

Chromate uptake characteristics of the pristine layered double hydroxides of Mg with Al

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Abstract

The layered double hydroxides (LDHs) of Mg with Al readily scavenge dissolved chromate ions under a wide range of conditions. While the chromate uptake is quantitative in the LDH containing 33 mol% Al, the uptake is only 58% of the stoichiometric value in the LDH containing 25 mol% Al. This indicates that the lower symmetry of the NO_3^- ions in the LDH with 33 mol% Al facilitates the intercalation of chromate ions even under conditions of equilibration with excess dissolved nitrate ions. The chromate uptake obeys the Langmuir adsorption isotherm suggesting that the entire interlayer region of the LDH behaves like a surface. This surface is structural rather than morphological as the chromate uptake correlates negatively with the BET surface area of the LDHs.

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1. Introduction

Layered double hydroxides constitute an important class of layered materials with potential applications for the remediation of anionic contaminants. The structure of LDHs is derived from that of mineral brucite, $\text{Mg}(\text{OH})_2$ [1]. Brucite comprises a close packing of hydroxyl ions in which Mg^{2+} ions occupy alternative layers of octahedral sites, leading to stacking of charge-neutral metal hydroxide slabs of composition $[\text{Mg}(\text{OH})_2]$ [2]. When a fraction, x , of Mg^{2+} ions is isomorphously substituted by a trivalent ion such as Al^{3+} or Fe^{3+} , the positive charge $x+$ generated on the metal hydroxide slab is compensated by the inclusion of anions, A^{n-} , in the interlayer region to give LDHs of composition $[\text{M}_{1-x}^{II}\text{M}_x^{III}(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ ($\text{M}^{II} = \text{Mg}, \text{Ca}, \text{Co}, \text{Ni}, \text{Zn}$; $\text{M}^{III} = \text{Al}, \text{Cr}, \text{Fe}$; $0.2 \leq x \leq 0.33$) [3]. We refer to these LDHs as $[\text{M}-\text{M}'-\text{A}]_x$. The subsequent exchangeability of the interlayer anion makes LDHs potential candidates for

sequestration of anionic contaminants such as chromates, arsenates, phosphates, iodides and selenates from solution. Chromates are among the common pollutants in industrial water and their remediation by the use of LDHs is of interest.

Although chromate-intercalated LDHs have been reported [4–6], there is a paucity of literature on the use of LDHs for remediation of anionic pollutants. There are several reasons for this.

1. Among all the anions, the most ubiquitous in industrial as well as natural water bodies is the CO_3^{2-} ion. Crystal chemical considerations favor the incorporation of CO_3^{2-} into the interlayer owing to (a) the matching of the symmetry of the CO_3^{2-} ion with the local symmetry of the interlayer site and (b) the strong hydrogen bonding between the hydroxyl ions of the layer with the carbonate ions. Consequently CO_3^{2-} containing LDHs do not participate in any anion exchange reactions [7].
2. Mineralization of the anionic contaminants would be successful only if the anion incorporated LDH is thermodynamically more stable than the precursor LDH. This is not often the case. Recent reports suggest that unlike the

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cationic clays, the LDHs have a relatively soluble ‘framework’ [8]. Consequently chromate containing LDHs redissolve and the anion is leached out partially or completely [9]. There is an equal likelihood for the formation of unitary (comprising a single metal ion) salts of the incoming anion. Thus phosphates tend to combine with the metal ions to yield metal phosphates, rather than phosphate intercalated LDHs [10,11].

On account of the difficulties arising due to carbonate interference, many authors report the sorption of chromate ions by the oxide residue obtained from the thermal decomposition of the LDHs [12–15]. On thermal decomposition, the LDH of Mg with Al yields an oxide residue having the structure of periclase, with Al^{3+} partially substituting for Mg^{2+} [16]. The oxide residue has certain fundamental differences with the hydroxide precursor:

- (i) The precursor hydroxide is layered, while the oxide has a 3-D structure. The former has an active interlayer region, which the latter lacks. The layered structure is therefore expected to have a higher chromate uptake capacity.
- (ii) The precursor has surface basicity [17] while the oxide residue has surface acidic sites.
- (iii) The interlayer chemistry is reversible paving the way for possible recycling of the chromate.

Thus the nature of the interaction with the adsorbate is fundamentally different for a layered material as opposed to a 3-D oxide. The sequestration of the anions by means of anion exchange reactions depends upon several factors such as (a) solubility of the LDHs, (b) selective uptake of the anions, (c) the stability of the pristine LDHs relative to that of the exchanged product and (d) mechanistic and energetic aspects of uptake. The dearth of reports that aim to contribute towards understanding these factors suggests that there are fundamental problems limiting the use of LDHs in chromate scavenging applications despite its potential from the crystal chemical point of view. This paper aims to study the characteristics of chromate uptake by the pristine LDHs of Mg with Al having NO_3^- as the exchangeable anion by means of anion exchange reactions. We correlate the Al^{3+} content of the pristine LDH with the uptake characteristics and reflect upon the implications of these results on the nature of chemical reactivity in the interlayer region.

