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An Atomic Level Understanding of Orthophosphate Adsorption by Magnesium Aluminum Layered Double Hydroxides – A Multi-Technique Study

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Abstract

The phosphate (P) adsorption properties of three magnesium aluminum layered double hydroxides intercalated with nitrate and/or carbonate (MgAl-NO$_3$/CO$_3$ LDH) with targeted Mg:Al ratios of 2, 3, and 4 were investigated to understand how phosphate interact with the LDH using powder X-ray diffraction, solid state NMR, vibrational spectroscopy, scanning electron microscopy, and ICP-OES. The solid products after phosphate exposure contained four different phosphate species which were quantified by $^{31}$P MAS NMR: Phosphate intercalated in the interlayer (A), phosphate adsorbed to the surface of the LDH particles (B and C), and phosphate adsorbed to amorphous aluminum hydroxide (D). Their relative concentrations depend on the Mg:Al ratio, the phosphate loading, and the intercalated anion in the parent LDH. Surprisingly, phosphate intercalated by anion exchange, which has been assumed to be the dominant mechanism of P adsorption, is less than 30 %. Instead phosphate adsorbed to the surface of the LDH particles is the predominant site (52-88 %). Moreover, a non-negligible fraction (8-39 %) of phosphate is adsorbed to an amorphous aluminum hydroxide (AOH) impurity (Site D) especially at high phosphate concentration and exposure time. AOH is a known...
impurity in LDH prepared by co-precipitation at constant pH, the most commonly used method in phosphate removal studies. This indicates that MgAl-LDH have higher affinity for phosphate than AOH. Furthermore, no significant dissolution of the LDH followed by precipitation of phosphate minerals was observed by PXRD, $^{27}$Al and $^{31}$P MAS NMR.

**Introduction**

Phosphorus in the form of inorganic orthophosphate (P) is essential for plant growth and extensively used as a fertilizer. Currently, phosphate rocks obtained from mining activities is the major source, but the known deposits may be depleted within 50-100 years.\(^1\) Hence, phosphate rock is considered a critical resource by the European Union.\(^2\) One of the most promising alternative phosphate sources is domestic wastewater, which has a high concentration of phosphorus (5-20 mg/L). Furthermore, recovery of phosphate from wastewater treatment plants (WWTP) would benefit the phosphorus circular economy\(^3\) and simultaneously reduce the ecological impact (eutrophication) of the excessive P discharge into surface water reservoirs. Currently, phosphate present at WWTP is mainly concentrated in sludge, which is applied to agricultural fields. However, there is a growing concern about contamination from pathogens, toxic organic compounds, and heavy metals. Consequently, some European countries have banned application of sludge to fields.\(^3-4\) Alternative technologies to sludge application include the recovery of phosphate by controlled precipitation of, e.g., struvite (NH$_4$MgPO$_4$·6H$_2$O) or by phosphate selective adsorbents.\(^5-7\) Layered double hydroxides (LDH), a group of inorganic anion exchange materials related to the mineral hydrotalcite (Mg$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O), are one of the most promising sorbent materials due to their unique anion exchange properties and their high affinity for phosphate.\(^8-11\) The general formula for a LDH is [M$^{2+}$.\(_x\)M$^{3+}$.\(_y\)(OH)$_2$]$^{x+}$(A$^{n-x/n}$)$\_y$H$_2$O, abbreviated as M$^{2+}$M$^{3+}$-A, where M$^{2+}$, M$^{3+}$, and A represent cations and anions, respectively.\(^12\) Their structure consists of stacked, positively charged edge-sharing octahedra.
planes ([M$^{2+}_{1-x}$M$^{3+}_x$(OH)$_2$]$^{2+}$) separated by hydrated anionic species (A$^{n-x/n}$yH$_2$O) as illustrated in Figure 1. Inorganic phosphate anions have been fully intercalated by anion exchange reaction in LDH materials leading to pure phosphate containing LDH.$^{13-16}$ Moreover, phosphate adsorption by LDH have extensively been studied in the laboratory using pure phosphate solutions as well as solutions from wastewater, sewage sludge filtrate, and seawater.$^{9-11, 13, 15, 17-31}$ Furthermore, recyclability of LDH materials has been demonstrated although a lower capacity has been reported after regeneration.$^{10, 18, 20-21, 32}$

![Figure 1. Crystal structure of a Mg$_2$Al-NO$_3$ LDH and the different possible binding sites: Interlayer phosphate (A) and surface adsorbed (B+C) related to the LDH, and phosphate adsorbed to aluminum hydroxide (D).](image)

