value than the LDH synthesized at room temperature (Fig 4.7). This decrease in d₀₀₃ spacing could be attributed to the decrease in water content due to better crystallinity at higher
temperature. For each anionic LDH synthesized at room temperature, the basal spacing of the hydrotalcites increased as follows:

Mg-Al-NO$_3$ > Mg-Al-Cl > Mg-Al-CO$_3$ and similarly the basal spacing of the hydrocalumite increased as follows: Ca-Al-NO$_3$ > Ca-Al –Cl.
Fig 4.1 X-ray diffraction patterns of Mg-Al-NO3 with different composition of layers.

Fig 4.2 X-ray diffraction patterns of Mg-Al-Cl with different composition of layers.
Fig 4.3 X-ray diffraction patterns of Mg-Al-CO$_3$ with different composition of layers.

Fig 4.4 X-ray diffraction patterns of Ca-Al-NO$_3$ with different composition of layers.
Fig 4.5 X-ray diffraction patterns of Ca-Al-Cl with different composition of layers.

Fig 4.6 X-ray diffraction patterns of commercial uncalcined and calcined carbonate form of hydrotalcite.
Fig 4.7 X-ray diffraction patterns of Mg-Al-CO$_3$ hydrothermal (urea method) vs. coprecipitation.
4.3.2 Arsenite uptake by hydrotalcite-type and hydrocalumite-type LDH: kinetic study of chloride forms

Tables 4.1 and 4.2 show the results of arsenite uptake by the chloride form of hydrotalcite and hydrocalumite (molar ratios of 3 and 2 for Mg/Al and Ca/Al) at two different concentrations, and at different intervals of time. The uptake of arsenite from 1mM solution was in the range of 27-49% with hydrotalcites and in the range of 22-33% with hydrocalumites (Table 4.1). The uptake of arsenite from 2 mM solution was in the range of 16-41% with hydrotalcites and in the range of 28-77% with hydrocalumites (Table 4.2). Figures 4.8 and 4.9 show that the uptake of arsenite reached a plateau between 8 to 16 hrs.

The uptake of arsenite, in general, was higher in case of 3:1 chloride forms of hydrotalcite and hydrocalumite than the 2:1 chloride forms of hydrotalcite and hydrocalumite (Tables 4.1 and 4.2). This could be due to the fact that 3:1 contains a lower amount of Al$^{3+}$ compared to 2:1 and, therefore net positive charge on the hydroxide layers is lower in 3:1 compared to 2:1 samples, the latter with higher charge density. The space for incoming anion is larger in case of 3:1 chloride form of LDH than that of 2:1 and this larger interlayer space facilitated arsenite uptake in the former. Table 4.3 shows the uptake of arsenite by 4:1, 3:1 and 2:1 types of Mg: Al (Cl$^-$) LDH. The pH values of the equilibrated solutions are given in Table 4.3 and others to give an indication of As species expected. These results show that as the charge density increased, the uptake of AsO$_2^-$ decreased because of narrower interlayer spacing for higher charge LDH (Table 4.3). The anion exchange of chloride by arsenite led to little or no change in d$_{003}$ spacing (Figs 4.10-4.12) because they apparently have similar size in the interlayers. However,
the intensity of d_{003} spacing decreased after arsenite exchange with chloride forms of calumite (Figs. 4.13 and 4.14) indicating a dissolution reaction. The presence of calcite at 3.03 Å and gibbsite-like phase around 4.83 Å (Figs 4.14 and 4.15) also suggest dissolution reaction.
Table 4.1 Arsenite (AsO$_2^-$) uptake by chloride form of LDH (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>LDH</th>
<th>1mM AsO$_2^-$ uptake (%) as a function of time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4h</td>
</tr>
<tr>
<td>Mg:Al (3:1) Cl$^-$</td>
<td>45.1 ± 2.4</td>
</tr>
<tr>
<td>Mg:Al (2:1) Cl$^-$</td>
<td>26.8 ± 5.0</td>
</tr>
<tr>
<td>Ca:Al (3:1) Cl$^-$</td>
<td>22.1 ± 0.8</td>
</tr>
<tr>
<td>Ca:Al (2:1) Cl$^-$</td>
<td>28.6 ± 0.8</td>
</tr>
</tbody>
</table>

* average of duplicates while the others are triplicates

Table 4.2 Arsenite (AsO$_2^-$) uptake by chloride form of LDH (Initial concentration=2mM)

<table>
<thead>
<tr>
<th>LDH</th>
<th>2mM AsO$_2^-$ uptake (%) as a function of time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4h</td>
</tr>
<tr>
<td>Mg:Al (3:1) Cl$^-$</td>
<td>38.8 ± 2.2</td>
</tr>
<tr>
<td>Mg:Al (2:1) Cl$^-$</td>
<td>19.2 ± 2.7</td>
</tr>
<tr>
<td>Ca:Al (3:1) Cl$^-$</td>
<td>27.7 ± 7.6*</td>
</tr>
<tr>
<td>Ca:Al (2:1) Cl$^-$</td>
<td>48.9 ± 1.5</td>
</tr>
</tbody>
</table>

*average of duplicates while the others are triplicates

Table 4.3 Arsenite (AsO$_2^-$) uptake by chloride form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Mg:Al (Cl$^-$)</th>
<th>d-spacing</th>
<th>Uptake % AsO$_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.051</td>
<td>65.8 ± 5.1</td>
<td>9.4</td>
</tr>
<tr>
<td>3:1</td>
<td>7.770</td>
<td>48.8 ± 1.6</td>
<td>9.1</td>
</tr>
<tr>
<td>2:1</td>
<td>7.609</td>
<td>30.9 ± 3.7</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Fig 4.8 Effect of initial arsenite concentration and equilibration time for \( \text{AsO}_2^- \) uptake by (a) 3:1 and (b) 2:1 chloride forms of hydrotalcite.
Fig 4.9  Effect of initial arsenite concentration and equilibration time for $\text{AsO}_2^-$ uptake by (a) 3:1 and (b) 2:1 chloride forms of hydrocalumite.
Fig 4.10 X-ray diffraction pattern of Mg-Al (3:1)-Cl exchanged with AsO$_2^-$ at different intervals of time.

Fig 4.11 X-ray diffraction patterns of Mg-Al (2:1)-Cl exchanged with AsO$_2^-$ at different intervals of time.
Fig 4.12 X-ray diffraction patterns of Mg-Al (4:1)-Cl exchanged with AsO$_2^-$.

Fig 4.13 X-ray diffraction patterns of Ca-Al (3:1)-Cl exchanged with AsO$_2^-$ at different intervals of time.
Fig 4.14 X-ray diffraction patterns of Ca-Al (2:1)-Cl exchanged with AsO$_2^-$ at different intervals of time.

