Application of layered double hydroxides for removal of oxyanions: A review

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Abstract

Layered double hydroxides (LDHs) are lamellar mixed hydroxides containing positively charged main layers and undergoing anion exchange chemistry. In recent years, many studies have been devoted to investigating the ability of LDHs to remove harmful oxyanions such as arsenate, chromate, phosphate, etc. from contaminated waters by both surface adsorption and anion exchange of the oxyanions for interlayer anions in the LDH structure. This review article provides an overview of the LDH synthesis methods, the LDH characterization techniques, and the recent advancement that has been achieved in oxyanion removal using LDHs, highlighting areas of consensus and currently unresolved issues. Experimental studies relating to the sorption behaviors of LDHs with various oxyanions, and the kinetic models adopted to explain the adsorption rate of oxyanions from aqueous solution onto LDHs, have been comprehensively reviewed. This review discusses several key factors such as pH, competitive anions, temperature, etc., that influence the oxyanion adsorption on LDHs. The reusability of LDHs is discussed and some mechanistic studies of oxyanion adsorption on LDHs are highlighted. The sorption capacities of LDHs for various oxyanions are also compared with those of other adsorbents. In addition, this review critically identifies the shortcomings in current research on LDHs, such as the common weaknesses in the adopted methodology, discrepancies among reported results and ambiguous conclusions. Possible improvement of LDHs and potential areas for future application of LDHs are also proposed.

Keywords: Layered double hydroxides (LDHs), Hydrotalcite, Oxyanions, Adsorption, Anion Exchange

1. Introduction

Elevated levels of oxyanions have been found in the environment and they can be harmful to both humans and wildlife. In recent decades, a class of anionic clays known as layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTlc) has attracted substantial attention from both industry and academia. Although LDHs exist as naturally occurring minerals, they are also relatively simple and economical to synthesize. The structure of LDHs is based on positively charged brucite-like sheets and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions. LDHs have relatively weak interlayer bonding and, as a consequence, exhibit excellent ability to capture organic and inorganic anions. The most interesting properties of LDHs include large surface area, high anion exchange capacity (2–3 meq/g) that is comparable to those of anion exchange resins, and good thermal stability (Bish, 1980; Cavani et al., 1991; Vaccari, 1998; Das et al., 2004b).

LDHs have been studied for their potential use in a wide range of important areas, i.e. catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical science, and environmental application (Cavani et al., 1991; Newman and Jones, 1998; Rives, 2001; Li and Duan, 2005; Evans and Duan, 2006). LDHs have been applied in catalyzing the production of basic chemicals (Morioka et al., 2001; Tsyganok et al., 2003), catalyzing redox processes (Monzón et al., 1999; Nishimura et al., 2000), and catalyzing acid–base processes (Tichit et al., 1998; Roelofs et al., 2001), with improved activity and improved recuperation of immobilized catalysts (Sels et al., 2001). For applications in photochemistry, photodimerization and photoisomerization of the interlayer anions that occurred in the LDHs could yield useful photoresponsive materials (Shichi et al., 1996; Shimizu et al., 2006). LDHs have also been investigated for their use as electrode for alkaline secondary cells (Jayashree and Vishnu Kamath, 2002; Chen et al., 2003) and nanocomposite polymer electrolytes (Liao and Ye, 2004). In medical applications, LDHs have been potentially used in pharmaceutical formulations (Gardner, 1985) and development of new delivery systems in biomedical science (Rahman et al., 2004). Moreover, LDHs have been used as heat retention additives in plastic films (Evans and Duan, 2006), flame retardants (Shi et al., 2005; Wang et al., 2005), stabilizing agents for polymers (Van Der Ven et al., 2000; Lin et al., 2005), and precursors to magnetic materials (Sugimoto, 1999).

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

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

Overall, this review focuses on the following issues that arise:

- the extent to which the adsorption efficiencies of LDHs can be achieved under specific conditions;

- the recyclability of LDHs that can be attained by various desorption and regeneration methods and the possible ways for recovery of the oxyanions;
- the mechanisms that are responsible for the adsorption and desorption of oxyanions on LDHs;
- the main concerns and suggested solutions with regard to the practical application of LDHs in water and wastewater treatments, e.g. stability of LDHs, physical form of LDHs, separation of LDHs, etc.

The elucidation of the foregoing issues is made on the basis of

- a good understanding of the LDH materials and the adsorption processes;
- a consolidated summary of significant findings/observations/hypotheses reported in previous studies;
- an experimental study on the adsorption of several oxyanions on the LDHs synthesized by the authors.

2. Composition and structure of LDHs

LDHs are a class of two-dimensional nanostructured anionic clays. The structure of LDHs can be described as a cadmium iodide-type layered hydroxide (e.g., brucite, $Mg(OH)_2$), where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been isomorphously replaced by trivalent cations, giving positively charged sheets. The net positive charge is compensated by anions in the interlayer region between the brucite-like sheets. Some hydrogen-bonded water molecules may occupy the free space in this interlayer region (Cavani et al., 1991; Li and Duan, 2005; Evans and Duan, 2006). The structure of LDHs and a typical octahedral unit are shown in Fig. 1. The basal spacing (c') is the total thickness of the brucite-like sheet and the interlayer region. The octahedral units of M^{2+} or M^{3+} (sixfold coordinated to OH^{-}) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding.

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

Different stacking arrangements of the brucite-like sheets have been observed. The brucite-like sheets can be stacked either with two layers per unit cell in hexagonal symmetry (manasseite) or with three layers per unit cell in rhombohedral symmetry (hydrotalcite), or in less symmetrical arrangements (Carrado et al., 1988). In general, LDHs of rhombohedral symmetry have mainly been found. M^{2+} (Mg^{2+}, Fe^{2+}, Co^{2+}, etc.) and M^{3+} (Al^{3+}, Cr^{3+}, Fe^{3+}, etc.) ions that have ionic radius similar to that of Mg^{2+} can be accommodated in the holes of the close-packed configuration of OH groups in the brucite-like sheets to form LDHs. In addition, LDHs containing more than two species of the second cation have been synthesized (Nunan et al., 1989; Kooli et al., 1995). Another class of LDHs, which contains monovalent and trivalent matrix cations such as $[LiAl_2(OH)_6]^+A^- \cdot mH_2O$, has also been prepared (Besserguenev et al., 1997; Nayak et al., 1997; Williams et al., 2004; Kottegoda and Jones, 2005). The charge density and the anion exchange capacity of the LDHs may be controlled by varying the M^{2+}/M^{3+} ratio. The most common anion found in the naturally occurring LDHs is carbonate. In practice, however, a broad spectrum of charge-balancing anions may be incorporated, namely halides, oxyanions, silicates, polyoxometalate anions, complex anions, and organic anions (Newman and Jones, 1998).

3. Synthesis of LDHs

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

The simplest and most commonly used method is coprecipitation. In this method, aqueous solutions of M^{2+} and M^{3+} containing the anion that is to be incorporated into the LDHs are used as precursors, of which Mg and Al are the most frequently used metal precursors. In order to ensure simultaneous precipitation of two or more cations, it is necessary to carry out the synthesis under conditions of supersaturation. There are generally two types of coprecipitation conditions, namely coprecipitation at low supersaturation and coprecipitation at high supersaturation. Coprecipitation at low supersaturation is performed by slow addition of mixed solutions of divalent and trivalent metal salts at the selected ratio into a reactor containing an aqueous solution of the desired interlayer anion. A second solution of an alkali is then added into the reactor simultaneously at such a rate as to maintain the desired pH for coprecipitation of the two metallic salts. In a slight contrast to the former method, coprecipitation at high supersaturation requires the addition of a mixed salt solution to an alkaline solution containing the desired interlayer anion. Coprecipitation at high supersaturation generally gives rise to less crystalline materials compared to those with low supersaturation, due to the formation of a large number of crystallization nuclei. After precipitation at low and high supersaturation, a thermal treatment process is performed to increase the yields and crystallinity of the materials. This is followed by an aging process conducted for a period ranging from a few hours to several days (Cavani et al., 1991; He et al., 2005). In order to ensure the purity of the synthesized LDHs, the use of the decarbonated ultrapure water and the application of vigorous stirring in combination with nitrogen purging in the synthesis process are necessary.

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

A number of studies have reported the synthesis of LDHs using the urea hydrolysis method (Costantino et al., 1998; Ogawa and Kaiho, 2002; Oh et al., 2002). Urea has a few unique properties such as its weak brǿnsted base characteristic, high solubility in water, and its hydrolysis rate that can be easily controlled, making it an attractive agent to precipitate several metal ions as hydroxides or as insoluble salts when in the presence of a suitable anion (Vogel, 1989). The optimum conditions to prepare the LDHs with a good crystal quality in a relatively short time using this method have been suggested to involve dissolving solid urea in a 0.5 M solution of the chosen metal chlorides to give a urea/metal ion molar ratio of 3.3. The compounds prepared using this method display homogeneous sizes and platelet-like primary particles with well-defined hexagonal shapes, which may be very interesting from the viewpoint of nanotechnology since LDHs offer nano-size two-dimensional spaces for the creation of functional materials (Costantino et al., 1998).

LDHs can be also prepared by the ion exchange method. This method is useful when the coprecipitation method is inapplicable, e.g. when the divalent or trivalent metal cations or the anions involved are unstable in the alkaline solution, or when the direct reaction between the metal ions and the guest anions is more favorable. In this method, the guests are exchanged with the anions present in the interlayer regions of the LDHs to produce specific anion-pillared LDHs (Morel-Desrosiers et al., 2003).

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

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

Besides the aforementioned methods, other reported synthesis methods of LDHs include the secondary intercalation method (an intercalation method involving dissolution and the re-coprecipitation method), salt-oxide method, surface synthesis, template synthesis, and others (He et al., 2005).

4. Characterization of LDHs

A wide range of analytical techniques have been used to characterize LDHs. The routine analyses that are most frequently used are powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. Other routine analyses include thermogravimetry (TG), differential scanning calorimetry (DSC), differential thermal analysis (DTA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Among the specific characterization techniques are electron spin resonance (ESR), nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), Mössbauer spectroscopy, UV/VIS spectroscopy, neutron scattering, etc.

X-ray patterns generated by PXRD are normally obtained using randomly oriented powdered samples. The typical X-ray patterns of LDHs, as shown in Fig. 2, contain sharp basal ($00l$) reflections at low 2θ values corresponding to successive orders of basal spacing c'. On the other hand, relatively weak non-basal reflections are observed at higher values of 2θ. The true c value is a multiple of c' and depends on the layer stacking sequence. The interlayer spacing observed in Fig. 1 is the difference between basal spacing c' and the brucite-like sheet thickness of about 4.8 Å. The interlayer spacing is always dependent on the size and orientation of the charge-balancing anion. The ratio M^{2+}/M^{3+} of the LDHs may be deduced from the parameter a of the unit cell, which is calculated by the formula $a = 2d_{110}$, where d_{110} is the d-spacing of the 110 reflection. The measurement of d_{110}, together with the elemental analysis techniques, allows the prediction of an approximate chemical formula for the LDHs (Cavani et al., 1991;

Newman and Jones, 1998).

