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Sorption characteristics and mechanisms of oxyanions and oxyhalides having different molecular properties on Mg/Al layered double hydroxide nanoparticles

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Abstract

The sorption ability of fast-coprecipitated and hydrothermally-treated Mg/Al layered double hydroxide nanoparticles (FCHT-LDH) for various oxyhalides and oxyanions was evaluated. Interactions of oxyhalide such as monovalent bromate or oxyanions such as divalent chromate and divalent vanadate with FCHT-LDH were investigated using a combination of macroscopic (batch sorption/desorption studies and electrophoretic mobility (EM) measurements) and microscopic techniques (CHNS/O, XRD, FTIR, XPS, and EXAFS analyses). The sorption studies on various oxyanions and oxyhalides suggested that their sorption characteristics on FCHT-LDH were largely governed by their ionic potentials and molecular structures. Oxyanions which have ionic potentials higher than 7 nm^{-1} were found to be more readily sorbed by FCHT-LDH than oxyhalides with ionic potentials lower than 5 nm^{-1} . The results obtained also demonstrated that trigonal pyramid oxyhalides showed a lower degree of specificity for FCHT-LDH than the tetrahedral coordinated oxyanions. From the macroscopic and microscopic studies, monovalent oxyhalide sorption on FCHT-LDH was postulated to occur mainly via anion exchange mechanism with subsequent formation of outer-sphere surface complexes. For polyvalent oxyanion sorption on FCHT-LDH, the mechanisms were possibly associated with both anion exchange and ligand exchange reactions, resulting in the coexistence of outer-sphere and inner-sphere surface complexes.

1. Introduction

Inorganic anions have high solubilities in aqueous phase at the circumneutral to alkaline pH values typical of most subsurface environment. They are also less susceptible to sorption since most natural materials have negative surface charges. Oxyanions such as arsenate, chromate, molybdate, selenate, vanadate, etc. are toxic to both humans and wildlife at either $\mu\text{g/L}$ or mg/L levels [1–3]. Borate, another oxyanion, can stunt plant growth and cause disease in the nervous system of animals [4]. Oxyhalides such as bromate, chlorate, and iodate are disinfection by products (DBPs) in ozone-treated water that have been reported to be carcinogen, whereas perchlorate is well-known for inhibiting the production of thyroid hormones [5,6].

Among various anion treatment processes, sorption is considered to be less expensive than the membrane separation and less generation of secondary waste than the chemical precipitation [7]. In recent years, many conventional sorbents such as activated carbon, zeolite, and metal oxides have been used to remove oxyanions and oxyhalides from water. However, most of them are not selective and some have low sorption and regeneration efficiencies. Layered double hydroxides (LDHs), represented by the general formula $[\text{Ma(II)}_{1-x}\text{Mb(III)}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} m\text{H}_2\text{O}$ (Ma(II) = divalent cation; Mb(III) = trivalent cation; A^{n-} = interlayer anion with valence n ; $x = \text{Mb(III)}/(\text{Ma(II)} + \text{Mb(III)})$), are lamellar mixed hydroxides containing positively-charged main layers with charge-balancing anions in the interlayer region. They have favorable characteristics including large surface area, high anion exchange capacity, good thermal stability, and ability to recover from its calcined form to its layered structure through “memory effect” [8,9]. These make them excellent candidates for removing anions from aqueous solution. Engineered inorganic nanoparticles have recently been reported to enhance the sorption capacity of oxyanions since they have high specific surface area and chemical reactivity, and highly dispersed behaviors [10,11].

Some studies have indicated that LDHs have greater affinities for polyvalent anions than monovalent anions [12,13] but the interrelation between LDHs and valences of anions was not clearly elucidated. Indeed a systematic investigation on various oxyanions and oxyhalides sorption considering the relationship between molecular properties of anions and their sorption characteristics on LDHs could serve as the basis for predicting the selectivity of LDHs towards a wide range of anions. Most previous studies have focused on the anions sorption performance on LDHs under various environmental conditions [14–16], comparatively little is known about the interactions between anions and LDHs. Knowledge of LDH interaction with oxyanions and oxyhalides at the solid/aqueous interface is of paramount importance as it will allow the accurate prediction of the sorptive properties of the sorbent and subsequently lead to the optimization of the sorption and regeneration processes. Recent advancements in analytical techniques such as X-ray photoelectron spectroscopy (XPS) and extended X-ray adsorption fine structure (EXAFS) allow probing

into the surface chemistry and detailed structural information of the sorbed complexes at the solid/aqueous interface. One recent EXAFS study revealed that arsenate sorbed on the internal and external surfaces of the LDHs by forming outer-sphere complexes [17]. Nonetheless, almost no detailed microscopic study has been performed to examine the interaction between LDHs and other environmentally significant anions including bromate, chromate, and vanadate. These insights are vital for improving the sorbent functionality through novel synthesis.