Most studies have focused on the phosphate adsorption properties of the LDH under different conditions (pH, phosphate concentration, LDH composition, exposure time and competing anions) with emphasis on quantification of the amount of phosphate removed from the aqueous phase.$^{8-10, 17, 19-21, 24-25, 32}$ In contrast, detailed structural studies of the phosphate adsorption mechanism by LDH, i.e., exactly where and how phosphate species interact with the LDH have been limited, due to the low crystallinity of P containing LDH, which is caused by structural disorder of the P anions in the
interlayer domains. Powder X-ray diffraction (PXRD) of LDH intercalated with phosphate (M$^{2+}$M$^{3+}$-P LDH) display only a few reflections of low intensity, which prevents refinement of the PXRD profile. Thus, no crystal structure has been published for any of these M$^{2+}$M$^{3+}$-P LDH to our knowledge. Several phosphate adsorption mechanisms including intercalation by anion-exchange, surface adsorption, ligand complexation, and dissolution of the LDH followed by formation of different phosphate minerals such as hopeite (Zn$_3$(PO$_4$)$_2$·4H$_2$O) and newberyite (MgHPO$_4$·3H$_2$O) have been proposed based only on thermodynamic studies.$^{11, 18, 23, 26-27, 31}$ Adsorption is commonly understood as the overall uptake phenomenon irrespective of mechanism, whereas the term theoretical adsorption capacity (TAC) refers to the maximum anion exchange capacity both in the interlayer and on the surface of the LDH particles. The relative contribution from the suggested mechanisms is essential to design an efficient and recyclable filter material but have to our knowledge not been quantified. PXRD has extensively been used to probe intercalation of phosphate in the interlayer, seen as a shift of the (00l) reflections towards low 2θ values and always associated with a loss in crystallinity.$^{13, 15-16, 18, 22-23, 27-28}$ Moreover, PXRD clearly shows that the CaAl-LDH structure is destroyed upon exposure to phosphate resulting in the formation of calcium phosphates such as brushite (CaHPO$_4$·2H$_2$O) and hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH)).$^{23, 29-30}$ However, it has also become evident that the presence of amorphous phases are not detected by PXRD$^{26, 33}$ and sorption to the LDH surface cannot be probed by PXRD. Furthermore, the LDH used for phosphate adsorption are normally prepared by co-precipitation at constant pH or at increasing pH using thermal hydrolysis of urea (the so-called “urea method”).$^{34}$ These two synthesis methods result in variable quantities (10-60 %) of amorphous aluminum hydroxide (AOH) impurities.$^{33, 35}$ Such AOH has clearly been identified by $^{27}$Al SSNMR for MgAl- and ZnAl-LDH phases used for phosphate adsorption.$^{28, 36-38}$ Moreover, the presence of amorphous aluminum hydroxides is critical as these have a high affinity for phosphate$^{39-41}$ and will lower the actual Al content in the LDH,$^{33, 35-36, 42}$ i.e., result in a lower
TAC. Thus, experimental techniques with atomic level resolution, which do not require long-range order such as solid-state NMR spectroscopy (SSNMR), X-ray extended absorption spectroscopy (EXAFS), vibrational spectroscopy (FT-IR and Raman) is needed to probe surface complexation and amorphous phases.

SSNMR has provided valuable information about adsorption of phosphate by LDH and can be used for quantification of the different phosphate sites and has as well given detailed insight into phosphate sorption onto aluminum hydroxides. For example, SSNMR quantified phosphate adsorbed to AOH and aluminum phosphate formed by dissolution reprecipitation in our recent paper on removal of phosphate from acidified sludge by ZnAl-NO$_3$ LDH. Moreover, SSNMR of LDH identified ordering of the M(III) ions, structural defects, and amorphous impurities.

Few studies have investigated the phosphate adsorption by LDH using SSNMR. These report partial dissolution of the LDH at a pH $\leq 7$, which is accompanied by precipitation of phosphate minerals, e.g., aluminum phosphate (AlPO$_4$), bobierite (Mg$_3$(PO$_4$)$_2$·8H$_2$O), newberyite or brushite. Phosphate adsorption experiments under basic conditions show no precipitation of phosphate minerals according to SSNMR and/or PXRD. However, quantification of the different binding sites on the LDH as well as the contribution from the amorphous AOH phase has not been investigated in detail.

Here we report a detailed study of the phosphate adsorption properties of a series of Mg$_R$Al-NO$_3$ LDH ($R = 2, 3, 4$) using a combination of phosphate adsorption experiments with detailed characterization of the solid LDH products by PXRD, FT-IR, Raman, ICP-OES, and multi-nuclear ($^1$H, $^{25}$Mg, $^{27}$Al, and $^{31}$P) SSNMR as a function of phosphate loading to gain an atomic level understanding on how phosphate interact with the LDH as well as identify and quantify the different phosphate species. PXRD was used for identification of the intercalated anions and to monitor the
crystallinity of LDH as a function of phosphate loading, whereas $^{25}$Mg and $^{27}$Al MAS NMR provided information on the stability of the LDH and $^{31}$P MAS NMR was used for identification and quantification of the phosphate species (P-species).