2. Experimental

All reagents were of analytical grade (Merck, India) and were used without further purification. The $[\text{Mg}-\text{Al}-\text{NO}_3]_x$ LDHs ($x = 0.25$ and 0.33) were prepared by the drop-wise addition (3 ml min^{-1}) of a mixed metal salt solution $[\text{Mg}(\text{NO}_3)_2 + \text{Al}(\text{NO}_3)_3]$ into a reservoir containing 10 times the stoichiometric requirement of NO_3^- ions taken as its sodium salt. NaOH (2 M) was dispensed using a Metrohm model 718 STAT Titrino to maintain a constant pH (9.0) at precipitation.

N_2 gas was bubbled through the solution during precipitation and aging for 18 h at 65°C . The precipitate was rapidly filtered under suction and washed with deionized (10^{15} ohm cm specific resistance), decarbonated water and then dried at 80°C for 24 h.

All samples were characterized by powder X-ray diffraction using X’pert Pro Philips diffractometer (Cu $K\alpha_1$ source, $\lambda = 1.5405 \text{ \AA}$) fitted with a graphite monochromator. IR spectra in the transmission mode were recorded using a Nicolet model Impact 400D FTIR spectrometer ($4000\text{--}400 \text{ cm}^{-1}$, resolution 4 cm^{-1} , KBr pellet). Attenuated total reflectance (ATR) spectra were collected using a SMART ORBIT[®] ATR accessory and a Nicolet 6700 infrared spectrometer, Thermo Electron Corporation, USA. Diamond crystal (refractive index 2.4) was used to collect the spectra ($4200\text{--}200 \text{ cm}^{-1}$, resolution 4 cm^{-1} , DTGS Detector with KBr window, Ge coated KBr as beam splitter). Background spectrum was taken before the spectrum collection of each sample. TGA studies were carried out using a Mettler-Toledo 851^e TG/SDTA system driven by Star^c 7.1 software (heating rate 5°C min^{-1} , N_2 gas). The samples were first heated to 100°C in the TG balance for 0.5 h to drive away the adsorbed water before being ramped up to 800°C . The BET surface areas of the samples were measured using a NOVA 1000 Ver. 3.70 high speed gas sorption analyzer.

2.1. Chromate uptake studies

Pre-weighed (0.20 g) batches of the LDH were suspended in 25 ml of decarbonated water and stirred for 30 min to ensure complete wetting. To this slurry 25 ml of K_2CrO_4 solution (0.008–0.1 M, pH 8.5–9.0) was added and stirred for 5 h at the ambient temperature ($22\text{--}26^\circ\text{C}$) after which the slurry was centrifuged and the chromate concentration of the centrifugate determined by means of potentiometric titration versus standard (0.025–0.1 N) ferrous ammonium sulphate (FAS) solution. For low chromate concentrations ($\leq 0.00416 \text{ M}$), a larger volume (100–150 ml) of the K_2CrO_4 solution was used to affect the chromate uptake. The chromate uptake by the LDHs was calculated from the difference in the initial and final chromate concentrations and is reported in moles of chromate exchanged per mole of LDH taken. From this data, isotherms were plotted. Chromate uptake studies were also carried out at 4°C and 65°C in a similar manner. The precursors namely the LDH slurry and K_2CrO_4 solution were maintained at the respective temperatures for 30 min to attain constant temperature before mixing. Chromate uptake was also measured from K_2CrO_4 solutions which were made 1 M in KNO_3 to study the effect of relative activities of the anions on the uptake of chromate ions. The isotherms obtained under these conditions when the pristine LDH is in equilibration with the nitrate ions in solution were used to obtain Langmuir plots.

Conventional anion exchange reactions were carried out by suspending pre-weighed (0.20 g) batches of the LDH in 30 ml of K_2CrO_4 solution containing 10 times the stoichiometric requirement of chromate ions required to affect a complete

exchange of the anions in the pristine LDH. The reaction was carried out for 5 h with stirring after which the solid was separated by centrifugation and washed with deionized, decarbonated water. The chromate uptake observed in these experiments is referred to as the ‘chromate carrying capacity’ and is compared with the theoretical exchange capacity computed from the molecular formula. The chromate immobilized in the solid LDH was estimated by dissolving a pre-weighed (0.2 g) quantity of the sample in acid (2 ml of conc. H_2SO_4) and titrating against standard ferrous ammonium sulphate (0.025 N) solution potentiometrically. The CrO_4^{2-} content was estimated in equivalents of Cr to obviate the need of estimating independently the CrO_4^{2-} ($\text{pH} > 6$) and $\text{Cr}_2\text{O}_7^{2-}$ ($\text{pH} < 6$) species.