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

2. Experimental

2.1. Chemicals

Milli-Q ultrapure water (18.2 M Ω cm) was used throughout the study, and the water was decarbonated before use. Analytical reagent grade chemicals and decarbonated ultrapure water were used to prepare all the solutions. LDH precursors, i.e. purified magnesium nitrate hexahydrate (Mg(NO₃)₂ · 6H₂O, 99%) was obtained from HiMedia Laboratories Pvt. Ltd. while aluminum nitrate nanohydrate (Al(NO₃)₃ · 9H₂O, 98%) was from Fluka Chemika. The solutions of oxyanions (arsenate, borate, chromate, molybdate, selenate, and vanadate) were prepared using Na₂HAsO₄ · 7H₂O (Sigma, 99.4%), Na₂B₄O₇ · 10H₂O (Hayashi Pure Chemical, 99%), K₂CrO₄ (Merck, 99.5%), Na₂MoO₄ · 2H₂O (J.T. Baker, 100%), Na₂SeO₄ (Sigma, 99%), and Na₃VO₄ (Aldrich, 99.9%), respectively. The solutions of oxyhalides (bromate, chlorate, iodate, and perchlorate) were prepared from NaBrO₃ (Merck, 98%), KClO₃ (Merck, 99%), KIO₃ (Hayashi Pure Chemical, 99.5%), and KClO₄ (BDH, 99%) compounds.

2.2. Sorbents

The sorbents used in this study were Mg/Al LDH nanoparticles with nitrate intercalation prepared in our laboratory and commercial LDH particles supplied by Sinopharm Chemical. The Mg/Al LDH nanoparticles were synthesized via a combined fast

coprecipitation and hydrothermal treatment route and denoted as fast-coprecipitated and hydrothermally-treated Mg/Al layered double hydroxide nanoparticles (FCHT-LDH). In this method, a mixed salt solution containing 16 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 8 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was rapidly added (within a few seconds) into 40 ml of 1.4 M NaOH solution under vigorous stirring and nitrogen purging, and followed by several cycles of separation and washing with decarbonated ultrapure water. The aqueous suspension was subjected to hydrothermal treatment in an autoclave with a Teflon lining (Parr Instrument) under autogenous pressure at 80 °C for 16 h and subsequently freeze-dried. The commercial LDH particles were produced by conventional ion exchange method, in which carbonate was exchanged with the chloride present in the interlayer region of the preformed LDHs. The commercial LDH was given by the formula $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$.

2.3. Characterization

Magnesium and aluminium content in the LDH samples were analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optima 2000) after microwave-assisted acid digestion (EPA Method 3052). Carbon and nitrogen content in the LDHs were determined using CHNS/O analyzer of PerkinElmer 2400 Series II. QuantaChrome Autosorb-1 Analyzer was used to determine the BET surface area, pore volume, and pore size of the LDHs. Prior to measurements, all samples were outgassed at 200 °C under nitrogen flow for several hours. XRD patterns of the LDHs were obtained using Bruker AXS (D8 Advance) X-ray diffractometer ($\lambda = 1.54 \text{ \AA}$). FTIR spectra of the LDHs as KBr pellets were recorded with a PerkinElmer 2000 FTIR spectrometer. The spectra were collected in transmission mode at a resolution of 4 cm^{-1} , and 100 scans were recorded in the $4000\text{--}370 \text{ cm}^{-1}$ to ensure good signal to noise ratio. The transmission electron micrograph (TEM) images of the LDHs were recorded on a JEOL JEM-2100F operating at 200kV.

2.4. Batch sorption/desorption studies

Unless otherwise stated, all the experiments were carried out using the batch sorption technique at 25 °C and at pH 9.5 (the natural pH of the LDH suspension). The background electrolyte solution was prepared from NaNO_3 . Triplicate determinations of the sorption results were performed for most of the experiments. To minimize CO_2 dissolution, all the experiments were carried out in the air-tight system. For kinetic experiments, the container and the suspension were purged with nitrogen, then sealed, and wrapped in Parafilm to ensure CO_2 -free atmosphere for the reaction. The sample was extracted from the sealed container at each interval by the syringe needle through the Parafilm.

The sorption efficiencies of FCHT-LDH and commercial LDH for various oxyanions and oxyhalides were investigated in a single sorbate system by adding a predetermined dose of LDH into the solution of 0.2mM anion in a 50 mL centrifuge tube. The suspensions

were reacted for 24 h to enable complete equilibrium. The suspensions were subsequently centrifuged, filtered through 0.45 μm membrane filter, and the concentrations of oxyanions were determined by ICP-OES whereas the concentrations of oxyhalides were determined by ion chromatograph (IC, Dionex ICS-1000).