Fig 4.15 X-ray diffraction patterns of Ca-Al (4:1)-Cl exchanged with AsO$_2^-$
Table 4.4 shows the uptake of arsenite by the nitrate form of hydrotalcite. The difference in d spacing in 4:1, 3:1, and 2:1 is due to difference in number of interlayer species. The 2:1 has higher charge density than 3:1 and 4:1, and therefore requires larger number of large nitrate interlayer anions. Therefore d-spacing increased to avoid repulsion. Due to higher d-spacing in 2:1 than in 4:1 and 3:1 the uptake of arsenite was also higher compared to those of 4:1 and 3:1 nitrate forms of hydrotalcite. The 2:1 nitrate form of hydrotalcite removed 87.5% of arsenite. The anion exchange of nitrate with arsenite was confirmed by the change in d<sub>003</sub> spacing (Figs. 4.16- 4.18). The d<sub>003</sub> spacing decreased after exchange with arsenite due to smaller size of AsO<sub>2</sub><sup>-</sup> than NO<sub>3</sub><sup>-</sup>.

Hydrotalcites have a very high affinity for carbonate anion and it is very difficult to replace them with some other anion. Uptake of arsenite was, therefore, less in case of carbonate form of hydrotalcite, as the exchange of CO<sub>3</sub><sup>2-</sup> with AsO<sub>2</sub><sup>-</sup> was difficult. Table 4.5 shows the uptake of arsenite by carbonate form of hydrotalcite. The uptake of arsenite decreased with an increase in charge density due to the strong electrostatic interaction between positively charged layers and interlayers, and therefore smaller space is available for incoming anion. The exchange occurs mainly on the outer planar surfaces of LDH and at the edges of interlayers containing CO<sub>3</sub><sup>2-</sup>. After exchange with arsenite, the decrease in d<sub>003</sub> spacing is small because the exchange is mainly on the surfaces and at edges (Figs 4.19 to 4.21).
Table 4.4 Arsenite (AsO$_2^-$) uptake by nitrate form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Mg:Al (NO$_3^-$)</th>
<th>d-spacing</th>
<th>Uptake % AsO$_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.010</td>
<td>42 ± 10.5</td>
<td>7.5</td>
</tr>
<tr>
<td>3:1</td>
<td>8.155</td>
<td>52.3 ± 6.8</td>
<td>8.0</td>
</tr>
<tr>
<td>2:1</td>
<td>8.985</td>
<td>87.5 ± 0.7</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 4.5 Arsenite (AsO$_2^-$) uptake by carbonate form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Mg:Al (CO$_3^{2-}$)</th>
<th>d-spacing</th>
<th>Uptake % AsO$_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>7.951</td>
<td>41.7 ± 22.6</td>
<td>8.8</td>
</tr>
<tr>
<td>3:1</td>
<td>7.866</td>
<td>25.6 ± 3.6</td>
<td>8.4</td>
</tr>
<tr>
<td>2:1</td>
<td>7.534</td>
<td>17.4 ± 1.4</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Fig 4.16 X-ray diffraction patterns of Mg-Al (4:1)-NO$_3$ exchanged with AsO$_2^-$.

Fig 4.17 X-ray diffraction patterns of Mg-Al (3:1)-NO$_3$ exchanged with AsO$_2^-$.
Fig 4.18 X-ray diffraction patterns of Mg-Al (2:1)-NO$_3$ exchanged with AsO$_2^-$.  

Fig 4.19 X-ray diffraction patterns of Mg-Al (4:1)-CO$_3$ exchanged with AsO$_2^-$. 
Fig 4.20 X-ray diffraction patterns of Mg-Al (3:1)-CO$_3$ exchanged with AsO$_2^-$.

Fig 4.21 X-ray diffraction patterns of Mg-Al (2:1)-CO$_3$ exchanged with AsO$_2^-$.
Tables 4.6 and 4.7 show the uptake of arsenite by nitrate and chloride forms of hydrocalumites. The uptake of arsenite on Ca-Al-NO$_3$ is greater than on Ca-Al-Cl. This may be due to restricted interlayer space in case of chloride form of hydrocalumites which further affects the uptake of AsO$_2^-$ ions. In case of chloride form of hydrocalumite, d$_{003}$ spacing was unchanged but intensity was reduced (Figs. 4.13 and 4.14) after treatment with 1mM of arsenite solution. In case of nitrate form of hydrocalumite the d$_{003}$ spacing shifted, in general, towards lower values after treatment with arsenite solution (Figs. 4.22 to 4.24) indicating exchange with arsenite. The presence of calcite at about 3.03Å and gibbsite-like phase at about 4.76 to 4.82Å (Figs 4.22-4.24) again suggests a dissolution reaction along with exchange.

The X-ray diffraction (XRD) patterns (Fig. 4.25) show the high crystallinity of LDH synthesized by hydrothermal method and the d$_{003}$ spacing is unchanged after exchange because the exchange is mainly on the surfaces and edges. These results suggest that oxyanion uptake was less in case of the well crystallized, hydrothermally synthesized LDH as compared to that of the poorly crystallized materials (Table 4.8), because it is more difficult to break bonds in the former than in the latter. The LDH synthesized hydrothermally had less surface area due to large crystal size (see SEM pictures later) and therefore, uptake was also less.

The uptake also depends upon the type of interlayer anions. Hydrotalcite and hydrocalumite with same charge density and different interlayer anions showed differences in uptake. In case of hydrotalcite the order of uptake of arsenite was as follows Mg-Al-NO$_3$ > Mg-Al-Cl > Mg-Al-CO$_3$. In case of hydrocalumites the order was Ca-Al-NO$_3$ > Ca-Al –Cl. This is due to larger size of nitrate than chloride as reflected by
d_{003} spacing (Figs. 4.26 and 4.27). Several studies reported that divalent anions are more difficult to replace than monovalent anions verifying arsenite anion uptake results by LDH. Miyata (1983) reported the anion uptake on Mg-Al LDH in the following order: $\text{OH}^-> \text{F}^-> \text{Cl}^-> \text{Br}^-> \text{NO}_3^-> \text{I}^-$ for monovalent anions and $\text{CO}_3^{2-} > \text{SO}_4^{2-}$ for divalent anions and divalent anions are more selective than monovalent anions on LDH.
Table 4.6 Arsenite ($\text{AsO}_2^-$) uptake by chloride form of hydrocalumite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Ca:Al (Cl$^-$)</th>
<th>d-spacing</th>
<th>Uptake % $\text{AsO}_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>7.83</td>
<td>19.8 ± 6.5</td>
<td>10.9</td>
</tr>
<tr>
<td>3:1</td>
<td>7.78</td>
<td>32.8 ± 3.2</td>
<td>11.4</td>
</tr>
<tr>
<td>2:1</td>
<td>7.80</td>
<td>23.5 ± 3.5</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 4.7 Arsenite ($\text{AsO}_2^-$) uptake by nitrate form of hydrocalumite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Ca:Al (NO$_3^-$)</th>
<th>d-spacing</th>
<th>Uptake % $\text{AsO}_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.55</td>
<td>83.6 ± 16.2</td>
<td>10.4</td>
</tr>
<tr>
<td>3:1</td>
<td>8.65</td>
<td>54.5 ± 20.0</td>
<td>10.9</td>
</tr>
<tr>
<td>2:1</td>
<td>8.69</td>
<td>48.3 ± 6.0</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Table 4.8 Arsenite ($\text{AsO}_2^-$) uptake by carbonate form of hydrotalcite at different synthesis conditions (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Carbonate form of LDH</th>
<th>Uptake % $\text{AsO}_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coprecipitation</td>
<td>25.6 ± 3.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>19.3 ± 5.5</td>
<td>9.4</td>
</tr>
</tbody>
</table>
Fig 4.22 X-ray diffraction patterns of Ca-Al (4:1)-NO$_3$ exchanged with AsO$_2^-$