3. Results and discussion

3.1. Characterization of pristine LDHs

On account of their high solubility [8], the use of LDHs for water decontamination applications is limited to only those comprising benign cations such as Mg, Ca, Al and Fe. Fig. 1 shows the PXRD patterns of $[\text{Mg}-\text{Al}-\text{NO}_3]_{0.25}$ and $[\text{Mg}-\text{Al}-\text{NO}_3]_{0.33}$ LDHs. These patterns are indexed to a hexagonal cell. The basal reflections $00l$ at low angles correspond to the interlayer distances of 8.0 Å (11.0° , 2θ) and 8.9 Å (9.9° , 2θ) of the LDHs having $x = 0.25$ and 0.33 compositions, respectively. The 110 reflections appear at high angles (60.3° and 60.8° (2θ), respectively, for $x = 0.25$ and 0.33). The lattice parameters are estimated as $c = l \times d_{00l}$; $a = 2 \times d_{110}$ and agree well with the values reported in the literature (Table 1). The non-uniform broadening of lines in the mid- 2θ region (30° – 50°) is indicative of structural disorder.

The large difference in the interlayer distances points to differences in the mode of incorporation of nitrate ions into the interlayer region. A distance of 7.6–8.0 Å is characteristic

Table 1
Characterization of pristine and chromate-intercalated LDHs

LDH	Cell parameters		TGA mass loss ^a (%)	Chromate carrying capacity ^b	CrO_4^{2-} content (mol%)
	a (Å)	c (Å)			
$[\text{Mg}-\text{Al}-\text{NO}_3]_{0.25}$	3.056	23.97	46.7 (48.5)	0.073	—
$[\text{Mg}-\text{Al}-\text{NO}_3]_{0.33}$	3.049	26.93	47.3 (50.6)	0.165	—
$[\text{Mg}-\text{Al}-\text{CrO}_4]_{0.25}$	3.056	24.46	45.5 (41.7)	—	0.070
$[\text{Mg}-\text{Al}-\text{CrO}_4]_{0.33}$	3.049	9.07	37.3 (36.7)	—	0.155

^a Values in parentheses are the expected mass loss.

^b Mole of chromate per mole of LDH.

of a single atom thick interlayer which corresponds to the NO_3^- ion intercalated with its plane perpendicular to the c -crystallographic axis. In this mode of intercalation, the coordination symmetry of the NO_3^- ion in the interlayer is D_{3h} which matches with that of the free ion. The higher interlayer spacing of 8.9 Å is evocative of an interlayer which is 2–3 atoms thick. There have been two proposals in the literature to explain this higher interlayer spacing which is observed when $x = 0.33$:

- (1) The NO_3^- ion is intercalated with one of its N–O bonds parallel to the c -axis, i.e. the plane of the NO_3^- ion is parallel to the c -crystallographic axis [18,19]. Halford’s rule suggests that for a ‘molecule in a solid’ approach, the crystallographic axis is to be used as the principal axis of symmetry for the molecular fragment [20]. By this notion, the nitrate behaves as a ‘molecule’ with C_{2v} symmetry.
- (2) The NO_3^- ions are arranged in a bilayer, with their planes perpendicular to the c -crystallographic axis. The bilayer model, also called the ‘stick-lying’ model [21] retains the nitrate ions in the D_{3h} symmetry.

There is considerable discussion in the literature regarding the relative merits of the two models [22,23]. The two modes of coordination must in principle be distinguished by their IR spectra, as the NO_3^- ion in D_{3h} symmetry has only one allowed mode of vibration ν_3 (E' symmetry) in the 1500–1200 cm^{-1} region [24]. In the C_{2v} symmetry this mode is expected to split into two modes of A_1 and B_1 symmetries; the extent of split, $\Delta\nu$, is reflective of the strength of binding between the metal hydroxide slab and the N–O bond oriented towards it [25,26]. Weaker interactions are expected to yield a smaller splitting.

IR investigations of the $[\text{Mg}-\text{Al}-\text{NO}_3]$ LDHs have yielded conflicting results. Xu and Zeng [21] report identical spectra for $x = 0.25$ as well as for $x = 0.33$ compositions and their spectrum matches with that expected of the nitrate in the D_{3h} symmetry. Their proposal of the ‘stick-lying’ model is based on this observation. Wang and Wang [22] report a spectrum for the $x = 0.33$ composition which is very different from that of the $x = 0.25$ composition.

The difference in the results reported in the two papers is on account of the different manner in which the two groups have acquired their spectral data. The data of Xu and Zeng [21] is obtained in the transmission mode using a pressed KBr pellet.