FTIR spectroscopy is another useful tool for the characterization of LDHs, involving the vibrations in the octahedral lattice, the hydroxyl groups and the interlayer anions. These methods can be used to identify the presence of the charge-balancing anion in the interlayer, the type of bonds formed by the anions, and their orientations. For example, the absorption at 3500–3600cm^{-1} in the IR spectra of all LDHs is attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer (Cavani et al., 1991). The bending vibration of the interlayer water ($\delta_{\mathrm{H_2O}}$) occurs at 1600–1650cm^{-1}, giving a characteristic peak rarely overlapped by others. For common inorganic anions, the peaks at 1350-1380 (v_3), 850-880 (v_2), and 670-690 (v_4) cm^{-1} are indicative of $\mathrm{CO_3^{2-}}$. The case for $\mathrm{NO_3^-}$ is similar, with v_3 at ~1380, v_2 at ~830, and v_3 at 720–750cm^{-1}. $\mathrm{SO_4^{2-}}$ and $\mathrm{ClO_4^-}$ have IR active v_3 (at ~1100 cm^{-1}) and v_3 (at ~740cm^{-1}) modes, respectively. Raman spectroscopy can be seen as complementary to infrared spectroscopy, and both are often used together to characterize LDHs. The major difference between these two techniques is that Raman spectroscopy depends on the changes in polarizability of molecules, whereas infrared spectroscopy depends on the changes in dipole moments of molecules (Frost, 1996).

The thermal properties of the LDHs are commonly studied using TG, DSC, and DTA, while the morphologies of the LDHs are usually observed through SEM and TEM. TEM image as illustrated in Fig. 3 shows that the LDHs are smooth, well-shaped in hexagonal form, and overlapping crystals. For most transition metal ions that have unpaired electrons, the corresponding LDHs can show their own ESR signals. Several transition metal-containing LDHs have been examined by ESR spectroscopy, some investigating the effect of metal substitution in LDHs (Velu et al., 1999a), the thermal composition of LDHs (Ukrainczyk et al., 1994; Moujahid et al., 2002), and the arrangement of anions in the interlayer region (Auerbach et al., 2004). NMR spectroscopy has been used to study the protons with very different mobilities in LDHs, monitor the decomposition process of LDHs, examine the dynamic and structural behavior of interlayer and externally adsorbed anions, and identify the coordination of metal cations in LDHs (Auerbach et al., 2004).

EXAFS spectroscopy provides powerful means for assessing the local ordering of the cations in the brucite-like sheet (Intissar et al., 2002) and the local ordering of the anions in the interlayer region of LDHs (Evans and Slade, 2005). XANES spectroscopy has been proposed by Moggridge et al. (1994) as a potential analytical technique for determining the orientation of organic guests in the interlayer regions of LDHs. Another specific technique known as Mössbauer spectroscopy has been applied to a range of Fe-containing LDHs, specifically examining the difference in the Fe^{3+} local environment between two types of LDHs and studying the reduction reaction of LDH-derived MgFe- and MgFeAl-oxides (Auerbach et al., 2004). A number of studies have reported on the use of UV/VIS spectroscopy in the characterization of LDHs, e.g. Roussel et al. (2001) used UV/VIS spectroscopy to examine the formation of ZnCr–Cl-LDHs, while Velu et al. (1999a) utilized UV/VIS spectroscopy to investigate the spectral changes with Mn loading in Mn-containing MgAl-LDHs. Neutron scattering has been used by Kagunya et al. (1998) to investigate the vibrational modes of LDHs and the properties of water adsorbed on LDHs.

Other physicochemical methods include elemental analysis, CHN analysis, N2 adsorption–desorption study (surface area and porosity analysis), and photon correlation spectroscopy. Very little works have reported on the pH_{pzc} (pH of point of zero charge) and the acid buffer capacity of LDHs. A few published pH_{pzc} values of LDHs have been shown in Table 1. One suggestion for future research using LDHs as adsorbents is to determine pH_{pzc} and acid buffer capacity because they are fundamentally important properties used in explaining the interaction of solid surfaces with aqueous solutions and solutes.

5. Absorption of oxy anions on LDHs

In addition to the large surface area and high anion exchange capacity of LDHs, their flexible interlayer region that is accessible to various anionic species as well as polar molecular species is another important feature promising their high removal efficiencies of contaminants. In general, three different mechanisms have been proposed to control the removal of contaminants from aqueous medium to the LDHs, namely surface adsorption, interlayer anion exchange, and reconstruction of calcined LDH precursors by the memory effect (Li and Duan, 2005). The surface adsorption involves the adhesion of the contaminants to the surface of LDHs, thus allowing the formation of a molecular or atomic film. The anion exchange process of LDHs is mainly influenced by the charge-balancing anions in the interlayer and the layer charge density. The memory effect of LDHs will be discussed in greater detail in a subsequent section since it is one of their most attractive features as an adsorbent. In the past few years, many reports on adsorption of various contaminants on LDHs have been published. The contaminants include oxyanions (Kang et al., 1999; Toraishi et al., 2002; Zhang and Reardon, 2003; Wang et al., 2006b; Yang et al., 2006; Ay et al., 2007), monoatomic anions (Liu et al., 2006a; Lv et al., 2006a, b; Paredes et al., 2006), cations (Lehmann et al., 1999; Seida et al., 2001; Lazaridis, 2003), organics (Zhu et al., 2005; Bruna et al., 2006; Li et al., 2006), and gas (Cantu et al., 2005; Ritter et al., 2005).

Thus far, the oxyanions investigated are arsenite (H_3AsO_3 or $H_2AsO_3^-$), arsenate ($HAsO_4^{2-}$ or AsO_4^{3-}), chromate (CrO_4^{2-} or $Cr_2O_7^{2-}$), phosphate (PO_4^{3-}), selenite ($HSeO_3^-$ or SeO_3^{2-}), selenate ($HSeO_4^-$ or SeO_4^{2-}), borate (BO_3^{3-}), nitrate (NO_3^-), perrhenate (ReO_4^-), pertechnetate (TcO_4^-), iodate (IO_3^-), molybdate (MoO_4^{2-}), and vanadate (VO_4^{3-}). Table 2 shows the ionic radius of various oxyanions. The ionic radius of the oxyanions listed falls in the range of 0.19–0.26 nm. The ion exchange would reach its maximum when the interlayer region is large enough for the oxyanions to fit into the region for exchange process. The list of oxyanions which have been investigated for their adsorption characteristics with various LDHs is presented in Table 3.

5.1. Adsorption isotherms and adsorption capacities

Adsorption isotherm is pivotal to the design of adsorption systems because it describes how adsorbates interact with adsorbents and this information is essential in optimizing the use of adsorbents. Table 4 summarizes the reported adsorption capacities of LDHs for various oxyanions in the single-oxyanion aqueous systems. The affinities of LDHs for oxyanions can be generally grouped into the following ranges: 0.1–87.5 mg/g LDHs for arsenite (As(III)); 5–615 mg/g LDHs for arsenate (As(V)); 9–160mg/g LDHs for chromate (Cr(VI)); 7.3–81.6mg/g LDHs for phosphate (as P); 29–270mg/g LDHs for selenite (Se(IV)); 14–20mg/g LDHs for borate (as B); and 2.3–4.6 mg/g LDHs for nitrate (as N). The common adsorption isotherms employed to represent equilibrium LDHs–oxyanion adsorption data follow the order Langmuir > Freundlich > modified Langmuir > Redlich-Peterson ~Sips. To the best knowledge of the authors, as yet no adsorption system has reported on the incorporation of surface complexation models for describing the equilibrium oxyanion adsorption on LDHs. One of the advantages of these models over the adsorption isotherm equations is their ability to describe the adsorption as a function of solution pH. Examples of the surface complexation models that may be applied to the LDH adsorption system in the future study include constant capacitance model (Stumm et al., 1980), diffuse layer model, and triple layer model (Davis et al., 1978). Equilibrium speciation models such as MINTEQ, MINTEQA2, SOILCHEM, and HYDRAQL that incorporate surface complexation models could also be used to predict the chemical reactions in the LDH system.

It is also evident from Table 4 that the oxyanion adsorption on LDHs is strongly influenced by the calcination process during LDH synthesis. For example, the adsorption of As(V) increases from 105 to 615 mg/g when LDHs are calcined (LDHs dosage = 1g/L) (Lazaridis et al., 2002; Kiso et al., 2005). For Cr(VI), the adsorption capacities of the calcined LDHs (LDHs dosage ranging from 1 to 10 g/L) are generally reported as more than 50mg/g (Goswamee et al., 1998; Lazaridis et al., 2001; Lazaridis and Asouhidou, 2003; Martinez-Gallegos et al., 2004; Ye et al., 2004; Alvarez-Ayuso and Nugteren, 2005), whereas the Cr(VI) adsorption capacities of the uncalcined LDHs (LDHs dosage ranging from 1 to 4 g/L) are usually reported as less than 25 mg/g (Houri et al., 1998, 1999; Manju et al., 1999; Lazaridis et al., 2004; Terry, 2004; Alvarez-Ayuso and Nugteren, 2005). In the case of PO_4^{3-} adsorption on LDHs, the calcined LDHs also show generally higher adsorption capacities (34–82 mg/g, except one report) than the uncalcined LDHs (29–47 mg/g). The greater adsorption capacities of the calcined LDHs may be attributed to their larger surface areas of 198–287 m^2/g compared to 5–84 m^2/g for the uncalcined LDHs.

5.2. Adsorption kinetics and diffusion-controlled models

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

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

The studies investigating PO_4^{3-} and Se(IV) adsorption have shown that 70% of PO_4^{3-} was adsorbed by calcined LDHs within 1 d and the adsorption reached equilibrium only after 3 d (Chitrakar et al., 2005), whereas Se(IV) adsorption by uncalcined LDHs was a rapid process, and the adsorption equilibrium time increased with the Se(IV) loading (You et al., 2001a). The adsorption of boron on LDHs was relatively fast initially and then saturation was gradually reached after a few hours (Ferreira et al., 2006; Ay et al., 2007).

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

Among the models used to analyze the experimental results of oxyanion adsorption by LDHs, first-order kinetics or pseudo-first-order-kinetics is the most widely used (Table 4). Besides these models, diffusion-controlled models such as homogeneous diffusion model (HDM) and shrinking core model (SCM) have been used by Lazaridis et al. (2004) to describe Cr(VI) adsorption and desorption kinetics on LDHs. The classical homogeneous surface diffusion model (HSDM) and bidisperse pore model (BPM) have been utilized by Yang et al. (2006) to describe the adsorption kinetics of As(V) on LDHs. When HSDM is used to fit the experimental kinetic data, the estimated diffusivity values are dependent on the particle size. On the other hand, when BPM is applied to the same data, it predicts an intracrystalline diffusivity, which is invariable with the particle size.

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

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

5.3. Factors affecting adsorption of oxyanions on LDHs

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

5.3.1. pH

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

The As(V) adsorption on uncalcined chloride-Li–Al LDHs has been reported as sensitive to changes in pH between 4 and 7 (Liu et al., 2006b) whereas As(V) and Se(IV) adsorption on uncalcined Mg–Al LDHs could be sensitive to changes in a wider pH range of 2–11 (Yang et al., 2005). In another study carried out by the authors (unpublished), As(V) adsorption on nitrate-Mg–Al LDHs and commercial Mg–Al LDHs has shown to reduce with pH in the pH range of 7–12 and 5–12, respectively.

For Cr(VI) adsorption on uncalcined Mg–Al LDHs, a few studies have discovered that high adsorption occurred at about pH 2 (Manju et al., 1999; Terry, 2004), whereas low adsorption observed at pH values higher or lower than 2 (Terry, 2004). However, another study carried out on Cr(VI) has reported that high Cr(VI) adsorption by uncalcined carbonate-Mg–Al LDHs was favored at pH 6 (Lazaridis et al., 2004). The decline of Cr(VI) adsorption by LDHs with increasing pH was found to be independent of Cr(VI) speciation (Das et al., 2004a, b).