**Experimental**

The following reagents were used: magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$•6H$_2$O), aluminum nitrate nonahydrate (Al(NO$_3$)$_3$•9H$_2$O), dipotassium phosphate (K$_2$HPO$_4$), and sodium hydroxide (NaOH). All chemicals were of reagent grade. K$_2$HPO$_4$ (pKa = 7.21 for HPO$_4^{2-}$) was used as the source for phosphate to ensure alkaline condition and avoid dissolution of the LDH.

**Table 1.** Synthesis parameters (pH, aging time, and Mg:Al ratio of the metal salt solutions) and the properties of the parent Mg$_x$Al-LDH (Al content determined by ICP-OES, the Mg:Al ratio determined from ICP-OES (bulk) as well $^{27}$Al and $^1$H MAS NMR (LDH), the intercalated anion based on PXRD (intercalated), FT-IR, and Raman, the AOH content from $^{27}$Al MAS NMR, and the experimental adsorption capacity (EAC).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg:Al</th>
<th>pH</th>
<th>Bulk Al (%)</th>
<th>Mg:Al LDH ($^{27}$Al)</th>
<th>Mg:Al LDH ($^1$H)</th>
<th>Anion (PXRD)</th>
<th>Anion (FT-IR, Raman)</th>
<th>AOH (% Al)</th>
<th>EAC (mg P/gl)</th>
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</thead>
<tbody>
<tr>
<td>M2A</td>
<td>2.0</td>
<td>9.0(4)</td>
<td>34.6</td>
<td>2.7(6)</td>
<td>2.6(6)</td>
<td>NO$_3^-$</td>
<td>CO$_3^{2-}$, NO$_3^-$</td>
<td>30(6)</td>
<td>47</td>
</tr>
<tr>
<td>M3A</td>
<td>3.0</td>
<td>9.5(3)</td>
<td>26.7</td>
<td>3.9(6)</td>
<td>-</td>
<td>NO$_3^-$</td>
<td>CO$_3^{2-}$, NO$_3^-$</td>
<td>30(6)</td>
<td>46</td>
</tr>
<tr>
<td>M4A</td>
<td>4.0</td>
<td>10.0(3)</td>
<td>22.4</td>
<td>5.2 (6)</td>
<td>4.9(6)</td>
<td>CO$_3^{2-}$</td>
<td>CO$_3^{2-}$, NO$_3^-$</td>
<td>33(6)</td>
<td>17</td>
</tr>
</tbody>
</table>

**MgAl-LDH Syntheses:**

MgAl-NO$_3$ LDHs with a targeted Mg:Al ratio of 2:1, 3:1, and 4:1, respectively were synthesized by coprecipitation at constant pH,$^{33}$ as summarized in Table S1. The pH of the synthesis solution was increased with increasing Mg:Al molar ratio in order to insure a total precipitation of both Mg$^{2+}$ and
Al\(^{3+}\) cations. A solution of the metals salt with a total metal concentration of 1 M and the desired Mg:Al ratio was added by a peristaltic pump at a rate of 0.1 ml/min to deionized water in a reactor. A nitrogen (N\(_2\)) atmosphere was used to minimize carbonate contamination. The pH of the synthesis solution was kept constant by simultaneous addition of a 2 M NaOH solution by a peristaltic pump. Subsequently, the synthesis mixtures were aged for 61-62 h and then collected by centrifugation before the solid product was washed thrice with deionized water and dried at room temperature. Aging was chosen as post synthesis treatment over hydrothermal treatment to mimic large scale production of LDH. The parent materials were named according to the Mg:Al ratio of the metal salt solution: M2A, M3A, and M4A.

**Phosphate adsorption isotherms:** The adsorption experiments were carried out in 2 ml Eppendorf vials, which contained 10 mg LDH and 1 mL phosphate solution. The appropriate amount of phosphate was taken from a 0.05 M K\(_2\)HPO\(_4\) stock solution and deionized water was added to a total volume of 1 ml. The samples were shaken overnight after which the supernatant was separated by centrifugation. The supernatant was diluted by a factor of 50 prior to quantification of the HPO\(_4^{2-}\) concentration by ICP-OES. The equilibrium phosphate adsorption content, C\(_s\), was determined and plotted as a function of the equilibrium concentration, C\(_{eq}\).

\[
C_s = (C_0 - C_{eq}) \cdot \frac{v}{m}
\]

(1)

where C\(_0\) (mol·L\(^{-1}\)) is the initial P concentration, v (L) is the total volume, and m (g) is the mass of the LDH sample.

