

# 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  $\text{NO}_3^-$  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  $\text{Mg}^{2+}$  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  $\text{Mg}^{2+}$  ions is isomorphously substituted by a trivalent ion such as  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ , the positive charge  $x+$  generated on the metal hydroxide slab is compensated by the inclusion of anions,  $\text{A}^{n-}$ , 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  $\text{CO}_3^{2-}$  ion. Crystal chemical considerations favor the incorporation of  $\text{CO}_3^{2-}$  into the interlayer owing to (a) the matching of the symmetry of the  $\text{CO}_3^{2-}$  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  $\text{CO}_3^{2-}$  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  $\text{Al}^{3+}$  partially substituting for  $\text{Mg}^{2+}$  [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  $\text{NO}_3^-$  as the exchangeable anion by means of anion exchange reactions. We correlate the  $\text{Al}^{3+}$  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 ( $3 \text{ ml min}^{-1}$ ) 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  $\text{NO}_3^-$  ions taken as its sodium salt.  $\text{NaOH}$  (2 M) was dispensed using a Metrohm model 718 STAT Titrino to maintain a constant pH (9.0) at precipitation.

$\text{N}_2$  gas was bubbled through the solution during precipitation and aging for 18 h at  $65^\circ\text{C}$ . The precipitate was rapidly filtered under suction and washed with deionized ( $10^{15}$  ohm cm specific resistance), decarbonated water and then dried at  $80^\circ\text{C}$  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  $4 \text{ cm}^{-1}$ , KBr pellet). Attenuated total reflectance (ATR) spectra were collected using a SMART ORBIT<sup>®</sup> 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  $4 \text{ cm}^{-1}$ , 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<sup>e</sup> TG/SDTA system driven by Star<sup>c</sup> 7.1 software (heating rate  $5^\circ\text{C min}^{-1}$ ,  $\text{N}_2$  gas). The samples were first heated to  $100^\circ\text{C}$  in the TG balance for 0.5 h to drive away the adsorbed water before being ramped up to  $800^\circ\text{C}$ . 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  $\text{K}_2\text{CrO}_4$  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  $\text{K}_2\text{CrO}_4$  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  $4^\circ\text{C}$  and  $65^\circ\text{C}$  in a similar manner. The precursors namely the LDH slurry and  $\text{K}_2\text{CrO}_4$  solution were maintained at the respective temperatures for 30 min to attain constant temperature before mixing. Chromate uptake was also measured from  $\text{K}_2\text{CrO}_4$  solutions which were made 1 M in  $\text{KNO}_3$  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  $\text{K}_2\text{CrO}_4$  solution containing 10 times the stoichiometric requirement of chromate ions required to affect a complete

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