PO_4^{3-} removal by LDHs has been reported to reach a maximum at pH 5 by Das et al. (2006) and pH 7–9 by others (Kameda et al., 2002; Chitrakar et al., 2005). The removal of PO_4^{3-} by LDHs was also studied from the viewpoint of the pH buffering effect by Seida and Nakano (2001, 2002). They revealed that the pH buffering effect of LDHs worked effectively to enhance the PO_4^{3-} removal through dissolution–coagulation and/or dissolution–precipitation process.

A significant Se(IV) adsorption by uncalcined Mg–Fe LDHs was observed even at $pH \geqslant pH_{pzc}$, which indicated that the interaction between the surface sites and Se(IV) oxyanions was not necessarily of the electrostatic type alone; rather it was a combined effect of both chemical and electrostatic in nature (Das et al., 2002). The chemical interaction might proceed through the formation of monodentate or multidentate ligands with the hydroxyl surface. Two different phenomena were discovered for the pH influence on NO_3^- adsorption by uncalcined LDHs: (i) adsorption was nearly constant over a pH range between 5 and 10 (Tezuka et al., 2004b); and (ii) adsorption reached a maximum at pH 8, with low adsorption in the regions outside pH 6–9 (Tezuka et al., 2005). The adsorption of boron on uncalcined Mg–Al and Mg–Fe LDHs was pH independent according to Ferreira et al. (2006).

The discrepancies on the reported pH influences on oxyanion adsorption may be due to several reasons. One important reason is improper pH control throughout the sorption equilibration period, and another reason is pH adjustment, whereby complementary anions (Cl^-, NO_3^-, and SO_4^{2-}) of the added acid may influence the adsorption of oxyanions of interest, especially when pH has to be adjusted to less than 5. For example, to adjust pH to 3 from the initial pH 8 for LDHs, one would have to introduce at least 10^{-3} M of the complementary anions of the acid added; a greater amount would be added in most cases to overcome the acid-buffering capacity of LDHs. The interference arising from sorption competition might not have been taken into consideration by some of the previous investigators when they reported their results. In addition, some of the reported adsorption studies using LDHs did not indicate clearly whether the pH values shown were initial pH or the equilibrium pH, and whether pH was maintained throughout the sorption equilibration period.

5.3.2. Competitive anions

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

The effect of competing anions on As(III) adsorption by LDHs was found to reduce in the order $\mathrm{HPO_4^{2-}}$ > $\mathrm{SO_4^{2-}}$ > $\mathrm{CO_3^{2-}}$ > $\mathrm{F^-}$ > $\mathrm{Cl^-}$ > $\mathrm{Br^-}$ > $\mathrm{NO_3^-}$ (You et al., 2001b), while the interfering effects of competing anions on As(V) adsorption by LDHs were reported to follow the order $\mathrm{HCO_3^-}$ > $\mathrm{HPO_4^{2-}}$ > $\mathrm{SO_4^{2-}}$ > $\mathrm{Cl^-}$ (Kiso et al., 2005) and $\mathrm{HPO_4^{2-}}$ > ($\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$) > $\mathrm{SO_4^{2-}}$ > $\mathrm{NO_3^-}$ (Yang et al., 2005). Yang et al. (2005) observed that the competing ions had stronger effect on the As(V) adsorption on the uncalcined LDHs than on the calcined LDHs. For Se(IV) adsorption on uncalcined chloride-Mg–Al LDHs, the effect of competing anions was reported to follow the order $\mathrm{HPO_4^{2-}}$ > $\mathrm{SO_4^{2-}}$ > $\mathrm{CO_3^{2-}}$ > $\mathrm{NO_3^-}$ (You et al., 2001a; Yang et al., 2005). The adsorption behavior of Cr(VI) in the presence of various competing anions has also been studied (Goswamee et al., 1998; Das et al., 2004a). For example, the amount of Cr(VI) released from LDHs by different competing anions followed the order $\mathrm{CO_3^{2-}}$ > $\mathrm{Cl^-}$ > water (Goswamee et al., 1998). In the $\mathrm{PO_4^{3-}}$ adsorption by LDHs, the divalent anions were observed to have a profound interfering effect compared to the monovalent anions (Das et al., 2006).

A few studies have been carried out to investigate the effect of seawater matrix on the oxyanion adsorption by LDHs (Tezuka et al., 2004a, b; Chitrakar et al., 2005). The results showed that the calcined Mg–Mn LDHs and the uncalcined Ni–Fe LDHs had remarkably high selectivity for the adsorption of $\mathrm{PO_4^{3-}}$ (Chitrakar et al., 2005) and $\mathrm{NO_3^-}$ (Tezuka et al., 2004b, 2005) despite the existence of overwhelming $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$, and $\mathrm{CO_3^{2-}}$ in the seawater.

In general, it could be concluded that the anions of higher valence have a more significant interfering effect than the monovalent anions in the oxyanion adsorption by LDHs. Among the divalent anions, $\mathrm{HPO_4^{2-}}$ appears to be the most competitive anion that retards the adsorption of other oxyanions by LDHs. Unfortunately, most of the studies investigating the effect of competing anions on oxyanion adsorption by LDHs have not reported the pH of the system; thus, the speciation of the competing species that existed in the sorption system is not clear.

5.3.3. Dosage of adsorbent

Applying an optimum dosage of suitable adsorbent for adsorbate removal in a batch adsorption system is crucial for its cost-effective application. A dose of 2 g/L calcined Mg–Al LDHs was reported to be sufficient to reach the maximum percentage removal (99.5%) for Cr(VI) concentrations in the range of 57–239 mg/L, while for the higher concentrations of Cr(VI) (351 and 448 mg/L) a dose of 5 g/L was required to reach a maximum percentage removal of 97.5% (Alvarez-Ayuso and Nugteren, 2005). In another study, at least 4 g/L of uncalcined Mg–Al LDHs was found to be required for a maximum Cr(VI) removal of 96% from an initial concentration of 5 and 20 mg/L (Terry, 2004). The effect of LDHs dosage on boron adsorption has also been investigated (Ferreira et al., 2006; Ay et al., 2007). The amount of boron adsorbed from an initial concentration of 18 mg/L reached a maximum adsorption at around 92% when 2.5 g/L uncalcined Mg–Al LDHs was used (Ferreira et al., 2006). At a high initial boron concentration of 250 mg/L, the maximum adsorption (> 95%) was achieved at a rather high dose of 12 g/L uncalcined nitrate-Mg–Al LDHs (Ay et al., 2007).

5.3.4. Temperature

A change in temperature will change the equilibrium capacity of the adsorbent for particular adsorbate. Usually, the adsorbate uptake decreases with increasing temperature due to the exothermic nature of the simple adsorption reaction. The As(V) adsorption on both calcined and uncalcined LDHs was reported as an exothermic process (Yang et al., 2005). Das et al. (2006) observed that the percentage of $\mathrm{PO_4^{3-}}$ adsorption by calcined Mg–Al LDHs decreased with increasing temperature from 30 to 60˚C. The negative value of ΔH° obtained confirmed the exothermic nature of adsorption. The positive value of ΔS° reflected the affinity of LDHs toward $\mathrm{PO_4^{3-}}$ in aqueous medium and suggested some structural changes in the adsorbate and adsorbent. In the case of Se(IV) removal by uncalcined Mg–Fe LDHs, the adsorption process was also observed as exothermic (Das et al., 2002).

However, a number of studies have reported that the adsorption of oxyanions by LDHs appeared to be an endothermic process (Das et al., 2004a; Chitrakar et al., 2005; Tezuka et al., 2005; Yang et al., 2005). Examples of reported endothermic processes are adsorption of Se(IV) on calcined carbonate-Mg–Al LDHs (Yang et al., 2005), PO_4^{3-} adsorption on calcined Mg–Mn LDHs (Chitrakar et al., 2005), and NO_3^- adsorption on uncalcined Ni–Fe LDHs (Tezuka et al., 2005). The endothermic nature could be due to increased reactivity of the surface sites with temperature (Das et al., 2004a). However, it was unclear whether the observed endothermic adsorption processes could have been masked by the increased rate of intraparticle diffusion of oxyanions into the pores of LDHs at higher temperatures that gave rise to the observed increase in their adsorption.

Others have reported an insignificant influence of temperature on the oxyanion adsorption by LDHs. For example, Cr(VI) adsorption by the uncalcined Mg–Al LDHs (Terry, 2004) and Se(IV) adsorption by the uncalcined carbonate-Mg–Al LDHs (Yang et al., 2005) have been reported as temperature-independent.

5.3.5. Nature of precursor metals and crystallinity of LDHs

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

According to Wang and Gao (2006), the adsorption of on TcO_4^- uncalcined LDHs was correlated with the basal spacing d_{003} of the materials, which decreased with the radii of both divalent and trivalent cations. The adsorption seemed to take place at the edge sites of LDH layers, and it reached a maximum when the layer spacing was just large enough for a TcO_4^- to fit into a cage space among three adjacent octahedra of metal hydroxides at the edge. Moreover, the adsorption of TcO_4^- also increased with the crystallinity of the materials. For a given choice of metal cations and interlayer anions, the best crystalline LDH phase was generally obtained with an M^{2+}/M^{3+} ratio of 3:1. The results reported by Wang and Gao (2006) indeed help to establish a general structure–property relationship that will guide engineering LDH materials for removal of a specific oxyanion.

5.3.6. Layer charge and interlayer anion charge

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

A number of publications have reported the possibility of synthesizing LDHs containing tetravalent cations (Bhattacharyya et al., 1997; Velu et al., 1997, 1998, 1999b, c, 2000; Tichit et al., 2002). In particular, incorporation of Zr^{4+} into LDH layers and the adsorption of Cr(VI) and Se(IV) on Zr^{4+}-incorporated LDHs have been investigated by Das et al. (2004b). They found that Zr^{4+}-incorporated LDHs increased the adsorption capacity by up to 20%. Nevertheless, others have suggested that the Zr^{4+} ions may not actually be incorporated in the LDH layers in these materials and that they are in fact mixed phases (Intissar et al., 2003, 2004). These controversial findings highlight the needs for a comprehensive investigation of the material structure and the corresponding sorption mechanisms. For example, XANES and Mössbauer spectroscopies could be used to verify the incorporation of tetravalent cations into the LDH structure.

The charge and species of the interlayer anion can also affect the adsorption of guest oxyanions. Prasanna et al. (2006) discovered that carbonate-Ni–Fe LDHs did not exhibit any Cr(VI) adsorption compared to nitrate-Ni–Fe LDHs. This could be due to the strong electrostatic forces of CO_3^{2-} attraction to the host lattice, or formation of prismatic interlayer sites that strongly accommodate CO_3^{2-} ions with their planes parallel to the layers.

5.3.7. Calcination and memory effect

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

Numerous studies have reported that oxyanion adsorption by calcined LDHs was considerably higher than the adsorption by uncalcined LDHs (Goswamee et al., 1998; Lazaridis et al., 2001, 2002; Alvarez-Ayuso and Nugteren, 2005; Carja et al., 2005; Yang et al., 2005). The differences in behavior between calcined and uncalcined LDHs may be linked to several reasons: (i) increased surface area of the calcined products (Carja et al., 2005; Yang et al., 2005); (ii) increased porosity as a result of the calcination process (Lazaridis et al., 2001; Carja et al., 2005); and (iii) fewer carbonate anions in the interlayer of the calcined LDHs than in the uncalcined LDHs (Yang et al., 2005).