Fig 4.23 X-ray diffraction patterns of Ca-Al (3:1)-NO$_3$ exchanged with AsO$_2^-$
Fig 4.24 X-ray diffraction patterns of Ca-Al (2:1)-NO$_3$ exchanged with AsO$_2^-$

Fig 4.25 X-ray diffraction patterns of Mg-Al (3:1)-CO$_3$-hydrothermal exchanged with AsO$_2^-$
Fig 4.26 Arsenite uptake by hydrotalcite with same charge density (2:1) but different size of anions.

Fig 4.27 Arsenite uptake by hydrocalumites with same charge density (4:1) but different size of anions.
Table 4.9 shows the uptake of arsenite by uncalcined and calcined LDH. The poor exchange ability of uncalcined sample was due to strong interaction of carbonate anions with the hydroxide layer (Fig. 4.28). As mentioned before, calcination process resulted in the destruction of layered structures leading to the formation of amorphous phase of Mg and Al oxides (Fig 4.29). However, when the calcined material was exposed to arsenite solution, the layered structure of hydrotalcite was regenerated with incorporation of AsO$_2^-$ anions from solution (Fig 4.29). Several studies have reported that oxyanion uptake by calcined LDHs was higher than the uncalcined LDH (Goswamee et al., 1998; Lazaridis et al., 2001; Yang et al., 2005). This could be due to increased surface area of calcined products (Carja et al., 2005; Yang et al., 2005) and reformation of LDH with the uptake of oxyanions in question but without much competition from carbonate anions for the interlayers of calcined LDH than in uncalcined LDH (Yang et al., 2005).

In case of hydrotalcite the mechanism for anion exchange is topotactic. It involved breaking up of the electrostatic as well as the hydrogen bonds between the hydroxide layers and the outgoing anion and reformation of these bonds with incoming anions. In case of nitrate and chloride forms of hydrocalumites, the mechanism appeared to be initial exchange followed by dissolution-precipitation.

The XRD patterns of the products obtained from the anion exchange reactions of LDH with arsenite provided some evidence for both topotactic and dissolution-precipitation mechanism depending upon the type of synthetic LDH. In all forms of hydrotalcite the samples showed crystallinity after reaction with arsenite solution which suggests a preservation of the structure proving the topotactic mechanism.
Table 4.9 Arsenite ($\text{AsO}_2^-$) uptake by commercial carbonate form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Commercial carbonate form of LDH</th>
<th>Uptake % $\text{AsO}_2^-$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncalcined</td>
<td>$16.9 \pm 0.8$</td>
<td>9.3</td>
</tr>
<tr>
<td>Calcined</td>
<td>$78.2 \pm 15.6$</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Fig 4.28 X-ray diffraction patterns of commercial uncalcined Mg-Al (3:1)-CO$_3$ exchanged with AsO$_2^-$

Fig 4.29 X-ray diffraction patterns of calcined Mg-Al-CO$_3$ exchanged with AsO$_2^-$
Figures 4.13-4.15 show the products of anion exchange of chloride form of hydrocalumites with arsenite. It is clear from the figure that $d_{003}$ spacing of LDH increased slightly and was broadened (Fig 4.13) suggesting that some topotactic exchange is occurring. However, in case of Ca-Al (2:1) chloride form and Ca-Al-NO$_3$, the sample became amorphous and appearance of calcite peak at 3.03Å (Fig 4.14) and gibbsite peak at 4.76Å to 4.82Å in the XRD patterns after reaction with arsenite (Figs.4.22 -4.24) suggests that underlying mechanism could be initial exchange followed by dissolution-precipitation. Thus the nature of reactions seemed to be dependent upon the chemical composition of LDH.

SEM pictures also provided some evidence for dissolution-precipitation mechanism in case of nitrate form of hydrocalumites after reaction with AsO$_2^-$ . The morphology of the Ca-Al-NO$_3$ was changed after reaction with arsenite suggesting that it reacted with LDH and leading to formation of smaller particles (Figs. 4.30a and 4.30b). However, in case of chloride form of hydrocalumite (Fig 4.31), the change in morphology is not obvious. Hydrotalcite (carbonate form, urea method), on the other hand, did not show any change in morphology after exchange with arsenite solution (Fig 4.32).
Fig. 4.30 (a) SEM image of (3:1) nitrate form of hydrotalcite (untreated)

Fig. 4.30 (b) SEM image of (3:1) nitrate form of hydrotalcite (treated with arsenite)
Fig. 4.31 (a) SEM image of (3:1) chloride form of hydrocalumite (untreated)

Fig. 4.31 (b) SEM image of (3:1) chloride form of hydrocalumite (treated with arsenite)
Fig. 4.32 (a) SEM image of (3:1) carbonate form of hydrotalcite (hydrothermal)(untreated)

Fig. 4.32 (b) SEM image of (3:1) carbonate form of hydrotalcite (treated with arsenite)
4.4 Conclusions

This study showed that hydrotalcites and hydrocalumites can be used for removal of arsenite from solutions. Calcined carbonate form was also effective in removal of arsenite from contaminated water. In case of hydrotalcites the mechanism of uptake was topotactic. However the mechanism of uptake was complex in case of hydrocalumites and dependent on the type of interlayer anion and layer composition. The mechanism of arsenite uptake in calumite involves some topotactic exchange followed by dissolution and precipitation.
References


CHAPTER 5

UPTAKE OF ARSENATE BY SYNTHETIC HYDROTALCITE-TYPE AND HYDROCALUMITE-TYPE LAYERED DOUBLE HYDROXIDES

Abstract

The objectives of this study were to (i) synthesize cost-effective layered double hydroxides (LDH) or anionic clays to remove arsenate from water and (ii) quantify arsenate uptake by LDH and understand the mechanisms of uptake. We synthesized two types of LDH: hydrotalcite and hydrocalumite by coprecipitation at room temperature or higher with different compositions of layers and interlayers. The kinetic study showed that anion exchange process was very fast and apparently attained a steady-state in the range of 8-16 hrs. We achieved 100% and 99.9% removal of arsenate with nitrate form of hydrotalcite and hydrocalumite, respectively. We were also able to remove 50-90% of arsenate by chloride and carbonate forms of hydrotalcite and chloride form of hydrocalumite.