Two oxyanions (divalent chromate and vanadate) and an oxyhalide (monovalent bromate) were selected for investigation of sorption isotherms, kinetics, pH effect, ionic strength effect, and EM. Their selection was based on their environmental significance, different ionic charges, molecular structures, and molecular radii. In addition, they have only one predominant species at pH 9.5, thus reducing the number of dissolved anion species and possible adsorbing species, and subsequently minimizing ambiguity in the interpretation of sorption results. Sorption isotherms of these anions were studied by contacting FCHT-LDH with 0.008–0.391mM bromate solutions, 0.019–0.962mM chromate solutions, and 0.020–0.982mM vanadate solutions, respectively. The suspensions were reacted for 24 h at temperature-controlled shaker maintained at 25, 35, 45, and 55 $^{\circ}\text{C}$. The suspensions were then centrifuged, filtered, and the concentrations of anions were analyzed. Sorption kinetic experiments were conducted by adding LDH samples into 0.4mM bromate, chromate, and vanadate, respectively, and then stirring for 6 h with intermittent sampling. Bromate, chromate, and vanadate sorption on FCHT-LDH were examined as a function of pH ranging from 4.5 to 11 and ionic strength of 0.005 and 0.5 M NaNO_3 . LDH samples were hydrated in 0.005 and 0.5 M NaNO_3 solutions prior to the pH adjustment using either HNO_3 or NaOH solutions. An appropriate amount of bromate, chromate, or vanadate stock solution was added and the suspensions were then reacted with intermittent pH adjustment. The EM measurements were performed on a Zetasizer Nano ZS (Malvern Instrument). The suspensions containing FCHT-LDH in 0.01 M NaNO_3 was adjusted to pH 4.5–13.5. The suspensions were reacted with or without 0.2 mM bromate, chromate, or vanadate. The final pH and the EM of the mixed samples were measured. To provide more insights into the interactions of bromate, chromate, or vanadate with FCHT-LDH at the solid/aqueous interface, some selected samples were analyzed with CHNS/O, XRD, FTIR, XPS, and EXAFS. The efficiencies of different desorption solutions, namely 0.05 and 0.1 M NaOH , a mixture of 1 M NaNO_3 and 0.1 M NaOH , and 0.1 M Na_2CO_3 on bromate-loaded, chromate-loaded, or vanadate-loaded FCHT-LDH were investigated by reacting the anion-loaded sample with the solution at 1 g/L for 24 h. The desorption efficiency was defined as the ratio of the desorbed amount to the initial sorbed amount of the respective anions.

2.5. Analysis of XPS and EXAFS

The XPS surface measurements were performed in a Kratos AXIS Ultra spectrometer with a monochromatized Al $\text{K}\alpha$ X-ray source (1486.71 eV) operated at a reduced power of 150W (15kV and 10 mA). The base pressure in the analysis chamber was 2.66×10^{-7} Pa.

Binding energies were referenced to the C (1s) neutral C–C peak at 284.6 eV to compensate the effect of charging. Curve fitting of the spectra peaks was performed after a Shirley background subtraction by nonlinear least square fitting using a mixed Gaussian/Lorentzian function. The X-ray absorption near edge structure region or XANES and EXAFS measurements on chromate-loaded and vanadate-loaded FCHT-LDHs were performed at the XDD beamline of the Singapore Synchrotron Light Source (SSLS, Singapore) where a Si(1 1 1) channel-cut monochromator is equipped. The FCHT-LDH samples reacted with either chromate or vanadate solution at pH 9.5 were ground into fine powders, dispersed evenly on a clear sticky-tape, placed in a stainless steel cell, and measured in transmission mode at the Cr and V K-edge, respectively, at room temperature. The scanned energy was from 90 eV below the K-absorption edge ($E_0 = 5.989$ keV for Cr and $E_0 = 5.465$ keV for V) to 750 eV above the edge. Standards Cr-foil, Cr_2O_3 , K_2CrO_4 , K_2CrO_7 were used as references for samples with chromate, and for samples with vanadate V-foil, VO, V_2O_3 , VO_2 and V_2O_5 were analyzed. The EXAFS data were analyzed following the standard methods using the WINXAS code [18].

3. Results and discussion

3.1. Characteristics of the LDHs

Chemical compositions showed that the molar ratios of $\text{Mg}^{2+}/\text{Al}^{3+}$ in both commercial LDH and FCHT-LDH were close to the initial values of their starting salts (Table 1). Almost no change of $\text{Mg}^{2+}/\text{Al}^{3+}$ ratios for the anion-loaded FCHT-LDHs demonstrated insignificant loss of LDH crystallinity under the explored experimental condition. The CHNS/O analysis revealed the existence of N in FCHT-LDH, suggesting the successful intercalation of nitrate into the interlayer region. The relatively high C content in commercial LDH was consistent with its composition. A small amount of C in FCHT-LDH was likely originated from the atmospheric CO_2 and considered to pose insignificant effect to the anion exchange process. The surface area, pore volume, and pore size of FCHT-LDH were $127 \text{ m}^2/\text{g}$, $0.31 \text{ cm}^3/\text{g}$, and 8 nm, respectively, and they were higher by 2–8 times than those of commercial LDH having the surface area of $56 \text{ m}^2/\text{g}$, pore volume of $0.04 \text{ cm}^3/\text{g}$, and pore size of 3 nm. The XRD patterns of the fresh and anion-loaded FCHT-LDHs are illustrated in Fig. 1. The distinct reflections observed for the LDHs are (0 0 3), (0 0 6), (0 0 9), (0 1 5), (0 1 8), (1 1 0), and (1 1 3), indexed with R3m rhombohedral symmetry. Only hydrotalcite phase was observed in each sample and no other crystalline phase was detected. FCHT-LDH also showed a smaller crystallite size and a higher interlayer spacing (indicated by larger c value in Table 1) compared to the commercial LDH. FTIR spectra of the fresh and anion-loaded FCHT-LDHs were typical of hydrotalcitelike LDH material, as featured by a broad band at 3470 cm^{-1} (ν_{OH} for OH stretching vibration of hydrogen-