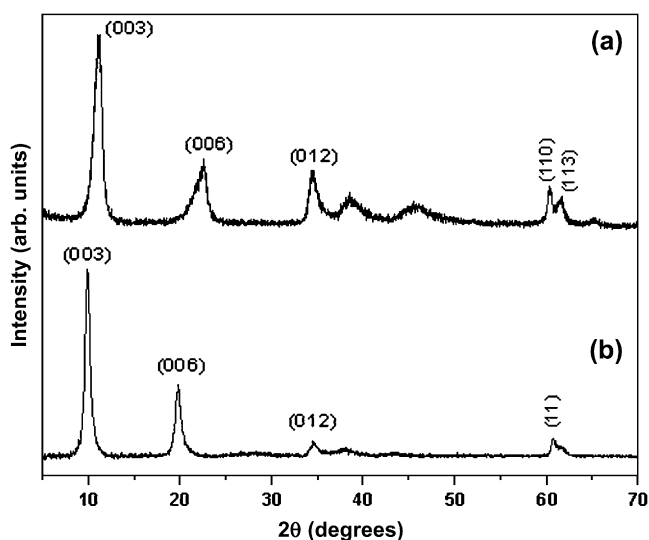


Fig. 1. PXRD patterns of (a) $[\text{Mg}-\text{Al}-\text{NO}_3]_{0.25}$ and (b) $[\text{Mg}-\text{Al}-\text{NO}_3]_{0.33}$ LDHs.

It is well known that during pelletization, the Br^- ion interacts strongly with the intercalated nitrate ion, replacing the latter [25,27]. Free nitrate is released from the LDH, which yields a spectrum corresponding to the D_{3h} symmetry. In Fig. 2(a), we show the vibrational spectra in $1500\text{--}1200\text{ cm}^{-1}$ region recorded in the transmission mode, using KBr pellets. It is evident that the ν_3 band at 1388 cm^{-1} in the $x = 0.33$ composition is very narrow (FWHM = 5 cm^{-1}), compared to the same band observed in the $x = 0.25$ composition (FWHM = 25 cm^{-1}). These spectra indicate that NO_3^- ions are released with greater ease from the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH, a point which we will return to later.

Wang and Wang [22] report data obtained from an ATR cell and clearly report the splitting of the ν_3 mode into two absorptions at 1350 cm^{-1} and 1426 cm^{-1} ($\Delta\nu = 75\text{ cm}^{-1}$) in the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH, expected of the nitrate in the C_{2v} symmetry. The $[\text{Mg-Al-NO}_3]_{0.20}$ LDH yields a smaller $\Delta\nu = 30\text{ cm}^{-1}$ showing only a minor departure from the D_{3h} symmetry. The $x = 0.25$ composition yielded a spectrum comprising both the kinds of NO_3^- ions. Polarized-ATR results clearly showed that the NO_3^- ions with the smaller $\Delta\nu$ are oriented with their planes nearly perpendicular to the c -crystallographic axis, while the NO_3^- ions with larger $\Delta\nu$ are coordinated with their planes nearly parallel to the c -crystallographic axis [22].

In Fig. 2(b) are shown our ATR measurements of the two LDHs. The spectra clearly show the lifting of degeneracy of the ν_3 (E') mode (1340 cm^{-1} and 1420 cm^{-1}) in the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH, whereas the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH exhibits a single absorption. These measurements provide evidence for the change in nitrate orientation with layer charge. These results are also supported by molecular dynamics calculations on the related $[\text{Ni-Al-NO}_3]_{0.25,0.33}$ LDHs [23]. The most probable tilt angle for the $[\text{Ni-Al-NO}_3]_{0.25}$ LDH is evaluated to be 15° (nearly D_{3h} symmetry) whereas

for the $[\text{Ni-Al-NO}_3]_{0.33}$ LDH, the tilt angles from 65° to 90° (nearly C_{2v}) are equally probable. Here the tilt angle refers to the angle made by the plane of the nitrate ion with the underlying metal hydroxide slab.

The NO_3^- ion in the D_{3h} symmetry occupies a larger number of interlayer sites [3]. As the positive charge ‘ x ’ on the layer increases from 0.25 to 0.33, large number of NO_3^- ions is required to restore charge neutrality. A reorientation in the C_{2v} symmetry provides a more tightly packed interlayer. Such transitions in the anion orientation are quite common among the LDHs [28]. This difference in the coordination symmetry, as we show later, profoundly affects the chromate uptake capacity of the two LDHs.

To conclude, IR spectra obtained by the KBr pellet technique vitiate the results and ATR spectra obtained directly from the LDH sample are representative of the actual state of bonding in the solid. The ATR spectra clearly show that the nitrate ion coordinates with a lower symmetry in the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH compared to the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH.

The line shapes of the hkl and $hk0$ reflections are indicative of structural disorder. The relatively well-resolved 110 and 113 reflections ($2\theta = 60\text{--}65^\circ$) in the PXRD pattern of $[\text{Mg-Al-NO}_3]_{0.25}$ are indicative of a greater degree of structural order. The PXRD pattern of $[\text{Mg-Al-NO}_3]_{0.33}$ LDH comprises a single feature in this region with asymmetric broadening on the high-angle side. This kind of broadening is characteristic of turbostratic disorder. The intercalated ions mediate structural order and anions coordinated in D_{3h} symmetry mediate an orderly stacking of the metal hydroxide slabs [29]. However, the peaks corresponding to the $00l$ reflections are narrower in the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH, indicative of a greater degree of crystal growth along the c -crystallographic direction in this LDH.