The uptake capacity of LDH synthesized by different methods was also compared. Layered double hydroxides synthesized by co-precipitation method had greater uptake capacity than those synthesized by hydrothermal method because of smaller crystal size in the former. We also observed higher oxyanion uptake with calcined LDH than with commercially available un-calcined carbonate form of LDH. Calcination of LDH produced intermediate non-stoichiometric oxides, which undergo rehydration and regeneration of the structure with the incorporation of these oxyanions.

In the presence of much larger concentrations of other anions, the uptake of arsenate was reduced but it is still selective on LDH. The results of uptake were confirmed by XRD, Raman spectroscopy, and scanning electron microscopy (SEM).
5.1 Introduction

Arsenic is a non-metal and ranks 20th in natural abundance, 14th in sea water, and 12th in human body (Mandal et al., 2002). It is commonly recognized as a toxic and carcinogenic metal compound (Bates et al., 1992; Smith et al., 1992). A long-term exposure to arsenic can cause cancer of skin, kidney, bladder and lung as well as neurological and cardiovascular problems (WHO 1981; Kiping et al., 1997; Jain et al., 2000; Mandal et al., 2002).

Arsenic can exist in four oxidation states: +5, +3, 0 and -3. In natural water the most common forms are inorganic oxyanions of trivalent arsenite and pentavalent arsenate (Brandhuber and Amy, 1998). The most common form of arsenic in surface water is arsenate. Soluble pentavalent or arsenate species are $\text{AsO}_4^{3-}$, $\text{HAsO}_4^{2-}$, $\text{H}_2\text{AsO}_4^-$ and $\text{H}_3\text{AsO}_4$. Arsenic speciation is controlled by two factors: redox potential and pH (Smedley et al., 2002). Under oxidizing conditions, arsenic (V) species dominate with $\text{H}_2\text{AsO}_4^-$ dominating at a pH less than 6.9, while $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$ species dominating at higher pH. The source of arsenic pollution is weathering of naturally occurring minerals of arsenic which solublize in oxidizing environment. An anthropogenic source of arsenic pollution is discharge from various industries such as smelting, petroleum refining, pesticides, herbicides, glass and ceramic manufacturing.

A number of materials such as yttrium carbonate (Wasay et al., 1996), zeolites (Qui et al., 2007), activated carbon (Chuang et al., 2005), iron containing granular activate carbon (Gu et al., 2005), hematite and feldspar (Singh et al., 1996), titania (Pena et al., 2005), activated alumina (Singh et al., 2004), iron oxides (Thirunavukkarasu et al., 2003), zero valent iron (Bang et al., 2005), goethite (Manning et al., 1998), and
lanthanum compounds (Wasay et al., 1996; Tokunaga et al., 1997; Jang et al., 2004) have been used to remove arsenic from water.

Hydrotalcites have been reported to remove arsenic from drinking water, but only investigated on a limited scale by (Bhaumik et al., 2004; Gillman, 2005). There is a need to study this important group of materials in a greater detail for removing arsenate from contaminated water because these materials may be cost-effective compared to other explored materials. The purpose of this study is to synthesize and use hydrotalcite and hydrocalumite with different composition of layers and interlayers to remove arsenate and to understand the mechanism of arsenate uptake.

5.2 Materials and methods

5.2.1 Synthesis of layered double hydroxides

Hydrotalcites having Mg-Al in the layers (Mg$^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2) and chloride, carbonate or nitrate in the interlayers and hydrocalumite with Ca-Al (Ca$^{2+}$/Al$^{3+}$ molar ratios 4, 3, and 2) in the layers and chloride or nitrate in the interlayers were prepared by coprecipitation. One LDH with carbonate in the interlayers and Mg$^{2+}$/Al$^{3+}$ molar ratio of 3 was synthesized by urea method as described in chapter 3.
5.2.2 Uptake of arsenate by layered double hydroxides

5.2.2.1 Kinetic study with chloride intercalated hydrotalcite and hydrocalumite

The uptake experiments were carried out in triplicate by batch equilibration technique. The first set of uptake experiments was conducted with chloride intercalated hydrotalcite and hydrocalumite.

Fifty milligrams of each LDH, was weighed into centrifuge tubes then mixed with 25 ml of sodium hydrogen arsenate solution at a concentration of 1mM or 2 mM. The initial pH of the solution was 7.8. The suspensions were shaken for 4h, 8h, and 16 h on a shaker. The tubes were then centrifuged, to separate solid and solution phases and arsenate concentration was determined in supernatants by atomic absorption spectroscopy (AAS). The solid phases were analyzed by XRD.

A second set of uptake experiments was done with nitrate and carbonate forms of hydrotalcite and nitrate form of hydrocalumite using the same procedure as for the first set of experiments except that the shaking was done for 16h because a steady-state has been achieved by this time.

5.2.2.2 Effect of competitive anions and determination of $K_d$ values.

Another uptake experiment was also carried out in presence of various competing anions. The effect of various competing anions such as Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$ was studied by equilibrating 50mg of each LDH i.e. (chloride and nitrate form of hydrotalcite and chloride form of hydrocalumite) with 25 ml of 1mM of sodium hydrogen arsenate solution containing 50 mM of Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$. These experiments were carried out in triplicate by batch equilibration technique. The suspensions were shaken for 16 h on a shaker. The tubes were then centrifuged, and arsenate uptake was
determined in supernatants by AAS. The distribution coefficient, $K_d$ values were calculated from analytical results using following formula:

$$K_d = \frac{(C_0 - C_i)}{C_i} \times \frac{V}{m}$$

Where $C_0$ and $C_i$ are the initial concentration and concentration after equilibration of arsenate anions, and $V$ is the volume of solution in ml, and $m$ is the mass of hydrotalcite or hydrocalumite used for equilibration.

5.2.3 Characterization of the synthesized product

5.2.3.1 X-ray Diffraction

The X-ray powder diffraction patterns of synthesized LDH were taken with a Scintag diffractometer operated at 35 kV voltage and 30 mA current using CuKα radiation. A step scan of 5° /min was used in the continuous method in a range of 5-40° 2θ.

5.2.3.2 Scanning Electron Microscopy

Some of the samples were characterized by scanning electron microscope (SEM) to determine the particle size and morphology. Scanning electron microscopy was done using a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with very thin carbon using a carbon coater. An accelerating voltage of 5 KV was used for observation with the microscope.