bonded groups in the brucite-like sheets and water in the interlayer space), a peak at 1637 cm^{-1} ($\delta_{\text{H}_2\text{O}}$ for water bending vibrations of the interlayer water), a strong peak at 1384 cm^{-1} ($\nu(\text{NO}_3^-)$ for NO_3^- intercalated in the inter-layer space), and bands at 780, 667, 556, and 448 cm^{-1} (due to M–O vibrations and M–O–H bending) (Fig. 2). FCHT-LDH was observed as well-formed and overlapping plate-like particles characteristic of layered structure with a uniform size of 40-100 nm and comprised nanocrystalline grains (see Fig.SI-1 in the Supporting information).

3.2. Comparative sorption studies of oxanions and oxyhalides having different molecular properties

Most oxyanions investigated in this study, i.e. arsenate, chromate, molybdate, selenate, and vanadate are divalent at pH 9.5 except borate whereas all of the oxyhalides including bromate, chlorate, iodate, and perchlorate are monovalent (Table SI-1). The molecular radii of the oxyanions (except borate) are generally more than 0.24 nm and their ionic potentials are about 8 nm^{-1} . The molecular radii of the oxyhalides range from 0.21 to 0.24 nm and their ionic potentials are less than 5 nm^{-1} . All the oxyanions are of tetrahedral structure while most oxyhalides are of trigonal pyramid structure. Anion selectivity is generally governed by the mobility of anions in the interlayer region of the LDH [19] which is likely dependent on the ionic charge, molecular radius, and molecular structure of the anion.

Fig. 3 depicts that FCHT-LDH attained considerably higher removal efficiency than commercial LDH for all the oxyanions and oxyhalides, primarily owing to its higher surface area, better porous nature, smaller crystallite size, and nanocrystalline property. Almost 100% of divalent arsenate, chromate, molybdate, selenate, and vanadate were successfully sorbed by FCHT-LDH whereas monovalent borate and oxyhalides (i.e. bromate, chlorate, iodate, and perchlorate) sorbed by FCHT-LDH were 55% and <20%, respectively. Apparently, the divalent anions were more favorably sorbed by FCHT-LDH compared to the monovalent anions. Based on the sorption results, the anions can be generally grouped into two classes: (1) anions favorably sorbed by FCHT-LDH which ionic potentials are higher than 7 nm^{-1} (oxyanions with $z = 2$) and (2) anions unfavorably sorbed by FCHT-LDH which ionic potentials are lower than 5 nm^{-1} (oxyanions and oxyhalides with $z = 1$). The ionic potential (μ) is defined as z/r , where z is the ionic charge and r is the molecular radius [20]. The ionic potential will greatly influence the degree to which water dipoles are attracted to the ion, and thus will also determine the mobility of the anion in aqueous solution. The tetrahedral oxyanions appeared to be more preferably sorbed by FCHT-LDH than the trigonal pyramid oxyhalides. Tetrahedral coordinated anions have also been reported to show a higher degree of specificity for the surface of precipitated hydrous iron oxides than the trigonal planar anions in a previous study [21]. The relatively low sorption efficiency of FCHT-LDH for borate was partially due to a transition in its coordination from tetrahedral $\text{B}(\text{OH})_4^-$ to trigonal HBO_3^{2-} during the

incorporation of B(OH)_4^- into FCHT-LDH (at $\text{pH} > 9.2$) which would require elimination of an energy barrier [22].

3.3. Sorption characteristics of bromate, chromate, and vanadate

The equilibrium sorption capacity of bromate on FCHT-LDH decreased with the increasing temperature from 25 to 55 °C (Fig. SI-2). In contrast, the sorption capacities of both chromate and vanadate increased with temperature, attributable to increased diffusivity and activity of the oxyanions that facilitated their incorporation into FCHT-LDH. Overall, Langmuir isotherm fitted the equilibrium data of anions better than Freundlich isotherm, on the basis of the linear coefficient of determination (R^2) and nonlinear Chi-square (χ^2) statistical test (Table 2). The characteristics of a Langmuir isotherm can be described in terms of a dimensionless separation factor, R_L [23], which explains the type of isotherm and is defined by:

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

where K_L is the Langmuir sorption constant (L/cmol), C_0 is the initial concentration of anion (cmol/L), and if $R_L > 1 \Rightarrow$ unfavorable, $R_L = 1 \Rightarrow$ linear, $0 < R_L < 1 \Rightarrow$ favorable, and $R_L = 0 \Rightarrow$ irreversible.