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

5.3.8. Particle size

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

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

5.4. *Desorption, regeneration and recovery*

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

5.4.1. Desorption

Various alkaline solutions and salt solutions or the mixture of these solutions have been successfully used to desorb oxyanion-loaded LDHs. More than 85% of As(III) and Cr(VI) can be desorbed from the uncalcined carbonate-LDHs using 0.1 M NaOH (Manju et al., 1999; Manju and Anirudhan, 2000). The desorption of As(V) and Se(IV) was dependent on the anion species and their concentrations in the desorbing solutions (Yang et al., 2005). The abilities of various anions to desorb As(V) from calcined Mg–Al LDHs were reported to follow the order $\mathrm{HPO_4^{2-}}$ > $\mathrm{SO_4^{2-}}$ > carbonate > $\mathrm{NO_3^-}$, while the order was $\mathrm{SO_4^{2-}}$ > $\mathrm{HPO_4^{2-}}$ > carbonate > $\mathrm{NO_3^-}$ for Se(IV) desorption, which was consistent with their competitiveness in the adsorption by LDHs. The adsorbed Se(IV) was found to be desorbed completely from uncalcined chloride-Mg–Al LDHs with aqueous carbonate species (You et al., 2001a). The effective desorption of PO_4^{3-} from the LDHs could be achieved using a mixed solution of NaCl and NaOH (Chitrakar et al., 2005; Kuzawa et al., 2006), and a good PO_4^{3-} sorption has been exhibited even after seven cycles of the adsorption/desorption (Chitrakar et al., 2005).

5.4.2. Regeneration

A number of studies have shown that oxyanion-loaded LDHs could be regenerated with chloride and carbonate solutions or with subsequent calcination (Shin et al., 1996; Kovanda et al., 1999; Lazaridis et al., 2004; Bhaumik et al., 2005; Peng et al., 2005; Kuzawa et al., 2006). Lazaridis et al. (2004) showed that Cr(VI)-loaded uncalcined LDHs could be fully regenerated by Na_2CO_3 in ~20min and that these regenerated LDHs exhibited consistent adsorption capacity over 10 cycles of adsorption and desorption. As(V)-loaded Mg–Al LDHs can also be regenerated by the carbonate solution (Peng et al., 2005). Successful regeneration of LDHs with chloride solutions has been demonstrated by Bhaumik et al. (2005) and Kuzawa et al. (2006). Kuzawa et al. (2006) reported that PO_4^{3-}-loaded LDHs were effectively regenerated with $MgCl_2$ solution and the adsorption capacity after 10 regenerations was 60% of the initial one.

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

5.4.3. Recovery of adsorbates

Thus far only limited research works have reported on the recovery of oxyanions such as As(V), PO_4^{3-} and Cr(VI) from spent LDHs (Gillman, 2006; Kuzawa et al., 2006; Wang et al., 2006b). Gillman (2006) reported that the minute amount of As in the As-loaded LDHs could be easily recovered by saturating As-loaded LDHs with phosphate, in order to convert them into valuable phosphatic fertilizers. Kuzawa et al. (2006) proposed a scheme whereby the desorbed PO_4^{3-} in the spent desorption solution could be recovered as calcium phosphate precipitate by addition of

$CaCl_2$, and the remaining spent desorption solution could also be reused after supplementing additional NaOH (Fig. 4).

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

5.5. Mechanistic studies

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

For example, Liu et al. (2006b) deduced from the EXAFS analysis that the superior As(V) sorption by chloride-Li–Al LDHs was mainly resulted from the additional positive charge brought by the occupation of the Li cations in the vacant octahedral holes within $Al(OH)_3$, which transformed the surface of $Al(OH)_3$ layers into active sorption sites. Another example is the application of Raman spectroscopy in identifying the intercalation of PO_4^{3-} species into the uncalcined LDHs, and exploring the pH effect on the PO_4^{3-} intercalation into the LDHs (Frost et al., 2006).

Recently, Wang et al. (2006b) developed a mechanistic model to describe the adsorption and desorption of Cr(VI) on/from chloride-Li–Al LDHs (Fig. 5) in four steps:

(1) In Step 1, Cr(VI) in the solution is adsorbed rapidly through ion exchange, and the Cl^- on the surface of LDHs or at the edge of the interlayer is replaced by the adsorbed Cr(VI).
(2) In Step 2, the Cl^- at the edge of the interlayer and the Li^+ from the brucite-like sheets start diffusing out to the bulk solution.
(3) In Step 3, the deintercalation of Li–Al LDHs due to the increasing release of Li^+ results in

the desorption of both Cr(VI) (on the basal surfaces and/or edges of LDHs) and Cl^- (in the interlayers).

(4) In Step 4, the desorption rate of the Cr(VI) gradually decreases until the reaction reaches equilibrium.

5.6. Comparison of the adsorption capacity of LDHs with various adsorbents

A comparison of the adsorption capacity of LDHs with various adsorbents is presented in Table 5. The adsorbents are categorized based on the medium, that is, classifying the adsorbents as aluminas, biomaterials, carbon-based materials, clays, iron-based minerals/materials, LDHs, resins, sands, silicas, waste materials, zeolites, and other minerals/materials. Aluminas such as activated alumina, carbon-based materials such as activated carbon, and resins such as Amberlite IRA-743 have been used in commercial scale to remove certain oxyanions.

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

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

6. Problems, improvement, and potential application of LDHs

6.1. Stability of LDHs

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

6.2. Design of LDH adsorption systems

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

6.2.1. Powdered LDHs

If LDHs are applied in the powder form for their large surface area and rapid oxyanion adsorption rate, it may present appreciable problems in the subsequent solid/liquid separation process, e.g. blockage of the filter that causes pressure drops. For efficient powdered LDH application, sorptive flotation constitutes an interesting option because it combines the advantages of greater sorption capacity and faster sorption kinetics of the sorbents, without running into the solid/liquid separation problems that occur with the deadend filtration. In this way, treated water is produced as underflow and a foam concentrate is also generated. Recovery of oxyanions is also possible from the foam concentrate and, if required, the fine sorbents may be recycled after oxyanion desorption. The sorptive flotation system has been demonstrated by Lazaridis et al. (2001, 2002) for promising arsenate and chromate removal and effective particles separation. In another study, a 'porous pot' technique integrated with powdered LDHs for As removal has been demonstrated by Gillman (2006) and satisfactory results were obtained. He estimated that the production cost of LDHs could be about US$0.12 d^{-1} for a family consuming 20 L of drinking water, suggesting that LDHs may be an attractive adsorbent for water treatment in less-developed regions.

6.2.2. Granular LDHs

Apart from using sorptive flotation for separating suspended powdered LDHs, it would be a good alternative to use granular LDHs in a fixed-bed filter, especially where continuous application is required. Granular LDHs that are amenable to separation could be produced by harnessing LDHs and their aggregates within polymeric beads. While the LDH granules retain their intrinsic sorption/desorption properties, the robust polymeric support offers adequate mechanical strength, durability and favorable hydraulic properties in them flow-through systems. Granular LDH flow-through systems may be designed to operate in a conventional downflow filtration mode or in an upflow mode. Though a few studies have indicated that the LDH granules are able to reduce relatively high concentrations of oxyanions to levels that would be acceptable in practice (Gillman, 2006; Kuzawa et al., 2006), additional studies may be required to further confirm the physical stability of the LDHs. The possibility of hybridizing LDHs with other potential mechanically and chemically stable materials should also be explored.

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

6.3. Multi-oxyanion system

In waters and wastewaters, several oxyanions co-exist, together with other constituents such as cations and humic substances that potentially influence the chemistry of LDHs and the speciation of oxyanions in the aqueous system. Thus, an understanding of the adsorption performance of LDHs in the multi-oxyanion system consisting of various oxyanions and matrices of interest is needed. To date, there are limited reports on oxyanion adsorption by LDHs in the solution matrices that are practical to water and wastewater treatment. This information is useful for assessing the viability of using LDHs for water and wastewater treatment. Future research should aim to fill this knowledge gap.

7. Conclusions

LDHs offer technical as well as economical merits in treating waters and wastewaters containing harmful oxyanions. One of the most competitive advantages of LDHs is that they consist of hydroxides of common and abundant metals on the earth and can be synthesized economically. Oxyanion adsorption process using LDHs also shows considerably faster kinetics in comparison to most of the biological treatment processes. The main advantages of LDHs over the conventional anionic exchange resins include their higher anion exchange capacity for certain oxyanions and their good thermal stability. Furthermore, LDHs can be fully regenerated in a short time for reuse.

In general, LDHs exhibit better oxyanion adsorption at pH lower than pH_{pzc}, which typically ranges from 9 to 12. Other important factors that may influence the efficiency of oxyanion adsorption on LDHs include the presence of competitive anions, LDHs/oxyanions ratio, temperature, nature of LDH precursor metals, crystallinity of LDHs, layer charge and interlayer anion charge of LDHs, LDH particle sizes, and calcination effect.

However, LDHs have several shortcomings that may limit their large-scale applications for oxyanion removal. First, precursor metals of LDHs could release into the solution, particularly at lower pH values. Second, regeneration of the spent LDHs can be costly. Third, high basicity would be introduced to the product water if the calcined LDHs are used.

Prior to full-scale application of LDHs in water and wastewater treatment, additional studies are still required to (i) develop the most economical synthesis method to mass-produce the LDHs with the optimum surface area, anion exchange capacity, and thermal stability; (ii) better understand the oxyanion adsorption by LDHs in solution matrices practical to water and wastewater treatment; (iii) obtain an archive of different oxyanion adsorption performances by tuning the particular LDHs and the reaction conditions; with this archive, 'fine tuning' could be employed to accurately control the LDHs and optimize them for oxyanion adsorption; and (iv) develop integrated treatment systems combining the LDH adsorption unit with other technologies to improve the overall efficiency of oxyanion removal.