5.2.3.3 Raman Spectroscopy

Some samples were characterized by Raman spectroscopy for identifying the presence of arsenate in the interlayer or on the surface of LDH. Samples were pressed to form pellets and spectra were collected by RS 2000 Raman spectrophotometer.
5.3 Results and Discussion

5.3.1 Powder X-ray diffraction results

Figures 5.1-5.5 show the XRD patterns of various Mg-Al LDHs and Ca-Al LDHs with different composition of layers and interlayers. These figures are the same as figures 4.1-4.5 but given here again for convenience. The XRD patterns for all synthesized samples were characteristics of layered materials with sharp or broad peaks at lower 2θ values and less intense peaks at higher 2θ. Slight shifts were observed in major peaks towards higher 2θ by lowering molar ratio of Mg/Al and Ca/Al (Figs 5.2, 5.3, and 5.5) which also indicates higher charge density and decreased interlayer distance and unit cell parameters except in the case of nitrate forms of LDH. This decrease in interlayer distance could be due to an increase in the electrostatic interaction between positive layers and negative interlayers. In the case of nitrate forms of LDH, the (003) increased because of repulsion of large anions in the interlayers (Figs 5.1 and 5.4).

The XRD patterns of uncalcined and calcined LDH are shown in Fig 5.6. The XRD patterns of calcined LDH clearly showed that the layer structure was completely destroyed.

For an identical hydrotalcite and hydrocalumite the type of anion directly affects the thickness of one layer which can be seen by change of 003 and 006 reflections in the XRD spectra. Temperature of synthesis also affected the thickness of the layer. The LDH synthesized by urea method at 150°C had lower d₀₀₃ value than the LDH synthesized at room temperature (Fig 5.7). This decrease in d₀₀₃ could be attributed to the decrease in water content due to better crystallinity at higher temperature. The figures 5.6 and 5.7 are the same as figures 4.6 and 4.7 but given here again for convenience. For each anionic
LDH synthesized at room temperature, the basal spacing of the LDH increased as follows:

Mg-Al-NO₃ > Mg-Al-Cl > Mg-Al-CO₃ and similarly the basal spacing for hydrocalumite increased as follows: Ca-Al-NO₃ > Ca-Al–Cl
Fig 5.1 X-ray diffraction patterns of Mg-Al-NO3 with different composition of layers.

Fig 5.2 X-ray diffraction patterns of Mg-Al-Cl with different composition of layers.
Fig 5.3 X-ray diffraction patterns of Mg-Al-CO$_3$ with different composition of layers.

Fig 5.4 X-ray diffraction patterns of Ca-Al-NO$_3$ with different composition of layers.
Fig 5.5 X-ray diffraction patterns of Ca-Al-Cl with different composition of layers.

Fig 5.6 X-ray diffraction patterns of commercial uncalcined and calcined carbonate form of hydrotalcite.
Fig 5.7 X-ray diffraction patterns of Mg-Al-CO$_3$ hydrothermal (urea method) vs. coprecipitation.
5.3.2 Arsenate uptake by hydrotalcite-type and hydrocalumite-type LDH: kinetic study of chloride forms

Tables 5.1 and 5.2 show the results of arsenate uptake by the chloride form of hydrotalcite and hydrocalumite (molar ratios of 3 and 2 for Mg/Al and Ca/Al) at two different concentrations and at different intervals of time. The uptake of arsenate was in the range of 37-83% with hydrotalcites and in the range of 95-99% with hydrocalumites. Figures 5.8 and 5.9 show that the uptake of arsenate reached a plateau between 8 to 16 hrs.

The uptake of arsenate was higher in case of 3:1 chloride form of hydrotalcite and hydrocalumites than 2:1 chloride forms of hydrotalcite and hydrocalumite (Tables 5.1 and 5.2). This could be due to the fact that 3:1 contains a lower amount of Al$^{3+}$ compared to 2:1 and therefore net positive charge on the hydroxide layers is lower in 3:1 compared to samples (2:1) with high charge density. The space for incoming anion is larger in case of 3:1 chloride form of LDH than that of 2:1. Table 5.3 shows the uptake of arsenate by 4:1, 3:1 and 2:1 types of Mg:Al(Cl-) LDH. These results show that uptake of arsenate was higher in 3:1 than 4:1 and 2:1. This could be due to the fact that exchange in case of 2:1 sample may be mainly on the external surfaces and, in 3:1 and 4:1 cases it is both on external surfaces and interlayers. The reason why 4:1 shows lower uptake compared to 3:1 is not clear and further studies are needed to understand this aspect. The pH values of the equilibrated solutions are given in Table 5.3 and other tables to give an indication of As species expected. The anion exchange of chloride by arsenate led to little or no change in d$_{003}$ spacing (Figs 5.10-5.12). However the intensity of d$_{003}$ spacing decreased after arsenate exchange with chloride forms of calumites (Figs 5.13-5.15) possibly indicating
a dissolution reaction. However the decrease in intensity for 4:1 LDH is slight after exchange (Fig. 5.15). The presence of gibbsite-like phase (~4.83Å) after reaction in the XRD patterns (Figs. 5.13-5.15) supports a dissolution-precipitation reaction.
Table 5.1  Arsenate ($\text{HAsO}_4^{2-}$) uptake by chloride form of LDHs (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>LDH</th>
<th>1mM HAsO$_4^{2-}$ uptake (%) as a function of time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4h</td>
</tr>
<tr>
<td>Mg:Al (3:1) Cl-</td>
<td>84.8 ± 1.2</td>
</tr>
<tr>
<td>Mg:Al (2:1) Cl-</td>
<td>37.5 ± 3.3</td>
</tr>
<tr>
<td>Ca:Al (3:1) Cl-</td>
<td>61.5 ± 0.8</td>
</tr>
<tr>
<td>Ca:Al (2:1) Cl-</td>
<td>65.5 ± 4.1</td>
</tr>
</tbody>
</table>

Table 5.2  Arsenate ($\text{HAsO}_4^{2-}$) uptake by chloride form of LDHs (Initial concentration=2mM)

<table>
<thead>
<tr>
<th>LDH</th>
<th>2mM HAsO$_4^{2-}$ uptake (%) as a function of time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4h</td>
</tr>
<tr>
<td>Mg:Al (3:1) Cl-</td>
<td>61.4 ± 4.3</td>
</tr>
<tr>
<td>Mg:Al (2:1) Cl-</td>
<td>28.5 ± 2.6</td>
</tr>
<tr>
<td>Ca:Al (3:1) Cl-</td>
<td>55.4 ± 0.8</td>
</tr>
<tr>
<td>Ca:Al (2:1) Cl-</td>
<td>76.8 ± 0.6</td>
</tr>
</tbody>
</table>
Table 5.3 Arsenate (HAsO$_4^{2-}$) uptake by chloride form of hydrotalcite (Initial concentration 1mM)

<table>
<thead>
<tr>
<th>Mg:Al (Cl$^-$)</th>
<th>d-spacing</th>
<th>Uptake % HAsO$_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.051</td>
<td>49.4 ± 1.8</td>
<td>9.1</td>
</tr>
<tr>
<td>3:1</td>
<td>7.770</td>
<td>83.3 ± 2.1</td>
<td>7.6</td>
</tr>
<tr>
<td>2:1</td>
<td>7.609</td>
<td>37.9 ± .0001</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Fig 5.8 Effect of initial arsenate concentration and equilibration time for HAsO$_4^{2-}$ uptake by (a) 3:1 and (b) 2:1 chloride forms of hydrotalcite.
Fig 5.9  Effect of initial arsenate concentration and equilibration time for HAsO$_4^{2-}$ uptake by (a) 3:1 and (b) 2:1 chloride forms of hydrocalumite.
Fig 5.10 X-ray diffraction pattern of Mg-Al (3:1)-Cl exchanged with HAsO$_4^{2-}$ at different intervals of time.