The values of R_L were found to be less than 1 for bromate, chromate, and vanadate sorption on FCHT-LDH, suggesting that the sorption process was favorable (Table 2). The values of heterogeneity factor ($1/n$) were less than 1 for all the anions, confirming their favorable sorption on FCHT-LDH. Among the investigated anions, the sorption capacity for chromate on FCHT-LDH was the highest ($q_m = \sim 120$ cmol/kg), and followed by vanadate and bromate. The Freundlich constant related to the sorption capacity (K_F) for chromate and vanadate sorption was much larger than that of bromate. The higher sorption capacities of chromate and vanadate on FCHT-LDH were possibly due to their higher ionic potential and tetrahedral coordination compared to those of bromate.

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

$$\Delta G^\circ = -RT \ln K_c \quad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

where R is universal gas constant (8.314 J/mol K), T is temperature (K), and K_c is defined as the thermodynamic equilibrium constant. K_c values can be obtained by plotting $\ln(C_s/C_e)$

vs C_s and extrapolating C_s to zero, where C_s is the surface concentration of anion (cmol/kg) and C_e is the concentration of anion in bulk solution at equilibrium (cmol/L) (see details in the Supporting information). The values of ΔH° and ΔS° can be derived respectively from the slope and intercept of the van't Hoff plot (insets in Fig. SI-2). The negative values of ΔG° for all the anions indicated the spontaneous nature of their sorption on FCHT-LDH (Table 2). Higher negative ΔG° values of chromate and vanadate showed that their sorption on FCHT-LDH were more energetically favorable than that of bromate. The positive values of ΔH° and ΔS° indicated the endothermic nature of chromate and vanadate sorption on FCHT-LDH and suggested the increased randomness at the solid/aqueous interface during the sorption process. In the contrary, bromate sorption on FCHT-LDH was an exothermic process and resulted in decreased randomness at the solid/aqueous interface and degree of freedom of the sorbed species. The kinetic curves showed that anion sorption on FCHT-LDH was a rapid process with equilibrium generally attained within 4 h (Fig. 4). This type of fast sorption process involving LDHs has been reported to be due to ion exchange reactions [24]. Bromate sorption on FCHT-LDH was considerably faster than those of chromate and vanadate, indicating that molecular property of an anion had a significant effect on their sorption rate on FCHT-LDH and also on their equilibrium sorption capacity.

Fig. 5a illustrates the effects of pH and ionic strength on bromate, chromate, and vanadate sorption on FCHT-LDH. At the ionic strength of 0.005 M, more than 90% of the chromate was sorbed by FCHT-LDH in the pH range of 4.4–10.2, and the sorption decreased drastically at higher pH. Vanadate sorption was more than 95% at pH 5–7, but decreased significantly at pH >7, which coincided approximately with the second pK_a (7.3) of H_3VO_4 [25]. The sorption of bromate was about 19% at pH 4.5 and reduced gradually to 14% as the pH increased to 11. The insensitivity of bromate sorption to pH change was probably due to the presence of single negatively charged bromate species at pH ranging from 4.5 to 11 ($HBrO_3 \leftrightarrow BrO_3^- + H^+$; $pK_a = 1.87$) [26]. The lower sorption of chromate or vanadate at high pH values was owing to an increased Donnan exclusion between the more negatively charged chromate or vanadate species and negatively charged surface sites of FCHT-LDH. The competition between carbonate (from atmospheric CO_2) or hydroxide ion (from NaOH) and chromate or vanadate for the sorption sites on FCHT-LDH might also partially contribute to the lower anions sorption at high pH. The sorption of chromate decreased more gradually with increasing pH compared to vanadate because chromate has comparatively less negatively charged species at the same pH value, and therefore they do not exhibit as much repulsion as vanadate with the FCHT-LDH. These results confirmed that both chromate and vanadate have stronger affinities for FCHT-LDH than bromate over a broad pH range.