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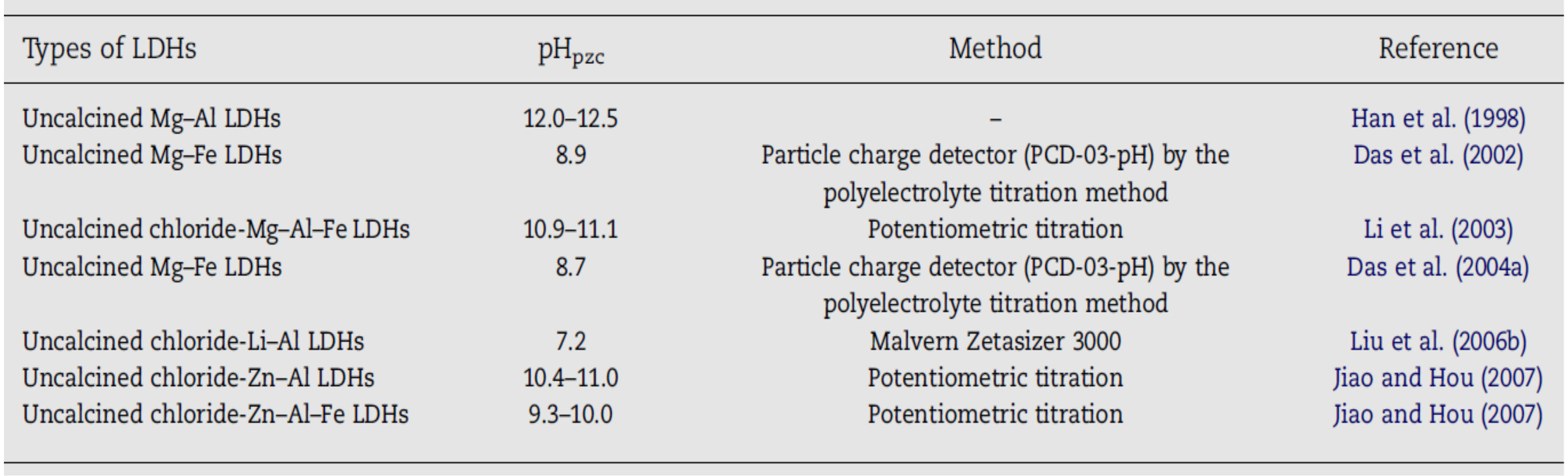
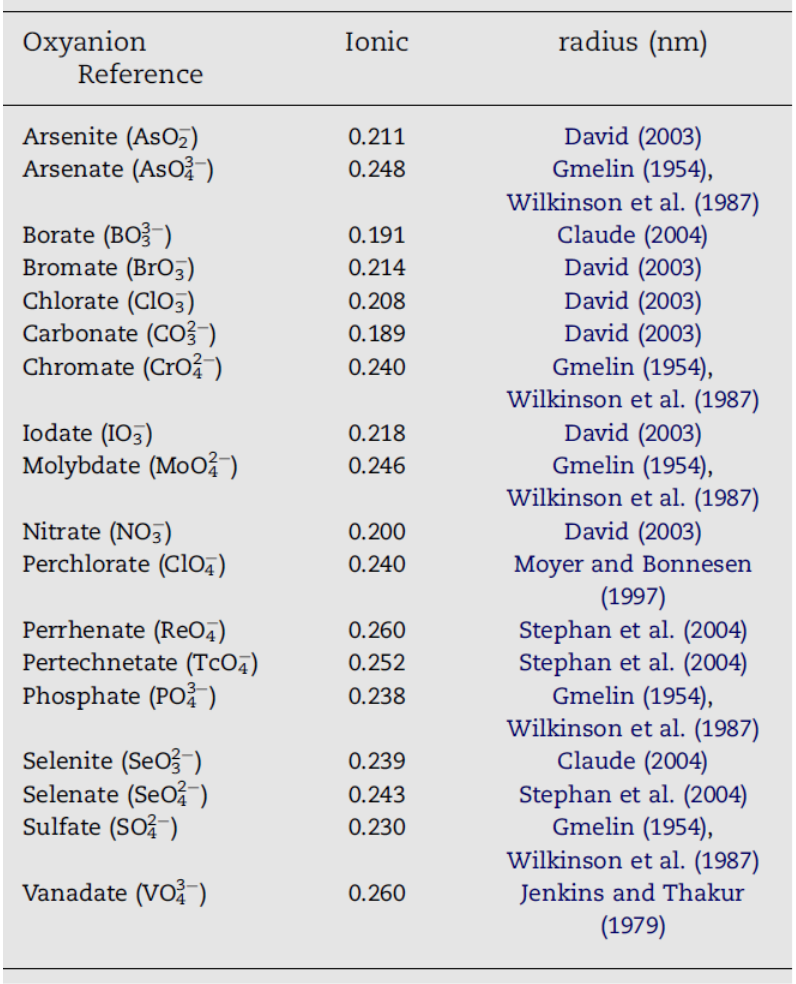
Fig. 5 A proposed mechanism for the adsorption and desorption of Cr(VI) in Li–Al LDHs (modified from Wang et al., 2006b).



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

Table 1 Reported pH_{pzc} values of LDHs in the literature



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

Table 2 Ionic radius of various oxyanions

Oxyanion	Types of LDHs	Reference
Arsenite	Uncalcined carbonate-LDHs	Manju and Anirudhan (2000)
Arsenite	Uncalcined chloride-LDHs, uncalcined carbonate-LDHs, and calcined LDHs	You et al. (2001b)
Arsenite	Uncalcined and calcined Mg–Al LDHs	Yang et al. (2005)
Arsenite	Calcined Mg–Al LDHs and calcined Mg–Fe LDHs	Ye et al. (2005)
Arsenite	Uncalcined nitrate-LDHs, uncalcined chloride-LDHs, and uncalcined carbonate-LDHs	Gillman (2006)
Arsenite	Uncalcined and calcined Mg–Al LDHs	Shibata and Murayama (2006)
Arsenate	Calcined Mg–Al LDHs	Kovanda et al. (1999)
Arsenate	Uncalcined and calcined Mg–Al LDHs	Lazaridis et al. (2002), Dousová et al. (2003), Bhaumik et al. (2005)
Arsenate	Uncalcined Mg–Al LDHs	Bryan et al. (2003)
Arsenate	Uncalcined and calcined Mg–Fe–Al LDHs	Carja et al. (2005)
Arsenate	Uncalcined Mg–Al LDHs	Kiso et al. (2005), Peng et al. (2005), Romanova et al. (2005)
Arsenate	Uncalcined and calcined Mg–Al LDHs	Yang et al. (2005)
Arsenate	Uncalcined nitrate-LDHs, uncalcined chloride-LDHs, and uncalcined carbonate-LDHs	Gillman (2006)
Arsenate	Uncalcined chloride-Li–Al LDHs	Liu et al. (2006b)
Arsenate	Uncalcined and calcined Mg–Al LDHs	Shibata and Murayama (2006)
Arsenate	Conditioned calcined Mg–Al LDHs	Yang et al. (2006)
Chromate	Calcined Mg–Al LDHs	Rhee et al. (1997), Lazaridis and Asouhidou (2003), Martinez-Gallegos and Bulbulian (2004)
Chromate	Uncalcined and calcined Mg–Al, Ni–Al and Zn–Cr LDHs	Goswamee et al. (1998)
Chromate	Uncalcined chloride-Zn–Al LDHs	Houri et al. (1998)
Chromate	Uncalcined chloride-Mg–Al, chloride-Zn–Al, and chloride-Zn–Cr LDHs	Houri et al. (1999)
Chromate	Calcined Mg–Al LDHs	Kovanda et al. (1999)
Chromate	Uncalcined Mg–Al LDHs (commercial)	Lehmann et al. (1999), Terry (2004)
Chromate	Uncalcined carbonate-Mg–Al LDHs	Manju et al. (1999), Chen et al. (2004), Lazaridis et al. (2004)
Chromate	Uncalcined and calcined Mg–Al LDHs	Lazaridis et al. (2001), Ye et al. (2004), Alvarez-Ayuso and Nugteren (2005), Bakhti and Ouali (2005), Shibata and Murayama (2006)
Chromate	Uncalcined hydroxide-Ca–Al LDHs and carbonate-Ca–Al LDHs	Zhang and Reardon (2003)
Chromate	Uncalcined Mg–Fe LDHs	Das et al. (2004a)
Chromate	Uncalcined and calcined Zn–Al–Zr and Mg–Al–Zr LDHs	Das et al. (2004b)
Chromate	Uncalcined and calcined Mg–Al LDHs	Martinez-Gallegos et al. (2004)
Chromate	Uncalcined Ni–Fe LDHs	Prasanna et al. (2006)
Chromate	Uncalcined Li–Al LDHs	Wang et al. (2006b)
Phosphate	Uncalcined and calcined Mg–Al LDHs	Shin et al. (1996), Lazaridis (2003), Bakhti and Ouali (2006)
Phosphate	Uncalcined chloride-Zn–Al LDHs	Badreddine et al. (1999)
Phosphate	Uncalcined Mg–Fe and Ca–Fe LDHs	Seida and Nakano (2001), Seida and Nakano (2002)
Phosphate	Uncalcined Mg–Al LDHs	Kameda et al. (2002), Nomura et al. (2003), Frost et al. (2006)
Phosphate	Uncalcined and calcined Mg–Mn LDHs	Tezuka et al. (2004a)
Phosphate	Calcined Mg–Mn LDHs	Chitrakar et al. (2005)
Phosphate	Uncalcined Mg–Al, Mg–Fe, and Ni–Fe LDHs	Chitrakar et al. (2006)
Phosphate	Uncalcined and calcined Mg–Al, Zn–Al, Ni–Al, Co–Al, Mg–Fe, Zn–Fe, Ni–Fe, and Co–Fe LDHs	Das et al. (2006)

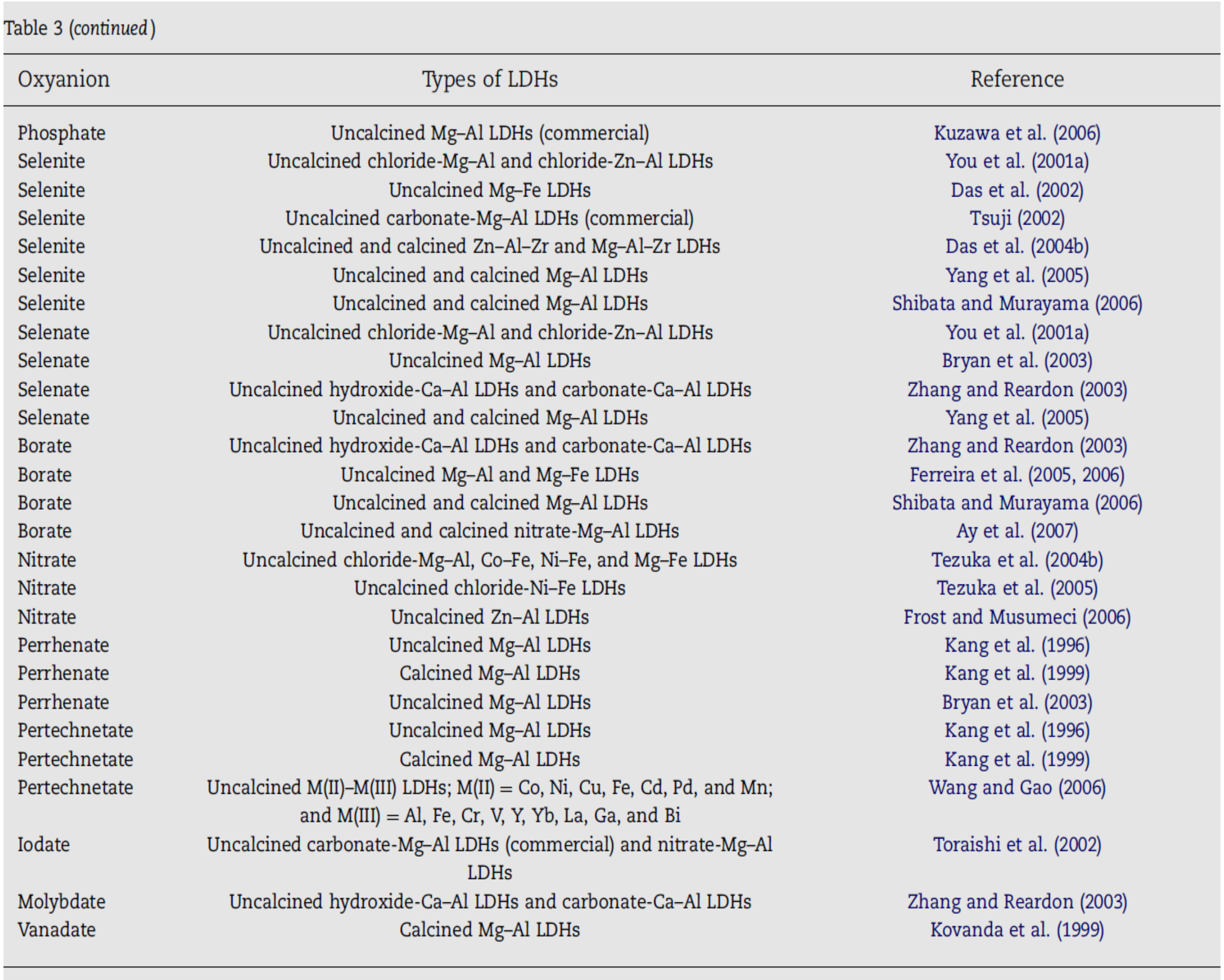


Table 3 (*continued*)