Fig 5.11 X-ray diffraction pattern of Mg-Al (2:1)-Cl exchanged with HAsO$_4^{2-}$ at different intervals of time.
Fig 5.12  X-ray diffraction patterns of Mg-Al (4:1)-Cl exchanged with HAsO$_4^{2-}$.

Fig 5.13  X-ray diffraction patterns of Ca-Al (3:1)-Cl exchanged with HAsO$_4^{2-}$ at different intervals of time.
Fig 5.14 X-ray diffraction patterns of Ca-Al (2:1)-Cl exchanged with HAsO$_4^{2-}$ at different intervals of time.

Fig 5.15 X-ray diffraction patterns of Ca-Al (4:1)-Cl exchanged with HAsO$_4^{2-}$. The peak at 16.3° 2θ indicates an artifact from zero background slide.
Table 5.4 shows the uptake of arsenate by the nitrate form of hydrotalcite. The difference in d spacing in 4:1, 3:1, and 2:1 is due to difference in number of interlayer species. The 2:1 has higher charge density than 3:1 and 4:1 so it requires larger number of large nitrate interlayer anions. Therefore d-spacing increased to avoid repulsion. Due to higher d-spacing in 2:1 than in 4:1 and 3:1 the uptake of arsenate was also higher compared to those of 4:1 and 3:1 nitrate forms of hydrotalcite. The 2:1 nitrate form of hydrotalcite removed 100% of arsenate. The anion exchange of nitrate with arsenate was confirmed by change in $d_{003}$ spacing (Figs 5.16-5.18). The $d_{003}$ spacing decreased after exchange with arsenate due to higher charge on arsenate than in nitrate. This is due to the fact that higher charge of arsenate resulted in increased electrostatic attraction between layers and interlayers and the reduced number of arsenate anions led to lower d-spacing.

Hydrotalcite has a very high affinity for carbonate anion and it is very difficult to replace it with some other anion. So exchange of $\text{CO}_3^{2-}$ with $\text{HAsO}_4^{2-}$ is expected to be difficult. Table 5.5 shows the uptake of arsenate by carbonate form of hydrotalcite. The uptake of arsenate was highest in 2:1. This could be due to the fact that the exchange occurs mainly on the outer planner surfaces of LDH containing $\text{CO}_3^{2-}$. The 2:1 carbonate form has higher charge density than 3:1 and 4:1 and thus the 2:1 has more positive charge on the external surfaces so number of carbonate ions on the external surfaces is more than 3:1 and 4:1. Therefore, more exchange of carbonate by arsenate has taken place in 2:1 case. After exchange with arsenate on external surfaces there is little or no increase in $d_{003}$ spacing (Fig 5.19-5.21).
Table 5.4 Arsenate ($\text{HAsO}_4^{2-}$) uptake by nitrate form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Mg:Al (NO$_3^-$)</th>
<th>d-spacing</th>
<th>Uptake % $\text{HAsO}_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.010</td>
<td>98.7 ± 0.8</td>
<td>9.0</td>
</tr>
<tr>
<td>3:1</td>
<td>8.155</td>
<td>99.3 ± 0.06</td>
<td>8.9</td>
</tr>
<tr>
<td>2:1</td>
<td>8.985</td>
<td>100 ± 0</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Table 5.5 Arsenate ($\text{HAsO}_4^{2-}$) uptake by carbonate form of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Mg:Al (CO$_3^{2-}$)</th>
<th>d-spacing</th>
<th>Uptake % $\text{HAsO}_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>7.951</td>
<td>56.6 ± 3.3</td>
<td>9.1</td>
</tr>
<tr>
<td>3:1</td>
<td>7.866</td>
<td>82.4 ± 3.4</td>
<td>8.9</td>
</tr>
<tr>
<td>2:1</td>
<td>7.534</td>
<td>89.2 ± 1.6</td>
<td>8.9</td>
</tr>
</tbody>
</table>
Fig 5.16 X-ray diffraction patterns of Mg-Al (4:1)-NO$_3$ exchanged with HAsO$_4^{2-}$. The peak at 16.3° 2θ indicates an artifact from zero background slide.

Fig 5.17 X-ray diffraction patterns of Mg-Al (3:1)-NO$_3$ exchanged with HAsO$_4^{2-}$. The peak at 16.3° 2θ indicates an artifact from zero background slide.
Fig 5.18 X-ray diffraction patterns of Mg-Al (2:1)-NO$_3$ exchanged with HAsO$_4^{2-}$.

Fig 5.19 X-ray diffraction patterns of Mg-Al (4:1)-CO$_3$ exchanged with HAsO$_4^{2-}$. 
Fig 5.20 X-ray diffraction patterns of Mg-Al (3:1)-CO$_3$ exchanged with HAsO$_4^{2-}$. The peak at 16.3° 2θ indicates an artifact from zero background slide.

Fig 5.21 X-ray diffraction patterns of Mg-Al (2:1)-CO$_3$ exchanged with HAsO$_4^{2-}$.
Tables 5.6 and 5.7 show the uptake of arsenate by chloride and nitrate forms, respectively of hydrocalumites. There is an almost complete removal of arsenate by these two forms of hydrocalumites. In case of chloride form of hydrocalumite after treatment with 1mM of arsenate, 003 d-spacing shifted towards higher values (Figs 5.13-5.15). In case of nitrate form of hydrocalumite, d_{003} spacing shifted toward lower value and intensity was reduced after treatment with 1mM of arsenate solution (Figs 5.22-5.24). This reduction in intensity may suggest a dissolution reaction. The presence of gibbsite after reaction at about 4.83Å (Figs 5.22-5.24) supports the above proposed mechanism. The presence of 5.4Å peak (Figs 5.22-5.24) indicates an artifact from zero background slide.