3.4. Sorption mechanisms

The reduction of N in FCHT-LDH was more significant for the sorption of chromate and vanadate which have higher ionic potentials compared to that of the lower ionic-potential bromate (Table 1). This result indicated the occurrence of ion exchange process between the guest anions and the interlayer nitrate in FCHT-LDH. The anion-loaded FCHT-LDHs showed the shift of (0 0 3) reflection peaks in the XRD patterns to a lower 2θ and slight increased interlayer spacing after the sorption process (Fig. 1 and Table 1), further suggesting the exchange of anion with nitrate in the interlayer region. Marginal increase of interlayer spacing of LDHs after incorporation of chromate has also been reported by some researchers [27,28]. The increment of interlayer spacing was larger for the FCHT-LDHs loaded with higher concentration of anions, implying the expansion of interlayer region to accommodate more guest anions for the exchange process. The broad peak with lower intensity observed at 22.5° for chromate-loaded FCHT-LDHs was probably due to the slight structural disorder arising out of stacking faults. The FTIR band of interlayer nitrate (1384cm^{-1}) for all the anion-loaded FCHT-LDHs became weaker after the sorption process, while new bands corresponding to Br–O stretching vibration, Cr–O stretching vibration and V–O stretching vibration, appeared at 791 cm^{-1} , 883 cm^{-1} , and 824 cm^{-1} , respectively (Fig. 2). All the results of CHNS/O, XRD, and FTIR have demonstrated that anion exchange played a significant role in the sorption mechanism of bromate, chromate, and vanadate onto FCHT-LDH.

The study of ionic strength effect on sorption at the solid/aqueous interface and EM measurements can be used to indirectly distinguish between the formation of outer-sphere and inner-sphere complexes [29]. Both bromate and chromate sorption appeared to be sensitive to the changes in ionic strength in the pH range of 4.5–11 (Fig. 5a). Vanadate sorption was unaffected by the changes in ionic strength in the pH range of 5–7, but decreased slightly with increasing ionic strength at pH 7–11. These findings suggested that bromate and chromate might predominantly form outer-sphere complexes on FCHT-LDH at pH 4.5–11, while the formation of outer-sphere vanadate complexes on FCHT-LDH was predominant at pH 7–11. Vanadate sorption on FCHT-LDH was less influenced by ionic strength compared to those of bromate and chromate, probably due to the energetic sorption activity of vanadate (indicated by higher negative ΔG° values) that led to weaker competition between the electrolyte ion and vanadate for the available surface sites on FCHT-LDH. The formation of outer-sphere complexes on FCHT-LDH by these anions was resulted from the anion exchange process (an electrostatic Coulombic interaction). Fig. 5b shows that the isoelectric point (IEP) of FCHT-LDH was ~ 13.5 . Sorption of bromate resulted in insignificant EM change and IEP shift. Sorption of chromate and vanadate however resulted in lower EM between pH 7–13 but did not significantly shift the IEP. These EM measurements again implied that bromate predominantly formed outer-sphere complexes on FCHT-LDH at pH 4.5–13.5. The relatively larger reduction in EM for chromate and vanadate sorption on FCHT-LDH (at pH > 7) can be explained by either the formation of outer-sphere complexes or the formation of both outer-sphere and inner-

sphere complexes.

Among the desorption solutions, the highest desorption rate were attained by desorbing anion-loaded FCHT-LDHs in Na_2CO_3 , i.e. ~100% for bromate, ~90% for chromate, and ~58% for vanadate. The high bromate desorption rate suggested that bromate sorption on FCHT-LDH was reversible and non-specific, mainly due to its low ionic potential and weaker affinity for FCHT-LDH. It could be therefore deduced that bromate sorbed on FCHT-LDH via predominant anion exchange mechanism and formed outer-sphere complexes and this hypothesis was supported by the study of ionic strength effect and the EM measurements. In contrast, a significant fraction of vanadate (~42%) was not displaceable by Na_2CO_3 . A small fraction of non-displaceable chromate (~10%) was also observed. These results generally suggested the occurrence of irreversible and specific adsorption of vanadate and chromate to the FCHT-LDH surface through ligand exchange mechanism which would subsequently form inner-sphere complexes of vanadate and chromate in addition to the predominant outer-sphere complexes formed by the anion exchange mechanism. The exchange of chromate or vanadate with the OH ligands on the FCHT-LDH surface was possible since these ligands are hard bases which preferably react with hard acids like Al^{3+} center, based on Pearson's hard and soft acid-base theory. The singly coordinated OH groups at the edges of FCHT-LDH were believed to be primarily responsible for the ligand exchange mechanism whereas the less-reactive OH groups, i.e. doubly coordinated OH at the edges and triply coordinated OH on the planar surfaces might play a secondary role, based on the observations reported for mineral surfaces [30,31].

3.5. Surface structures

Additional spectral evidence and structural data were collected using XPS and EXAFS spectroscopies to provide more direct information on the formation of anion complexes on FCHT-LDH. The XPS spectra of Mg 2p of FCHT-LDH before and after bromate, chromate, and vanadate sorption showed insignificant change, indicating that Mg atoms might not take part in their sorption (Fig. 6a). In comparison with Mg 2p, a noticeable increase of the Al 2p spectra intensity of FCHT-LDH was observed after chromate and vanadate sorption, showing their strong interaction with Al atoms (Fig. 6b). Conversely, the Al 2p spectra showed almost no change following bromate sorption on FCHT-LDH. These results suggested that Al atoms played a key role in chromate and vanadate sorption, but not in bromate sorption. O 1s narrow scans showed that the O 1s spectra of FCHT-LDH and anion-loaded FCHT-LDHs were quite different (except for bromate-loaded FCHT-LDHs), demonstrating that the oxygen constituents of FCHT-LDH changed after chromate and vanadate sorption (Fig. 6c). The disappearance of the peak at 406.5 eV (N 1s) following chromate and vanadate sorption implied the successful exchange of nitrate

with chromate and vanadate (Fig. 6d). On the other hand, the N 1s spectra of bromate-loaded FCHT-LDHs were almost unchanged and bromate was not detected on FCHT-LDH surface after the sorption process, indicating weak surface interaction between bromate and FCHT-LDH.