The thermogravimetric analysis (TGA) and Differential thermal gravimetry (DTG) profiles of the two pristine LDHs are presented in Fig. 3. The profiles are evocative of the different coordination symmetries of the intercalated NO_3^- ion and are consistent with other reports in the literature [30]. The mass loss is complete below 700°C for both compositions. However, the decomposition of the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH occurs at a higher temperature ($450\text{--}460^\circ\text{C}$) than the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH. The higher thermal stability of $[\text{Mg-Al-NO}_3]_{0.33}$ LDH is attributed to the grafting (direct coordination of the anion with the metal) of the NO_3^- ion to the metal hydroxide layer, which is facilitated by the C_{2v} symmetry [31]. These results are in agreement with our own earlier work [32] which has shown that the thermal stabilities are often at variance with the stability in solution.

3.2. Characterization of the chromate containing LDHs

Fig. 4 shows the PXRD patterns of the LDHs obtained after chromate exchange. The exchanged products essentially retain most of the features of the pristine LDHs except for the broadening of the lines. The success of the exchange reactions can be inferred by the wet chemical analysis of the exchanged products

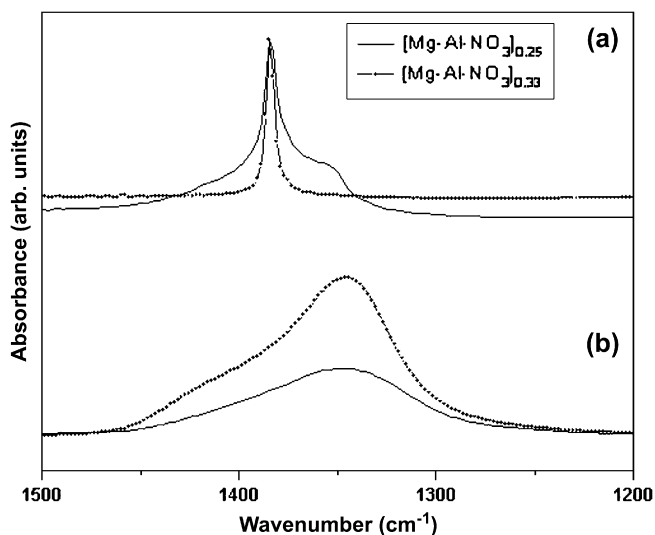


Fig. 2. IR spectra in the (a) transmission geometry and (b) attenuated total reflectance geometry of pristine $[\text{Mg-Al-NO}_3]_{0.25}$ and $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs.

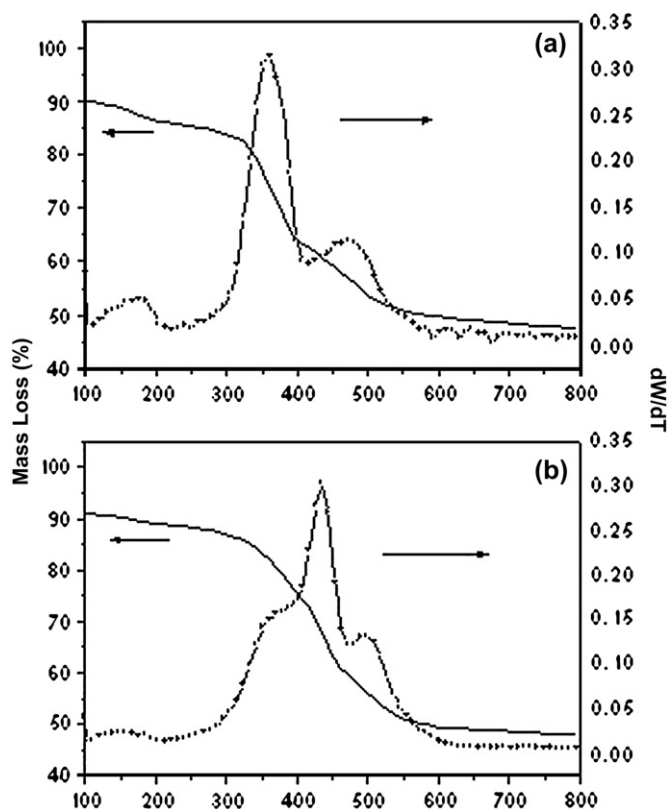


Fig. 3. TGA/DTG profiles of (a) $[\text{Mg-Al-NO}_3]_{0.25}$ and (b) $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs.