The X-ray diffraction (XRD) patterns (fig 5.25) show the high crystallinity of LDH synthesized by hydrothermal method and d_{003} spacing is unchanged after exchange because the exchange is mainly on the surfaces and edges. These results suggest that oxyanion uptake was less in case of the well crystallized hydrothermally synthesized LDH compared to that of the poorly crystallized materials (Table 5.8), because it is more difficult to break bonds in the former than in the latter. The LDH synthesized hydrothermally has less surface area due to large crystal size (see SEM pictures later) and therefore, the uptake was also less.
Table 5.6 Arsenate (HAsO$_4^{2-}$) uptake by chloride form of hydrocalumite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Ca:Al (Cl)</th>
<th>d-spacing</th>
<th>Uptake % HAsO$_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>7.83</td>
<td>93.8 ± 6.3</td>
<td>9.6</td>
</tr>
<tr>
<td>3:1</td>
<td>7.78</td>
<td>95.2 ± 0.28</td>
<td>11.0</td>
</tr>
<tr>
<td>2:1</td>
<td>7.80</td>
<td>99.1 ± 0.04</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 5.7 Arsenate (HAsO$_4^{2-}$) uptake by nitrate form of hydrocalumite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Ca:Al (NO$_3^-$)</th>
<th>d-spacing</th>
<th>Uptake % HAsO$_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>8.55</td>
<td>99.9 ± 0.1</td>
<td>10.8</td>
</tr>
<tr>
<td>3:1</td>
<td>8.65</td>
<td>97.9 ± 0.7</td>
<td>10.8</td>
</tr>
<tr>
<td>2:1</td>
<td>8.69</td>
<td>99 ± 0.8</td>
<td>10.8</td>
</tr>
</tbody>
</table>
Table 5.8 Arsenate (HAsO$_4^{2-}$) uptake by commercial carbonate form of hydrotalcite

(Initial concentration=1 mM)

<table>
<thead>
<tr>
<th>Commercial carbonate form of LDH</th>
<th>Uptake % HAsO$_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coprecipitation</td>
<td>82.4 ± 3.5</td>
<td>8.9</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>9.04 ± 4.9</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Fig 5.22 X-ray diffraction patterns of Ca-Al (4:1)-NO$_3$ exchanged with HAsO$_4^{2-}$.

Fig 5.23 X-ray diffraction patterns of Ca-Al (3:1)-NO$_3$ exchanged with HAsO$_4^{2-}$.
Fig 5.24 X-ray diffraction patterns of Ca-Al (2:1)-NO₃ exchanged with HAsO₄²⁻.

Fig 5.25 X-ray diffraction patterns of Mg-Al (3:1)-CO₃-hydrothermal exchanged with HAsO₄²⁻.
Table 5.9 shows the uptake of arsenate by uncalcined and calcined LDH. The poor exchange ability of uncalcined sample is due to strong interaction of carbonate anions with the hydroxide layer (Fig 5.26). As mentioned before calcination process resulted in the collapse of layered structures and resulted in formation of amorphous phase of Mg and Al oxides (Fig 5.27). However, when the calcined material was exposed to arsenate solution the layered structure of hydrotalcite was regenerated with incorporation of HAsO$_4^{2-}$ anions from solution (fig 5.27). Several studies have reported that oxyanion uptake by calcined LDHs was higher than uncalcined LDH (Goswamee et al., 1998; Lazaridis et al., 2001; Yang et al., 2005). This could be due to increased surface area of calcined products (Carja et al., 2005; Yang et al., 2005) and competition from fewer carbonate anions for the interlayers of calcined LDH than in uncalcined LDH (Yang et al., 2005).

In case of hydrotalcite the mechanism for anion exchange is topotactic. It involved breaking up of electrostatic interactions as well as the hydrogen bonds between the hydroxide layers and the outgoing anion and reformation of these bonds with incoming anions and in case of nitrate form of hydrocalumites the mechanism appears to be dissolution-precipitation.
Table 5.9 Arsenate (HAsO$_4^{2-}$) uptake by commercial carbonate of hydrotalcite (Initial concentration=1mM)

<table>
<thead>
<tr>
<th>Commercial carbonate form of LDH</th>
<th>Uptake % HAsO$_4^{2-}$</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncalcined</td>
<td>24.9 ± 4.3</td>
<td>9.2</td>
</tr>
<tr>
<td>Calcined</td>
<td>99.4 ± 0.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>
Fig 5.26 X-ray diffraction patterns of commercial uncalcined Mg-Al (3:1)-CO$_3$ exchanged with HAsO$_4^{2-}$.

Fig 5.27 X-ray diffraction patterns of calcined Mg-Al-CO$_3$ exchanged with HAsO$_4^{2-}$.
The XRD patterns of products obtained from the anion exchange reactions of LDHs with arsenate provided some evidence for both topotactic and dissolution-precipitation mechanism depending upon the type of synthetic LDH. All forms of hydrotalcite samples showed crystallinity after reaction with arsenate solution which suggests a preservation of the structure proving topotactic mechanism.

Fig 5.13 shows the products of anion exchange of chloride form of hydrocalumites with arsenate. It is clear from the figure that 003 d-spacing of LDH slightly increased and became broadened (Fig 5.12) suggesting that underlying mechanism was topotactic. However in case of Ca-Al (2:1 and 4:1) chloride form (Fig 5.14-5.15) and with Ca-Al- NO₃, the sample became amorphous and appearance of calcite at 3.03Å and gibbsite at 4.82Å in the XRD patterns after reaction with arsenate (Fig 5.22-5.24) suggests that underlying mechanism could be dissolution-precipitation. Thus the nature of reactions seemed to be dependent upon the chemical composition of LDH.

SEM pictures also provided some evidence for dissolution-precipitation mechanism in case of nitrate form of hydrocalumites after reaction with arsenate. The morphologies of the Ca-Al- NO₃ and Ca-Al-Cl changed after reaction with arsenate suggesting that they reacted with LDH leading to formation of smaller particles (Figs 5.28, 5.29). In case of carbonate form of hydrotalcite (Fig 5.30), the morphology did not change after exchange with arsenate solution.
Fig. 5.28 (a) SEM image of (3:1) nitrate form of hydrotalcite (untreated)

Fig. 5.28 (b) SEM image of (3:1) nitrate form of hydrotalcite (treated with arsenate)
Fig. 5.29 (a) SEM image of (3:1) chloride form of hydrocalumite (untreated)

Fig. 5.29 (b) SEM image of (3:1) chloride form of hydrocalumite (treated with arsenate)
Fig. 5.30 (a) SEM image of (3:1) carbonate form of hydrotalcite (urea hydrothermal) (untreated)

Fig. 5.30 (b) SEM image of (3:1) carbonate form of hydrotalcite (treated with arsenate)
Raman spectroscopy also provided evidence of uptake of arsenate by hydrotalcite and hydrocalumite. Fig 5.31 shows the Raman spectra of 2:1 nitrate form of hydrotalcite before and after exchange with arsenate. After exchange, a new band was observed at ~810 cm\(^{-1}\). Fig 5.32 shows the Raman spectra of 4:1 nitrate form of hydrocalumite before and after uptake. A new band showed up ~ 810 cm\(^{-1}\) after uptake of arsenate.
Fig 5.31 Raman spectra of Mg-Al (2:1)-NO$_3$ (a) - as synthesized (b) after exchange with HAsO$_4^{2-}$.