Fig. 7 presents the valence band photoelectron spectra of FCHT-LDH before and after anion sorption. The spectra of bromate-loaded FCHT-LDH were similar to that of fresh FCHT-LDH. It was observed that chromate and vanadate sorption influenced the nature of the valence band spectrum more substantially than that of bromate. The valence bands of chromate-loaded and vanadate-loaded FCHT-LDHs were shifted by about 2 eV to less negative binding energy relative to FCHT-LDH, whereas the intensity of the peaks were considerably higher. This spectroscopic variation suggested the formation of inner-sphere chromate and vanadate complexes on FCHT-LDH [32]. Furthermore, the stoichiometric ratio of OH⁻ between the fresh FCHT-LDH and anion-loaded FCHT-LDH was 1.8:1 for chromate-loaded FCHT-LDH and 1.9:1 for vanadate-loaded FCHT-LDH (Table 3), respectively, which was close to the configuration of the inner-sphere bidentate surface complexes [30]. The insignificant change of the content of OH⁻ for bromate-loaded FCHT-LDH further confirmed the absence of the inner-sphere surface complex.

The XANES spectra as well as the energies of the absorption edge (determined from the related zero crossing of the derivative spectrum (points) for a series of references with known oxidation states) of chromate sorbed on FCHT-LDH appeared to be the same as reference Cr(VI) (K₂Cr₂O₇ and K₂CrO₄) whereas those of vanadate sorbed on FCHT-LDH was located at energy value that was similar to that determined for V₂O₅ (Fig. SI-3). These XANES data confirmed that chromate sorbed on FCHT-LDH in the form of Cr(VI) and vanadate sorbed in the form of V(V), showing no reduction of chromate or vanadate after their sorption. In the EXAFS analysis, the first peaks in the Fourier transformed spectra in Fig. 8a and b were resulted from the Cr–O and V–O shells, respectively. The average interatomic distance (*R*) was 1.66 Å for chromate-loaded FCHT-LDH and 1.72 Å for vanadate-loaded FCHT-LDH. The average coordination number (CN) of oxygen was about 4 for both chromate and vanadate samples, confirming the tetrahedral geometry of these oxyanions. The second peaks centered at 2.5–3.0 Å with the CN of about 1 were attributed to chromate and vanadate bonding with Al. The EXAFS features indicated that chromate and vanadate were possibly adsorbed on FCHT-LDH by forming inner-sphere bidentate surface complexes, which was consistent with the previous EXAFS studies of the association of polyvalent oxyanions on similar mineral surfaces [29,33]. The inner-sphere bidentate complexes involved ionic bonding, covalent bonding or some combinations of covalent and ionic bonding [34]. The exact bonding mechanism at different experimental conditions can be further determined by a combined and comprehensive XANES and EXAFS analyses [35].

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

Conversely, two mechanisms have been found responsible for the sorption of chromate or vanadate on FCHT-LDH, i.e. primary anion exchange and secondary ligand exchange mechanisms, resulting in a mixture of outer-sphere and inner-sphere complexes of chromate or vanadate. These postulated mechanisms and surface complexes are described in the following equations:

Mechanism 1 (anion exchange) :

Mechanism 1 (anion exchange) :

Mechanism 2 (ligand exchange) :

Mechanism 2 (ligand exchange) :

4. Conclusions

The Mg/Al LDH nanoparticles prepared in this study (FCHTLDH) have shown excellent potential for use as a new sorbent for harmful anions removal from aqueous solution owing to its simple preparation method, high sorption capacity, and reusability. Both molecular properties of the anions and physicochemical properties of the LDH nanoparticles can play important roles in the sorption process. FCHT-LDH exhibited a much higher sorption capacity for divalent oxyanions (i.e. chromate and vanadate) than monovalent oxyhalides (i.e. bromate), attributable to their higher ionic potential and tetrahedral coordination. Chromate and vanadate sorption on FCHT-LDH were endothermic, while bromate sorption was exothermic. Sorption of chromate and vanadate were more sensitive to changes in pH than bromate. The kinetic study showed that the sorption of bromate, chromate, and vanadate on FCHT-LDH was a rapid process with equilibrium generally attained within 4

h. Macroscopic and microscopic studies suggested that monovalent oxyhalide sorption on FCHT-LDH was occurred through anion exchange mechanism with formation of outer-sphere complexes whereas polyvalent oxyanion sorption involved anion exchange and ligand exchange reactions with formation of both outer-sphere and inner-sphere complexes. The chemical bond in the inner-sphere complexes can be ionic, covalent, or a combination of the two.