(see Table 1). The interlayer distances observed for the chromate-intercalated LDHs (8.15 Å and 9.07 Å) agree well with the values reported in the literature (8.1 Å and 9.02 Å) [5,6]. The IR spectrum of the exchanged products confirms the intercalation of the chromate ion. The IR spectrum (data not shown, see Ref. [6]) of the exchanged product shows that the vibrations due to NO_3^- ions are extinguished and a new absorption is

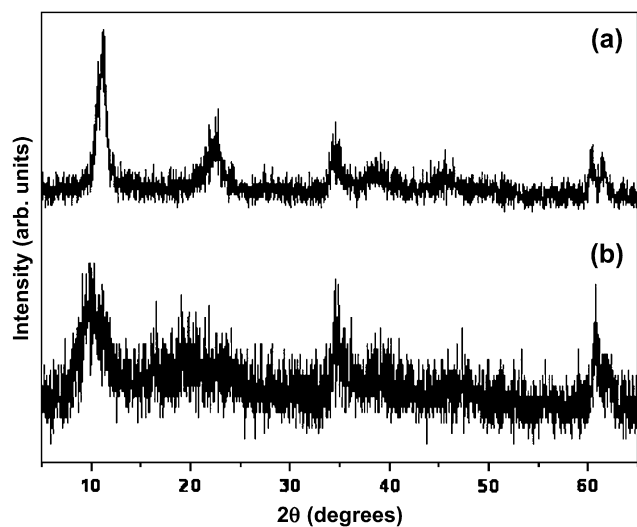


Fig. 4. PXRD patterns of the products obtained by chromate exchange from (a) $[\text{Mg-Al-NO}_3]_{0.25}$ and (b) $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs.

observed at 866 cm^{-1} due to the ν_3 mode of the intercalated chromate ion. The exchange reactions yield chromate carrying capacities of 0.073 mol and 0.165 mol of CrO_4^{2-} per mole of LDH for the $[\text{Mg-Al-NO}_3]_{0.25}$ and $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs, respectively. The chromate carrying capacity of the latter matches well with the theoretical exchange capacity (0.165 mol of CrO_4^{2-} per mole of LDH), while that of the former is 58% of the expected value (0.125 mol of CrO_4^{2-} per mole of LDH). The wet chemical analysis of the exchanged product and the TGA data (see Table 1) are consistent with these values.

Anions stabilize the LDH through (a) Coulombic interactions with the metal hydroxide layer and (b) hydrogen bonding interactions [33]. The Coulombic interactions are governed by the charge on the layer and the charge on the anion. The strength of hydrogen bonding is governed by the coordination symmetry of the anion and is contingent on the matching of the anion symmetry with the symmetry of the interlayer site [29]. Therefore with increase in charge on the metal hydroxide layer (x), the Coulombic interactions are stronger. Consequently the anion $(\text{A}^{n-})_{x/n}$ becomes a poor leaving group when x is large. At the same time, the NO_3^- ion in D_{3h} coordination symmetry ($x = 0.25$) is better matched with the trigonal prismatic symmetry of the interlayer site than the NO_3^- ion in C_{2v} symmetry ($x = 0.33$). Although the NO_3^- ion is expected to be a poorer leaving group in the $x = 0.33$ composition compared to that in the $x = 0.25$ composition by the yardstick of Coulombic interactions, from the point of view of hydrogen bonding it is weakly bound. Hydrogen bonding is the key factor contributing to LDH stability as Coulombic interactions are non-directional and are compensated by any incoming anion irrespective of its shape or symmetry. Considering the totality of these factors, it turns out that the NO_3^- ion in the $x = 0.33$ composition is a better leaving group than in the $x = 0.25$ composition, thus accounting for the greater chromate carrying capacity found in the former.

3.3. Chromate uptake characteristics of $[\text{Mg-Al-NO}_3]_{0.25}$ and $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs

Fig. 5 shows the results of chromate uptake by $[\text{Mg-Al-NO}_3]_{0.25}$ and $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs carried out at the ambient temperature (22–25 °C). Both LDHs were found to readily take up chromate ions from solution over the entire range of concentrations studied. At low initial concentrations the uptake is small which gradually increases with increase in chromate concentration. Eventually the uptake attains a saturation value at the initial chromate concentration of 0.008 M. The corresponding isotherm is of Type I. The saturation uptake value of both the LDHs agrees well with the chromate carrying capacity observed by anion exchange reactions. Chromate uptake was also measured from 1 M KNO_3 solutions containing different concentrations of the chromate ion. These experiments were designed to ensure that the concentration of the NO_3^- ions in solution remains nearly constant. Under these conditions, the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH takes up a negligible amount (<0.8 mmol per mole of LDH) of CrO_4^{2-} ion. This can be attributed to the contributions from the surface through adsorption.