Oxyanion	Types of LDHs	Reference
Phosphate	Uncalcined Mg–Al LDHs (commercial)	Kuzawa et al. (2006)
Selenite	Uncalcined chloride-Mg–Al and chloride-Zn–Al LDHs	You et al. (2001a)
Selenite	Uncalcined Mg–Fe LDHs	Das et al. (2002)
Selenite	Uncalcined carbonate-Mg–Al LDHs (commercial)	Tsuji (2002)
Selenite	Uncalcined and calcined Zn–Al–Zr and Mg–Al–Zr LDHs	Das et al. (2004b)
Selenite	Uncalcined and calcined Mg–Al LDHs	Yang et al. (2005)
Selenite	Uncalcined and calcined Mg–Al LDHs	Shibata and Murayama (2006)
Selenate	Uncalcined chloride-Mg–Al and chloride-Zn–Al LDHs	You et al. (2001a)
Selenate	Uncalcined Mg–Al LDHs	Bryan et al. (2003)
Selenate	Uncalcined hydroxide-Ca–Al LDHs and carbonate-Ca–Al LDHs	Zhang and Reardon (2003)
Selenate	Uncalcined and calcined Mg–Al LDHs	Yang et al. (2005)
Borate	Uncalcined hydroxide-Ca–Al LDHs and carbonate-Ca–Al LDHs	Zhang and Reardon (2003)
Borate	Uncalcined Mg–Al and Mg–Fe LDHs	Ferreira et al. (2005, 2006)
Borate	Uncalcined and calcined Mg–Al LDHs	Shibata and Murayama (2006)
Borate	Uncalcined and calcined nitrate-Mg–Al LDHs	Ay et al. (2007)
Nitrate	Uncalcined chloride-Mg–Al, Co–Fe, Ni–Fe, and Mg–Fe LDHs	Tezuka et al. (2004b)
Nitrate	Uncalcined chloride-Ni–Fe LDHs	Tezuka et al. (2005)
Nitrate	Uncalcined Zn–Al LDHs	Frost and Musumeci (2006)
Perrhenate	Uncalcined Mg–Al LDHs	Kang et al. (1996)
Perrhenate	Calcined Mg–Al LDHs	Kang et al. (1999)
Perrhenate	Uncalcined Mg–Al LDHs	Bryan et al. (2003)
Pertechnetate	Uncalcined Mg–Al LDHs	Kang et al. (1996)
Pertechnetate	Calcined Mg–Al LDHs	Kang et al. (1999)
Pertechnetate	Uncalcined M(II)–M(III) LDHs; M(II) = Co, Ni, Cu, Fe, Cd, Pd, and Mn; and M(III) = Al, Fe, Cr, V, Y, Yb, La, Ga, and Bi	Wang and Gao (2006)
Iodate	Uncalcined carbonate-Mg–Al LDHs (commercial) and nitrate-Mg–Al LDHs	Toraishi et al. (2002)
Molybdate	Uncalcined hydroxide-Ca–Al LDHs and carbonate-Ca–Al LDHs	Zhang and Reardon (2003)
Vanadate	Calcined Mg–Al LDHs	Kovanda et al. (1999)

Table 3 List of oxyanions investigated for their adsorption characteristics with various LDHs

Oxyanion	Types of LDHs (calcination temp. in parenthesis)	Synthesis method^{a}	Surface area (m^2/g)	Ads. capacity (mg/g); isotherm^{b}	C_0 (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model^{c}	Reference
Arsenite	Uncalcined carbonate-LDHs			L	75	pH 8.5; room		F	Manju and Anirudhan (2000)
Arsenite	Calcined Mg–Fe LDHs	C		87.5		Room			Ye et al. (2005)
Arsenite	Uncalcined chloride-LDHs	C		0.086^{d}	0.432^{d}		1:200		Gillman (2006)
Arsenate	Calcined Mg–Al LDHs (450 °C)			L		Neutral; 20			Kovanda et al. (1999)
Arsenate	Uncalcined Mg–Al LDHs	C		32.6; R-P, L, F	10–70	Natural; 30	1:1000		Lazaridis et al. (2002)
Arsenate	Calcined Mg–Al LDHs (500 °C)	C		615; R-P, L, F	50–700	Natural; 30	1:1000		Lazaridis et al. (2002)
Arsenate	Calcined Mg–Al LDHs (450 °C)	C		99.6^{d}	149.8^{d}	Neutral; 20	1:1000		Dousová et al. (2003)
Arsenate	Calcined Mg–Fe LDHs (450 °C; high N_2 flow)	C	287.4	202^{d}	206^{d}	pH 6.5; 25	1:1000		Carja et al. (2005)
Arsenate	Uncalcined chloride-Mg–Al LDHs			105; ML		Neutral			Kiso et al. (2005)
Arsenate	Uncalcined Mg–Al LDHs	H		F				LP-S	Peng et al. (2005)
Arsenate	Calcined Mg–Al LDHs (500 °C)	C	198	5.609^{d}; F, L	$0.01–0.2^{d}$	pH 4.2–5.4; 25	1:8333	M	Yang et al. (2005)
Arsenate	Uncalcined chloride-Li–Al LDHs	C	18.8	24.2^{d}; L	$3–150^{d}$	pH 5	1:400		Liu et al. (2006b)
Arsenate	Calcined Mg–Al LDHs (500 °C; conditioned)	C and CO		$\sim 5.25^{d}$; S	$0.06–0.3^{d}$	pH ~6.7; 25	1:25,000		Yang et al. (2006)
Chromate	Calcined Mg–Al LDHs (450 °C)	C		117.7^{d}; F	$0–1570^{d}$	Room	1:100	F	Goswamee et al. (1998)
Chromate	Uncalcined chloride-Zn–Al LDHs	C		23.3^{d}	$6.7–134.5^{d}$				Houri et al. (1998, 1999)
Chromate	Calcined Mg–Al LDHs (450 °C)			L		Neutral; 20			Kovanda et al. (1999)
Chromate	Uncalcined Mg–Al LDHs (commercial)		34.8	~160	200	pH 4	1:1000		Lehmann et al. (1999)
Chromate	Uncalcined carbonate-Mg–Al LDHs			23.2				F	Manju et al. (1999)
Chromate	Calcined Mg–Al LDHs (500 °C)	C		110	10.4^{d}		1:1000		Lazaridis et al. (2001)
Chromate	Calcined Mg–Al LDHs			120; F			1:1000	P-F, M-S, E	Lazaridis and Asouhidou (2003)
Chromate	Uncalcined Mg–Fe LDHs	C	62	L		30–60		F	Das et al. (2004a)
Chromate	Calcined Mg–Al–Zr (450 °C)	C	200	24; L	60	pH 6; 30	1:2000		Das et al. (2004b)
Chromate	Uncalcined carbonate-Mg–Al LDHs	C	84	17; F		pH 6; 30	1:1000	S	Lazaridis et al. (2004)
Chromate	Calcined Mg–Al LDHs (500 °C)	C		78^{d}		20	1:200		Martinez-Gallegos et al. (2004)
Chromate	Uncalcined Mg–Al LDHs (commercial)			$\sim 9^{d}$; F	5–40	pH 2.0–2.1; 24	1:250	P-F	Terry (2004)
Chromate	Calcined Mg–Al LDHs			73					Ye et al. (2004)
Chromate	Uncalcined Mg–Al LDHs	C		16.3; L	11–57	Natural; 22	1:500		Alvarez-Ayuso and Nugteren (2005)
Chromate	Calcined Mg–Al LDHs (500 °C)	C		128; L	57–448	Natural; 22	1:500		Alvarez-Ayuso and Nugteren (2005)
Chromate	Uncalcined nitrate-Ni–Fe LDHs	H	71.2	93.6^{d}		pH 8.2; 22-25	1:250		Prasanna et al. (2006)
Phosphate	Uncalcined chloride-Mg–Al LDHs			29.2^{d}					Shin et al. (1996)
Phosphate	Uncalcined Ca–Fe LDHs	C		28.8; L	1–1500	pH 8.4	1:2000		Seida and Nakano (2002)
Phosphate	Calcined Mg–Al LDHs (500 °C)	C		81.6^{d}; S, L, F		pH 7–7.5; 30	1:4000	LP-F	Lazaridis (2003)
Phosphate	Calcined Mg–Mn LDHs (300 °C)	C and AO		34.1^{d}		pH 8			Tezuka et al. (2004a)
Phosphate	Calcined Mg–Mn LDHs (300 °C)	C		7.3; F	0.3	Room	1:40,000		Chitrakar et al. (2005)
Phosphate	Calcined Mg–Al LDHs	C		49.6^{d}	2.5–50			F-R	Bakhti and Ouali (2006)
Phosphate	Calcined Mg–Al LDHs	C	210	44; L, F	50	pH 6; 30	1:2500	F	Das et al. (2006)

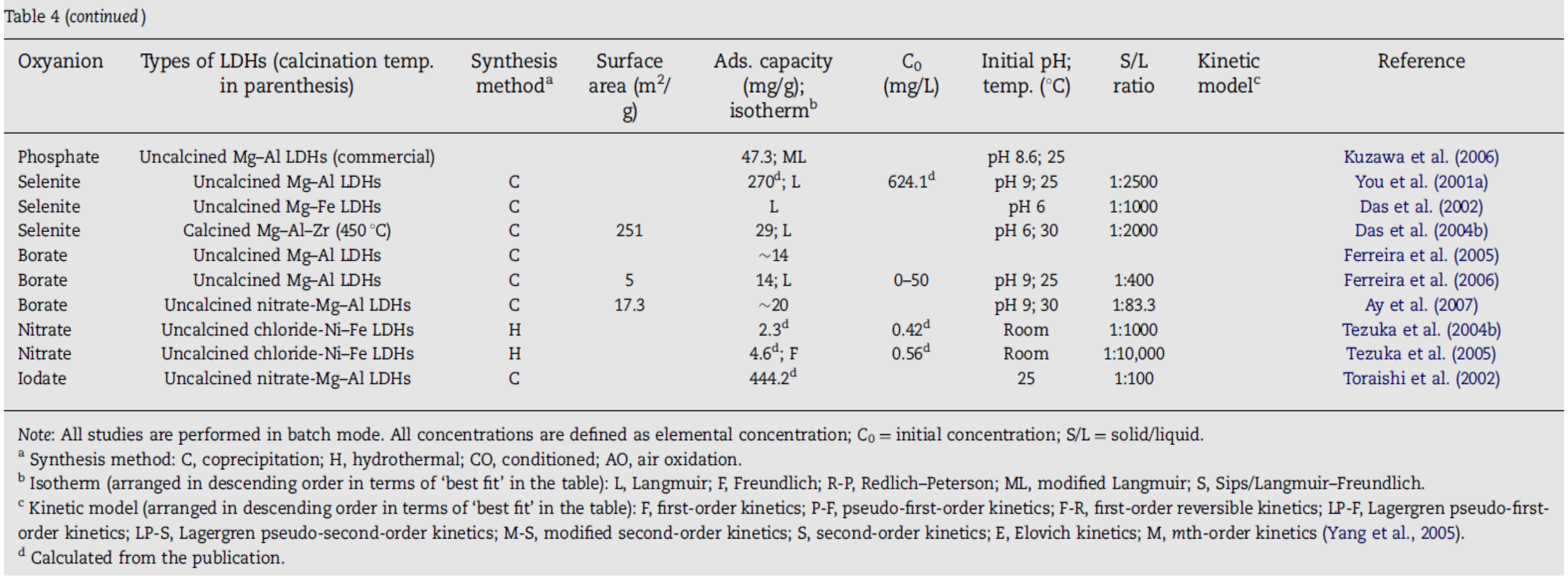


Table 4 (*continued*)