Despite the promising performances of the FCHT-LDH in the sorption of polyvalent oxyanions, the chemical stability of this material and their sorption ability in the aqueous matrix (e.g., the presence of carbonate) may be crucial for its application in water treatment. Therefore future research should deliberately focus on studying the influences of diverse co-existing ions on anions sorption by FCHT-LDH, examining the solubility of FCHT-LDH under various environmental conditions, and further enhancing its crystallinity through novel synthesis in order to ensure sorbent stability and sorption ability for prolonged application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jhazmat.2010.03.077](https://doi.org/10.1016/j.jhazmat.2010.03.077).

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Table 1

Sample	Composition	Lattice parameter			
		$\text{Mg}^{2+}/\text{Al}^{3+}$ (molar ratio)	C (wt%)	N (wt %)	Crystal size ^c (nm)
Commercial LDH	3.1/1	9.2	1.4	3.04	22.67
FCHT-LDH (fresh)	2.0/1	0.7	3.3	3.04	23.53
Bromate-loaded (20 mg/L)*	1.9/1	0.8	2.1	3.05	23.51
Bromate-loaded (100 mg/L)	1.9/1	0.8	2.0	3.05	23.53
Chromate-loaded (20 mg/L)	1.9/1	0.6	0.8	3.05	23.65
Chromate-loaded (100 mg/L)	1.8/1	0.6	0.5	3.04	23.85
Vanadate-loaded (20 mg/L)	1.9/1	0.9	0.9	3.06	23.82
Vanadate-loaded (100 mg/L)	1.8/1	1.2	0.8	3.06	24.01

^a $a = 2 \times d(110)$.

^b $c = 3 \times d(003)$.

^c Average size determined from fwhm of peak (003) and (006) using Scherer equation.

* Numbers in parentheses denote the initial concentrations of oxyanion or oxyhalide used for sorption equilibration with FCHT-LDH.

Anion	Temperature (°C)	Freundlich isotherm ^a				Langmuir isotherm ^b				Thermodynamics			
		$(K_F \text{ (cmol/kg)}/(\text{cmol/L})^{1/n})$	n	R^2	χ^2	$K_L \text{ (L/cmol)}$	$q_m \text{ (cmol/kg)}$	R_L^c	R^2	χ^2	$\Delta G^\circ \text{ (kJ/mol)}$	$\Delta H^\circ \text{ (kJ/mol)}$	$\Delta S^\circ \text{ (J/mol K)}$
Bromate	25	46	1.74	0.986	0.26	55	10	0.32	0.979	0.56	-4.65	-4.64	-0.028
	35	32	1.67	0.992	0.09	46	7	0.36	0.974	0.31	-4.57		
	45	29	1.71	0.979	0.17	48	7	0.35	0.953	0.31	-4.71		
	55	46	1.33	0.941	0.54	36	6	0.42	0.976	0.21	-4.60		
Chromate*	25	704	1.71	0.963	7.41	108	116	0.09	0.996	1.16	-5.60	3.00	29
	35	715	1.75	0.957	8.48	123	116	0.08	0.995	1.83	-5.89		
	45	640	1.89	0.927	14.48	142	118	0.07	0.984	7.34	-6.18		
	55	534	2.23	0.960	14.31	210	119	0.05	0.975	23.10	-6.47		
Vanadate*	25	290	2.36	0.913	15.83	408	61	0.02	0.960	8.36	-5.88	4.04	33
	35	323	2.41	0.922	13.35	480	69	0.02	0.954	19.77	-6.21		
	45	330	2.49	0.942	15.21	423	79	0.02	0.944	17.35	-6.54		
	55	299	2.95	0.920	20.77	1290	78	0.01	0.928	17.59	-6.88		

^a Freundlich isotherm: $q_e = K_F C_e^{1/n}$ where q_e is the amount of anion sorbed at equilibrium (cmol/kg), K_F is the Freundlich constant ((cmol/kg)/(cmol/L)^{1/n}), C_e is the concentration of anion at equilibrium (cmol/L), and $1/n$ is the heterogeneity factor.

^b Langmuir isotherm: $C_e/q_e = 1/(K_L q_m + C_e/q_m)$ where K_L is the Langmuir sorption constant (L/cmol) and q_m signifies sorption capacity (cmol/kg).

^c $R_L = 1/(1 + K_L C_0)$ where $C_0 = 0.039 \text{ cmol/L}$ for bromate, 0.096 cmol/L for chromate, and 0.098 cmol/L for vanadate.

* Concurrent monitoring of the solution pH showed a slight pH increment of about 0.5 during chromate and vanadate sorption equalization.

Table 2

Table 3

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

Note: All the peaks modeled as 70:30 Gaussian:Lorentzian.

^a Surface species: O²⁻ indicates oxygen bonded to metal; OH⁻ indicates hydroxyl bonded to metal; H₂O indicates surface and interlayer water.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8