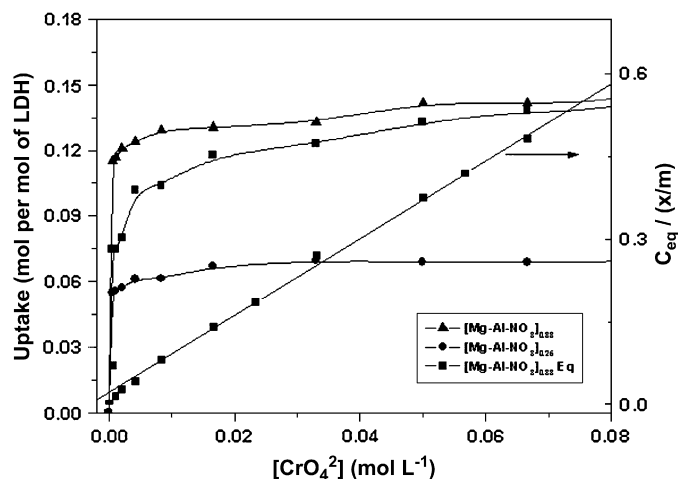


Fig. 5. Chromate uptake isotherms of $[\text{Mg-Al-NO}_3]_{0.25}$ and $[\text{Mg-Al-NO}_3]_{0.33}$ LDHs. Chromate uptake by the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH in equilibration with nitrate and the corresponding Langmuir plot is also shown.

However, $[\text{Mg-Al-NO}_3]_{0.33}$ LDH exchanges CrO_4^{2-} ion completely and the corresponding chromate carrying capacity (0.163 mol of CrO_4^{2-} per mole of LDH) matches well with that observed in the absence of dissolved nitrates. The chromate uptake measured at different initial concentrations is listed in Table 2. It may be noted that the chromate carrying capacities of the two LDHs correlate negatively with the BET surface area (see Table 2).

The chromate uptake measured in the presence of dissolved nitrates allowed us to process the data within the limits of the Langmuir adsorption isotherm. The Langmuir plot of $[C_{\text{eq}}/(x/m)]$ against C_{eq} should define a straight line. The result is presented in Fig. 5. Linear behavior is observed for the entire range of concentrations studied. The X_m value, 0.151 mol per mol of LDH, obtained from the slope of the Langmuir plot compares well with the value, 0.155 mol per mol of LDH, obtained from wet chemical estimation of CrO_4^{2-} ion

Table 2
Chromate uptake^a by the pristine LDHs under different conditions

[K ₂ CrO ₄], mol/L	[Mg-Al-NO ₃] _{0.25} (22.0 m ² /g)	[Mg-Al-NO ₃] _{0.33} (17.6 m ² /g)			
		Ambient ^b	Ambient ^b	Equilibrated	
				4 °C	Ambient ^b
0.00052	0.055	0.115	0.072	0.075	0.075
0.00104	0.055	0.117	0.079	0.075	0.075
0.00208	0.057	0.121	0.077	0.080	0.079
0.00416	0.061	0.124	0.105	0.102	0.107
0.00833	0.061	0.129	0.102	0.104	0.101
0.0166	0.067	0.130	0.121	0.118	0.120
0.0333	0.069	0.132	0.116	0.123	0.128
0.05	0.069	0.141	0.139	0.133	0.130
0.0666	0.069	0.141	0.134	0.138	0.140
0.0833	0.069	0.141	0.140	0.138	0.140
0.10	0.072	0.165	0.163	0.163	0.168

Values in parentheses are the specific surface areas.

^a Uptake expressed as mole of CrO_4^{2-} exchanged per mole of LDH taken.

^b Temperature: 22–26 °C.

in the solid (see Table 1). Sorption experiments were also performed at 4 °C and 65 °C to study the contributions arising from temperature (Table 2). The results show that there is no significant change in the chromate uptake characteristics with variation in the temperature. This is suggestive of a low barrier uptake and exchange is facilitated by the local structure of the interlayer site.

4. Conclusions

The following salient conclusions can be drawn:

- (1) The $[\text{Mg-Al-NO}_3]_{0.33}$ LDH has a chromate uptake capacity equal to that expected of a stoichiometric incorporation of chromate ions into all the crystallographically defined sites in the interlayer. This capacity is retained even under conditions of equilibration with the dissolved nitrate ions in solution.
- (2) The chromate uptake data obtained under conditions of equilibration with dissolved nitrates obey the Langmuir adsorption characteristics, thus showing that the entire interlayer region of the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH behaves like a surface. This behavior is on account of the higher interlayer spacing observed in this LDH owing to the incorporation of the nitrate ions in the C_{2v} coordination symmetry.
- (3) The $[\text{Mg-Al-NO}_3]_{0.25}$ LDH on the other hand behaves differently with only a partial participation of the interlayer region in the chromate uptake process. Under conditions of equilibration with dissolved nitrate ions, this LDH does not show any significant uptake of chromate ions indicating that the uptake observed under other conditions is also not a Langmuir-like process. This difference in behavior is on account of the smaller interlayer spacing observed in the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH.
- (4) The fact that the $[\text{Mg-Al-NO}_3]_{0.25}$ LDH has a higher BET surface area compared to the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH shows that the uptake does not correlate with the surface exposed by the macroscopic particles of the sample. The greater efficacy of the $[\text{Mg-Al-NO}_3]_{0.33}$ LDH has its origin in the structural rather than the morphological nature of the surface.