Oxyanion	Types of LDHs (calcination temp. in parenthesis)	Synthesis method[a]	Surface area (m^2/g)	Ads. capacity (mg/g); isotherm[b]	C_0 (mg/L)	Initial pH; temp. (°C)	S/L ratio	Kinetic model[c]	Reference
Phosphate	Uncalcined Mg–Al LDHs (commercial)			47.3; ML		pH 8.6; 25			Kuzawa et al. (2006)
Selenite	Uncalcined Mg–Al LDHs	C		270[d]; L	624.1[d]	pH 9; 25	1:2500		You et al. (2001a)
Selenite	Uncalcined Mg–Fe LDHs	C		L		pH 6	1:1000		Das et al. (2002)
Selenite	Calcined Mg–Al–Zr (450 °C)	C	251	29; L		pH 6; 30	1:2000		Das et al. (2004b)
Borate	Uncalcined Mg–Al LDHs	C		~14					Ferreira et al. (2005)
Borate	Uncalcined Mg–Al LDHs	C	5	14; L	0–50	pH 9; 25	1:400		Ferreira et al. (2006)
Borate	Uncalcined nitrate-Mg–Al LDHs	C	17.3	~20		pH 9; 30	1:83.3		Ay et al. (2007)
Nitrate	Uncalcined chloride-Ni–Fe LDHs	H		2.3[d]	0.42[d]	Room	1:1000		Tezuka et al. (2004b)
Nitrate	Uncalcined chloride-Ni–Fe LDHs	H		4.6[d]; F	0.56[d]	Room	1:10,000		Tezuka et al. (2005)
Iodate	Uncalcined nitrate-Mg–Al LDHs	C		444.2[d]		25	1:100		Toraishi et al. (2002)

Note: All studies are performed in batch mode. All concentrations are defined as elemental concentration; C_0 = initial concentration; S/L = solid/liquid.

[a] Synthesis method: C, coprecipitation; H, hydrothermal; CO, conditioned; AO, air oxidation.

[b] Isotherm (arranged in descending order in terms of 'best fit' in the table): L, Langmuir; F, Freundlich; R-P, Redlich–Peterson; ML, modified Langmuir; S, Sips/Langmuir–Freundlich.

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

[d] Calculated from the publication.

Table 4 Adsorption characteristic of various oxyanions with LDHs

Adsorbent	Surf. area (m^2/g)	Adsorption capacity (mg/g)							C_0 (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO_4^-)				
Aluminas												
Activated alumina	116–118	3.5	15.9						0.8–4.9 for As(III); 2.9–11.5 for As(V)	pH 7 for As(III); pH 5.2 for As(V); 25		Lin and Wu (2001)
Alumina						127.8[a]				pH 5.2; 30		Parida and Gorai (2003)
Biomaterials												
Biomass		13.2							1–10	pH 2; 28		Teixeira and Ciminelli (2005)
				15.6						pH 5; 28		Sekhar et al. (1998)
Bio-polymeric beads				0.83					86.7[a]	pH 6; 25		Bajpai et al. (2004)
Chitosan			58						400	pH 4; 25		Mcafee et al. (2001)
				11.3		34.5				pH 3 for Cr(VI); pH 4 for Se(VI); 25		Qian et al. (2000)
Carbon-based materials												
Activated carbon	522		3.1						0.025–0.2	pH 5; 24		Chuang et al. (2005)
	1210			186.1					5–200	pH 3; 40		Khezami and Capart (2005)
	1200						1.4		28–100			Rajaković and Ristić (1996)
Char carbon	36.5	89	34.5						193–992 for As(III); 157–737 for As(V)	pH 2–3; 25		Pattanayak et al. (2000)
$ZnCl_2$-activated coir pith carbon					1.7[a]				10–40	pH 4; 35	Des. ~50% (after 1 cycle)	Namasivayam and Sangeetha (2004)
Bituminous granular activated carbon	925							2.42	2	; 20		Chen et al. (2005)
Clays	15.6			13.9						pH 4.6; 25		Bhattacharyya and Gupta (2006)
Iron-based minerals/ materials												
Bead cellulose loaded with iron oxyhydroxide		99.6	33.2							pH 7; 25		Guo and Chen (2005)

Table 5 (*continued*)

Adsorbent	Surf. area (m^2/g)	Adsorption capacity (mg/g)							C_0 (mg/L)	pH; temp. (°C)	Des./reg. (%)	Reference
		Arsenite (as As(III))	Arsenate (as As(V))	Chromate (as Cr(VI))	Phosphate (as P)	Selenite (as Se(IV))	Borate (as B)	Perchlorate (as ClO_4^-)				
Ferrihydrite			68.8						0–150	pH 7		Lafferty and Loeppert (2005)
Goethite	39	22	4						0–60	pH 9; 22		Lenoble et al. (2002)
Hematite		0.2							1–10	2.8-5		Singh et al. (1988)
Hydrous ferric oxide	200	28	7						0–60	pH 9; 22		Lenoble et al. (2002)
Nanoscale zero-valent iron	37.2	2.5								pH 7; 35		Kanel et al. (2005)
Maghemite nanoparticles	178			19.2					5–200	pH 2–3; 25	Des. 87.7% (after 1 cycle)	Hu et al. (2005)
LDHs												
Calcined LDHs		87.5[1]			26.6[a2]					pH 7–7.5 for PO_4^{3-}; room for As(III); 30 for PO_4^{3-}		[1]Ye et al. (2005); [2]Lazaridis (2003)
Nano-scale LDHs			78.1	33.8				~0.8	12–200 for As(V); 12–100 for Cr(VI); 0.02–5 for ClO_4^-	pH 8–9; room	Des. 78% (after 1 cycle); Reg. 50% (after 1 cycle)	Goh (2007)
Uncalcined LDHs						270[a1]	~20[2]		624.1[a] for Se(IV)	pH 9; 25 for Se(IV); 30 for B		[1]You et al. (2001a) [2]Ay et al. (2007)
Resins												
Monoclinic hydrous zirconium oxide (Zr resin)	373	112.4	89.9						74.9[a]	pH 9–10 for As(III); pH 4–6 for As(V); 25	Des. 99% (after 1 cycle)	Suzuki et al. (2001)
Ion exchange resin IRN97H				58.1					~20	pH 3.8; 25		Rengaraj et al. (2003)
Lewatit M610 anion exchange resin				22.1					20–100	pH 5; 25		Gode and Pehlivan (2005)
Amberlite IRA-743 resin							2.5		25	pH 9; 30		de la Fuente García-Soto and Muñoz Camacho (2005)
Diaion CRB 01 resin							3[a]		20	; 30		Kabay et al. (2004)
Polymer-supported amino-bis(*cis*-propane 2,3-diol)							18		~95[a]	Natural; room	Des. 53.3% (after 1 cycle)	Bicak et al. (2005)
Sands												
Aluminium-oxide-coated sand						1.1			63.2–142.1[a]	pH 4.8; 25		Kuan et al. (1998)
Silicas												

Table 5 Comparative evaluation of LDHs and various adsorbents for oxyanions removal

Amino-functionalized mesoporous silicas (MCM-41)	310		119.8						0–1500	pH 6; 25	Reg. 91% (after 1 cycle)	Yoshitake et al. (2003)
Ammonium-functionalized MCM-48	750				15[a]				100–700	; 5	Reg. 94% (after 5 cycles)	Saad et al. (2007)
Glucamine-modified MCM-41	250						8.7[a]		50–200		Des. 83% (after 1 cycle)	Kaftan et al. (2005)
Polyolfunctionalized SBA-15	224						6.8[a]		20–250	; 30		Wang et al. (2006a)
Waste materials												
Fly ash			27.8									Diamadopoulos et al. (1993)
	4.4			1.8					2–10	pH 2; 30		Banerjee et al. (2004)
Orange juice residue		70.4	67.4							pH 7–11 for As(III); pH 2–6 for As(V); 30		Ghimire et al. (2002)
Rice husk			19						100–600			Lee et al. (1999)
Activated sludge				18.9					50–500	pH 1; 25		Aksu et al. (2002)
Sawdust				1.5					0–100			Sumathi et al. (2005)
Blast furnace slag	0.4				2.1[a]				500	pH 8.5		Oguz (2004)
Weak anion exchanger prepared from lignocellulosic residue	111.3				23.7[a]				10–300	pH 5; 30	Reg. 87.3% (after 4 cycles)	Anirudhan et al. (2006)
Fe(III)/Cr(III) hydroxide sludge	147.4					15.6			12.4–37.3[a]	pH 6.5; 32	Des. <15% (after 1 cycle)	Namasivayam and Prathap (2006)
Manganese nodule leached residues	109.2					54.6			60	pH 5; 30	Des. 28.5% (after 1 cycle)	Dash and Parida (2007)
Aluminum-based drinking-water treatment residuals								0.03[a]	10–200	; 23		Makris et al. (2006)
Zeolites												
Shirasu-zeolite (SZP_1)	15.6		65.9						97.4[a]	pH 3–10; 24	Reg. 85% (after 2 cycles)	Xu et al. (2002)
Zeolite	500				25.9[a]					; 25	Des. 56% (after 1 cycle)	Onyango et al. (2007)
Other minerals/ materials												
Manganese dioxide		44										Chen et al. (1999)
Titanium dioxide	330	59.9	37.5							pH 7; 25		Pena et al. (2005)
Aluminum oxide hydroxide					~11.4[a]				95			Tanada et al. (2003)

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

[a] Calculated from the publication.

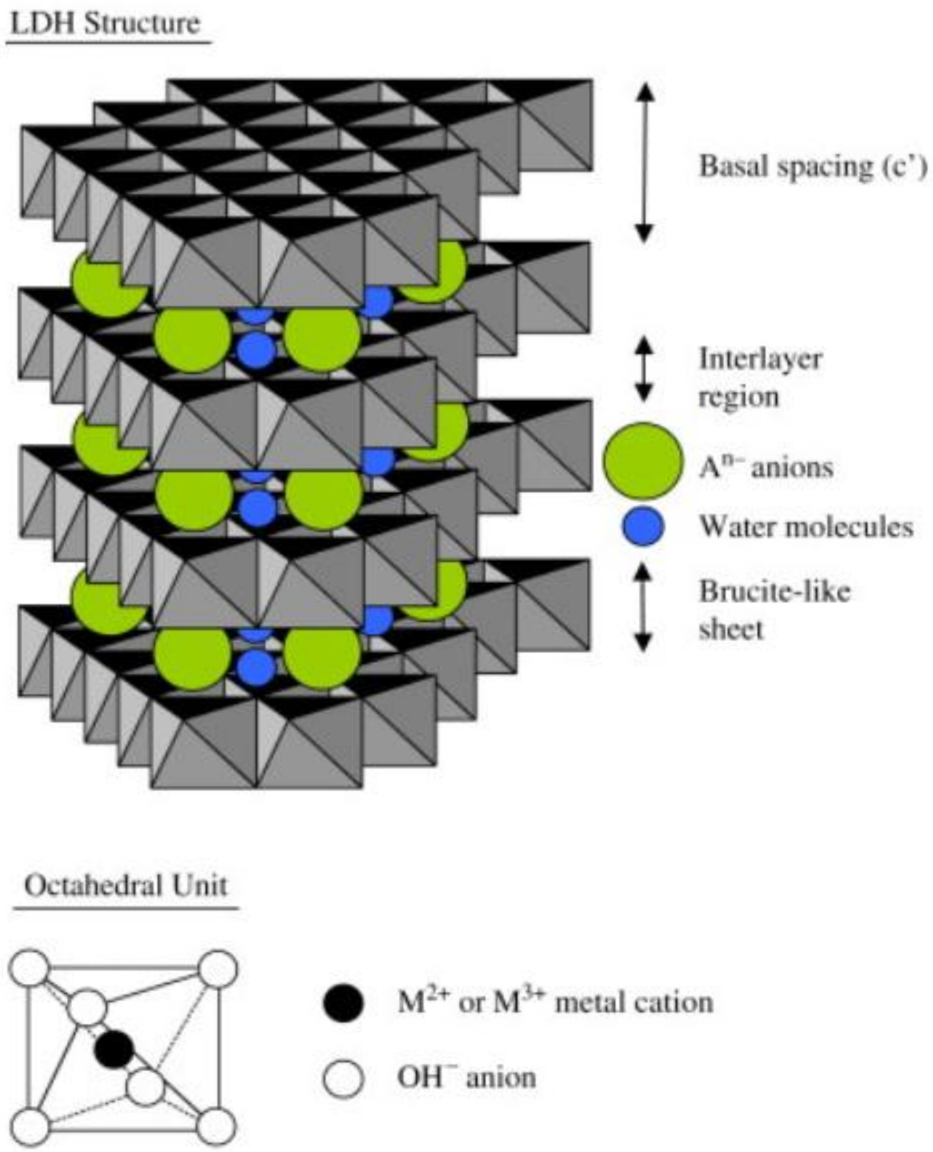


Fig. 1 Schematic representation of the LDH structure.