Fig 5.32 Raman spectra of Ca-Al (4:1)-NO$_3$ (a) - as synthesized (b) after exchange with HAsO$_4^{2-}$.
5.3.2.1 Effect of Competitive anions

Tables 5.10-5.12 show the effect of various competing anions such as Cl⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻ on uptake of arsenate by chloride and nitrate forms of hydrotalcite, and chloride form of hydrocalumite. The results indicated that divalent anion had more interfering effect on uptake of arsenate than monovalent anion. Among the divalent anions the CO₃²⁻ had higher effect on arsenate uptake than SO₄²⁻. The interfering effect of competing anions on arsenate uptake by hydrotalcite followed the order: CO₃²⁻ > SO₄²⁻ for divalent anions and NO₃⁻ > Cl⁻ for monovalent anions. In case of hydrocalumite the order was as follows for divalent ion CO₃²⁻ > SO₄²⁻ and for monovalent anion the order was Cl⁻ > NO₃⁻. Higher charge anion had more interfering effect on arsenate uptake than monovalent anion.

Tables 5.13-5.15 show the distribution coefficient after equilibration of hydrotalcite and hydrocalumite with different competing anions using a 1:50 arsenate to competing anion molar ratio. The results indicated that for hydrotalcite and hydrocalumite the highest $K_d$ value is when chloride is a competing anion followed by nitrate. $K_d$ values are less when competing anions are carbonate and sulfate i.e., these two compete more with arsenate in comparison to nitrate and chloride. The higher the $K_d$ value, the greater is the selectivity for the incoming arsenate anion (Tables 5.14-5.16). Thus arsenate anion appears to be selectively taken up by LDH even in the presence of large concentrations of competing anions.
Table 5.10 Effect of addition of foreign anions on the uptake of arsenate by (3:1) nitrate form of hydrotalcite.

<table>
<thead>
<tr>
<th>Anion added</th>
<th>Arsenate removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ alone</td>
<td>99.3</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + Cl-</td>
<td>98</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ - + NO$_3^{-}$</td>
<td>86.1</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>57</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Table 5.11 Effect of addition of foreign anions on the uptake of arsenate by (3:1) chloride form of hydrotalcite.

<table>
<thead>
<tr>
<th>Anion added</th>
<th>Arsenate removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ alone</td>
<td>49.4</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + Cl-</td>
<td>51</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ - + NO$_3^{-}$</td>
<td>47.3</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>20.3</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>16.2</td>
</tr>
</tbody>
</table>
Table 5.12 Effect of addition of foreign anions on the uptake of arsenate by (3:1) chloride form of hydrocalumite.

<table>
<thead>
<tr>
<th>Anion added</th>
<th>Arsenate removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ alone</td>
<td>96.7</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + Cl$^-$</td>
<td>64.7</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + NO$_3^-$</td>
<td>83.8</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>32</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Table 5.13 Effect of competing anions on Kd values for HAsO$_4^{2-}$ with nitrate form of hydrocalumite

<table>
<thead>
<tr>
<th>Anion added</th>
<th>HAsO$_4^{2-}$ Kd (ml/g) ± S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ + Cl$^-$</td>
<td>24357 ± 610</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + NO$_3^-$</td>
<td>2100 ± 564</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>684 ± 196</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>270 ± 9</td>
</tr>
</tbody>
</table>
Table 5.14 Effect of competing anions on Kd values for HAsO$_4^{2-}$ with chloride form of hydrotalcite

<table>
<thead>
<tr>
<th>Anion added</th>
<th>HAsO$_4^{2-}$ $K_d$ (ml/g) ± S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ + Cl$^-$</td>
<td>530 ± 119</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + NO$_3^-$</td>
<td>449 ± 25</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>128 ± 24</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>98 ± 31</td>
</tr>
</tbody>
</table>

Table 5.15 Effect of competing anions on Kd values for HAsO$_4^{2-}$ with chloride form of hydrocalumite

<table>
<thead>
<tr>
<th>Anion added</th>
<th>HAsO$_4^{2-}$ $K_d$ (ml/g) ± S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAsO$_4^{2-}$ + Cl$^-$</td>
<td>975 ± 371</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + NO$_3^-$</td>
<td>2619 ± 398</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>258 ± 184</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$ + CO$_3^{2-}$</td>
<td>79 ± 77</td>
</tr>
</tbody>
</table>
5.4 Conclusions

The present study showed that hydrotalcite and hydrocalumite could be used as effective anion exchangers for removal of arsenate from solutions. Kinetic study showed that 8-16 hrs were sufficient to reach equilibrium. Temperature of synthesis affected the uptake of arsenate. Competing anions such as SO$_4^{2-}$ and CO$_3^{2-}$ reduced arsenate uptake when present in a 50:1 competing anion to arsenate anion molar ratio but the arsenate uptake is still selective on LDH.
References


CHAPTER 6
SUMMARY AND CONCLUSIONS

• Nitrate form of hydrotalcite-type layered double hydroxides removed 100% of arsenate and 87.5% of arsenite; nitrate form of hydrocalumite-type layered double hydroxides removed 99.9% of arsenate and 83.6% of arsenite.

• Chloride forms of hydrocalumite and chloride and carbonate forms of hydrotalcite removed 17-65% of arsenite and 50-90% of arsenate.

• The arsenite and arsenate uptake process showed considerably fast kinetics and reached a steady-state in the range of 8-16 hrs.

• The layered double hydroxides synthesized at room temperature had higher uptake capacities for arsenite and arsenate than those synthesized hydrothermally by urea method due to large surface area of former than latter. The XRD results revealed that LDH synthesized at room temperature showed lower crystallinity than those synthesized at higher temperature by urea method.

• Calcined carbonate form of hydrotalcite was also effective in removal of arsenite and arsenate. The results showed that uptake by commercial carbonate form of hydrotalcite increased after calcination, because calcination resulted in loss of CO$_3^{2-}$ anion due to destruction of layer structure. The calcined product regenerated its original layer structure when exposed to solutions of arsenite and arsenate due to incorporation of these anions.
- Powder XRD patterns and SEM images were obtained for various samples after reaction with arsenite and arsenate solutions to know the mechanism of uptake. The results showed that mechanism of anion exchange was topotactic for all forms of hydrotalcite and in case of hydrocalumite the mechanism appeared to be initial exchange followed by dissolution–precipitation.

- Competing anions reduced arsenate uptake when present in 50:1 competing anion to arsenate anion molar ratio. The results showed that divalent anions had more profound effect on uptake than monovalent anions and that arsenate anion was still selective on LDH.

The results showed that LDH have high uptake capacity for arsenite and arsenate. The results presented here suggest that layered double hydroxides may provide cost effective alternative in treating waste water, drinking water, or ground water containing harmful oxyanions of arsenic.

**Future work**

There is a need to understand the mechanism of uptake of arsenic by hydrocalumite in greater detail. For example, what products/phases are formed after reaction of hydrocalumites with arsenite and arsenate solution? A recrystallization of the formed products at higher temperature may reveal the nature of the amorphous precursors. Uptake experiments will have to be conducted at different pH values to study uptake of different arsenate and arsenite species. Studies will have to be conducted to test whether we can reuse LDH by removing the exchanged arsenite and arsenate oxyanions i.e. test regenerability of spent LDH.