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References

- [1] F. Trifiro, V. Vaccari, in: G. Alberti, T. Bein (Eds.), Comprehensive Supramolecular Chemistry, Vol. 7, Pergamon, Oxford, 1997, p. 251 (Chapter 8).

- [2] H.R. Oswald, R. Asper, in: R.M.A. Leith (Ed.), *Preparation and Crystal Growth of Materials with Layered Structures*, D. Riedel Publishing Company, Dordrecht, 1977, p. 71.
- [3] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 173.
- [4] S. Miyata, A. Okada, *Clays Clay Miner.* 25 (1977) 14.
- [5] F. Malherbe, J.P. Besse, *J. Solid State Chem.* 155 (2000) 332.
- [6] F. Malherbe, L. Bigey, C. Forano, A. de Roy, J.P. Besse, *J. Chem. Soc., Dalton Trans.* (1999) 3831.
- [7] N. Iyi, T. Matsumoto, Y. Kaneko, K. Kitamura, *Chem. Mater.* 16 (2004) 2926.
- [8] R.K. Allada, A. Navrotsky, H.T. Berbeco, W.H. Casey, *Science* 296 (2002) 721.
- [9] S.V. Prasanna, P.V. Kamath, C. Shivakumara, *Mater. Res. Bull.* 42 (2007) 1028.
- [10] M. Badreddine, A. Legrouri, A. Barroug, A. deRoy, J.P. Besse, *Collect. Czech. Chem. Commun.* 63 (1998) 741. *Mater. Lett.* 38 (1999) 391.
- [11] A.V. Radha, P.V. Kamath, C. Shivakumara, *Solid State Sci.* 7 (2005) 1180.
- [12] N.N. Das, J. Konar, M.K. Mohanta, S.C. Srivastava, *J. Colloid Interface Sci.* 270 (2004) 1.
- [13] R.L. Goswamee, P. Sengupta, K.G. Bhattacharyya, D.K. Dutta, *Appl. Clay Sci.* 13 (1998) 21.
- [14] S. Martinez-Gallegos, S. Bulbulian, *Clays Clay Miner.* 52 (2004) 650.
- [15] F. Kovanda, E. Kovacsova, D. Kolusek, *Collect. Czech. Chem. Commun.* 64 (1999) 1517.
- [16] T. Sato, K. Kato, T. Endo, M. Shimada, *React. Solids* 2 (1986) 253.
- [17] V.R.L. Constantino, T.J. Pinnavaia, *Inorg. Chem.* 34 (1995) 883.
- [18] S. Miyata, *Clays Clay Miner.* 23 (1975) 369.
- [19] M. del Arco, S. Gutierrez, C. Martin, V. Rives, J. Rocha, *J. Solid State Chem.* 151 (2000) 272.
- [20] S.D. Ross, *Inorganic Infrared and Raman Spectra*, McGraw-Hill, London, 1972.
- [21] Z.P. Xu, H.C. Zeng, *J. Phys. Chem. B* 105 (2001) 1743.
- [22] S.L. Wang, P.C. Wang, *Colloids Surf A: Physicochem. Eng. Asp.* 292 (2007) 131.
- [23] H. Li, J. Ma, D.G. Evans, T. Zhou, F. Li, X. Duan, *Chem. Mater.* 18 (2006) 4405.
- [24] K. Nakamoto, *Infrared and Raman of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
- [25] F. Portemer, A. Delahaye-Vidal, M. Figlarz, *J. Electrochem. Soc.* 139 (1992) 671.
- [26] M. Rajamathi, P.V. Kamath, *J. Power Sources* 70 (1998) 118.
- [27] P. Genin, A. Delahaye-Vidal, F. Portemer, K. Tekaia-Elhsissen, M. Figlarz, *Eur. J. Solid State Inorg. Chem.* 28 (1991) 505.
- [28] M. Khaldi, A. de Roy, M. Chaouch, J.P. Besse, *J. Solid State Chem.* 130 (1997) 66.
- [29] A.V. Radha, P.V. Kamath, C. Shivakumara, *J. Phys. Chem. B* 111 (2007) 3411.
- [30] Z.P. Xu, H.C. Zeng, *Chem. Mater.* 13 (2001) 4564.
- [31] C. Vaysse, L. Guerlou-Demourgues, C. Delmas, *Inorg. Chem.* 41 (2002) 6905.
- [32] S. Britto, A.V. Radha, N. Ravishankar, P.V. Kamath, *Solid State Sci.* 9 (2007) 279.
- [33] H.F.W. Taylor, *Miner. Mag.* 39 (1973) 377.