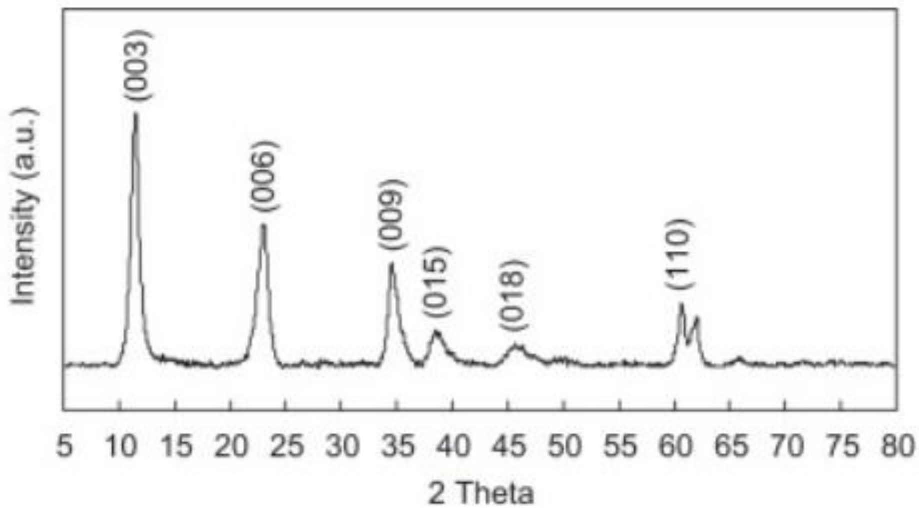


Fig. 2 Typical X-ray pattern of LDHs.

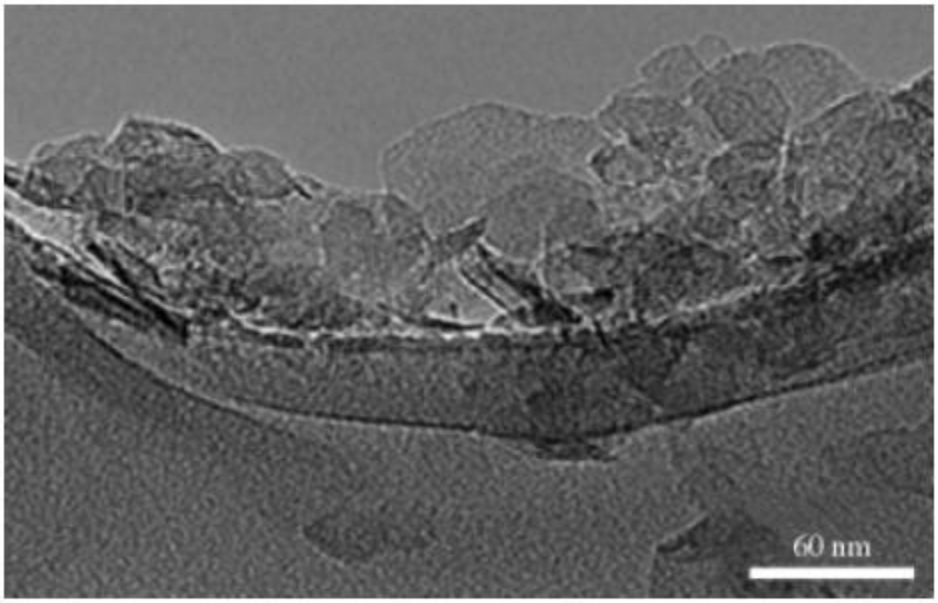


Fig. 3 TEM image of LDHs synthesized by the authors.

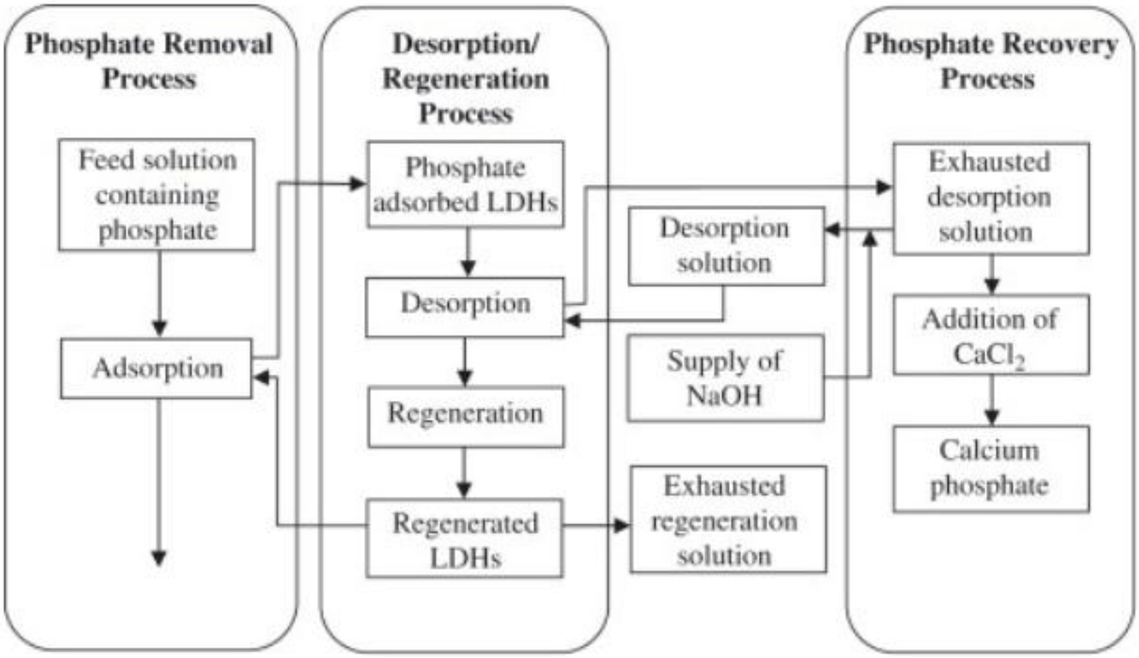


Fig. 4 Schematic diagram of the system for PO_4^{3-} removal/recovery, regeneration of LDHs, and regeneration of desorption solution (proposed by Kuzawa et al., 2006).

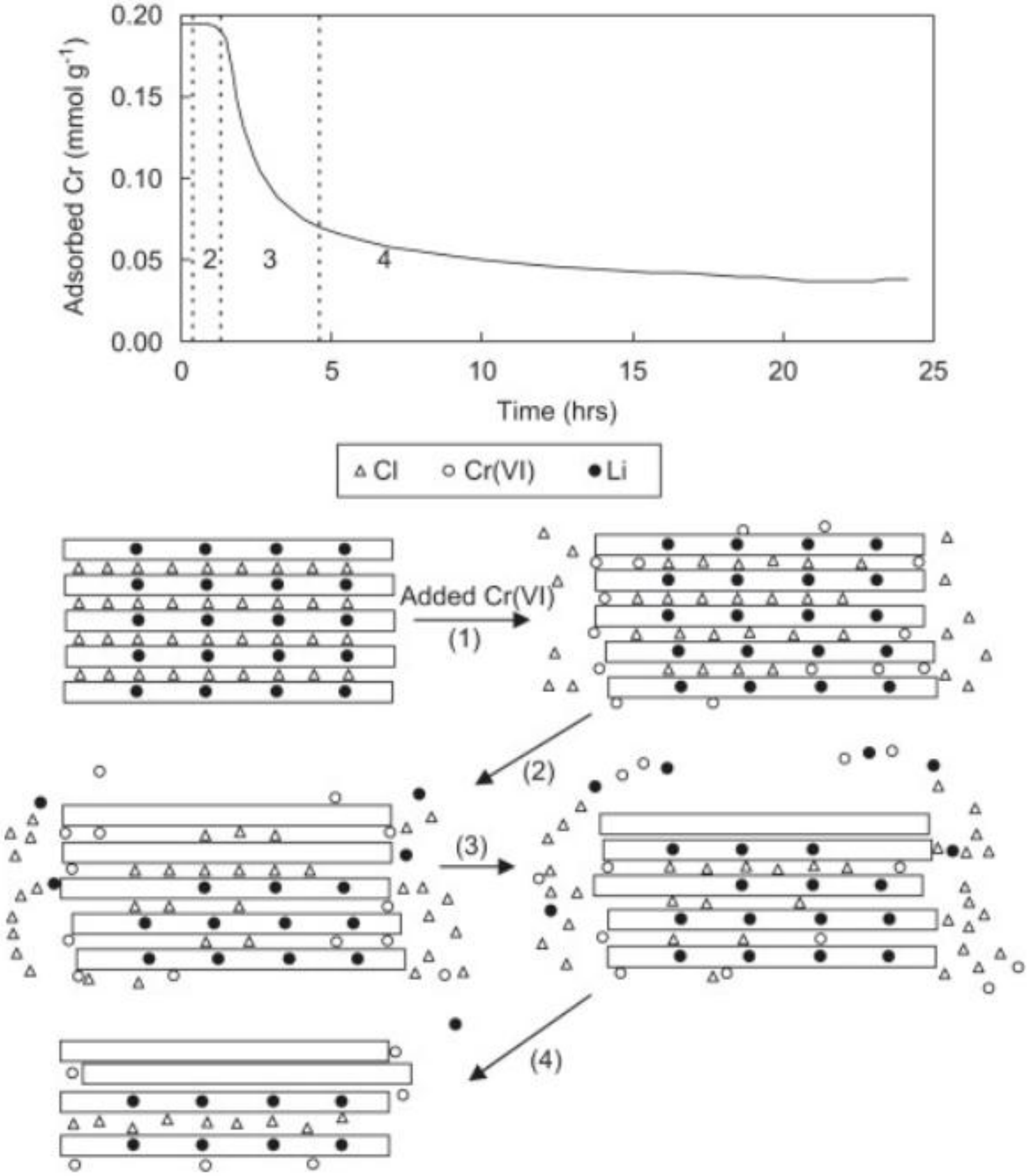


Fig. 5 A proposed mechanism for the adsorption and desorption of Cr(VI) in Li–Al LDHs (modified from Wang et al., 2006b).