**Preparation of phosphate loaded samples for characterization by PXRD, Raman, FTIR, ICP-OES, and SSNMR:**
0.300 g LDH was suspended in 50 ml deionized water in which a 1 M K$_2$HPO$_4$ solution was added in amount corresponding to 25, 50, 75, 100, and 400 % of the theoretical HPO$_4^{2-}$ anion exchange capacity (TAC) of the Mg$_6$Al-NO$_3$ LDH. The TAC was calculated under the assumption that nitrate can be completely exchanged for hydrogen phosphate (HPO$_4^{2-}$) by anion exchange and that the LDH contain two water molecules. See Tables S1 and S2 for further information. The 25, 50, 75, and 100 % samples were exposed to phosphate for five hours whereas the 400 % samples were exposed to phosphate for 62 h to ensure full saturation of the LDH. All adsorption experiments were performed under a N$_2$ atmosphere. The solid was collected by centrifugation and washed thrice with deionized water before dried at room temperature. The samples were named according the parent LDH (M2A, M3A, and M4A) and the initial P loading (Y): MRAYP. For example, M2A100P was synthesized with a Mg:Al ratio of two and exposed to a phosphate concentration corresponding to 100 % of the TAC.

Characterization of the solid samples:

**Powder X-ray Diffraction (PXRD):** The powder X-ray diffractograms were recorded on a Rigaku Miniflex 600 with Cu Kα radiation ($\lambda = 1.5418$ Å) in the 5-70 ° range using a step size of 0.02 ° and a speed of 10 °min$^{-1}$. In-situ powder X-ray diffractograms were recorded with a Philips X'Pert Pro diffractometer using CuKα radiation ($\lambda = 1.5405$ Å) over the 3–75 ° range at an accelerating voltage of 40 kV, a current of 30 mA and a scan speed of 2 °min$^{-1}$ using the XRD flow cell described elsewhere.$^{29}$

**FT-IR and Raman spectroscopy:** FT-IR spectra were recorded from 4000-400 cm$^{-1}$ on a Nicolet-5700 spectrophotometer by the KBr pellet method. The pellet was made by grinding approx. 2 mg of the sample and approx. 198 mg KBr. The Raman spectra were recorded from 150 to 1500 cm$^{-1}$ at room temperature using a confocal micro-Raman spectrometer (T64000 Jobin Yvon) with an excitation
wavelength of 514.5 nm (argon-ion laser-line). Spectra were acquired at a spectral resolution of 1 cm\(^{-1}\) with charge coupled device (CCD) multichannel detector cooled by liquid nitrogen to 140 K coupled with an Olympus confocal microscope.

**Scanning Electron Microscopy:** SEM images were recorded using a JSM-7500F FESEM operating at 3 KV with the samples mounted on conductive carbon adhesive tape and coated with a thin gold layer. Images were acquired at magnifications of x10,000 and x25,000. For each sample, SEM images did not show variation in size and morphology of particles then SEM images were selected in term of image quality (best contrast).

**SSNMR:** Single pulse \(^{27}\)Al and \(^{31}\)P MAS NMR spectra were recorded on a JEOL ECZ500CR MHz NMR spectrometer equipped with a 11.7 T Oxford magnet and a 3.2 mm double resonance MAS NMR probe using a spinning speed of 13 kHz. The \(^{31}\)P MAS NMR spectra were recorded with a 45° pulse and a relaxation time of 30-60 s, the latter was optimized for each sample to ensure full relaxation. The \(^{27}\)Al MAS NMR spectra were recorded with a relaxation time of 1 s and a 10° pulse angle to ensure quantitative spectra. The \(^{27}\)Al 3QMAS NMR spectra were recorded with a z-filter and a spinning speed of 14 kHz. \(^{25}\)Mg MAS NMR spectra were recorded on a Varian 600 MHz NMR spectrometer (14.1 T) with a 5 mm double resonance MAS NMR probe with a Hahn echo DFS pulse sequence, a relaxation delay of 1 s, and a spinning speed of 7-9 kHz. \(^1\)H MAS NMR spectra were recorded on Varian 600 MHz NMR spectrometer (14.1 T) with a 1.6 mm triple resonance MAS NMR probe. \(^1\)H MAS NMR spectra were recorded with a relaxation delay of 4-8 s and with 30-35 kHz as spinning speed. The \(^1\)H, \(^{25}\)Mg, \(^{31}\)P, and \(^{27}\)Al MAS NMR spectra were referenced from water (\(\delta_{\text{iso}}(\text{H}) = 4.6 \text{ ppm}\)), MgO in the rotor (\(\delta_{\text{iso}}(\text{Mg}) = 25 \text{ ppm}\)), 1 M AlCl\(_3\) solution (\(\delta_{\text{iso}}(\text{Al}) = 0 \text{ ppm}\)), and phosphoric acid H\(_3\)PO\(_4\) (\(\delta_{\text{iso}}(\text{P}) = 0 \text{ ppm}\)), respectively. The \(^{25}\)Mg and \(^{27}\)Al MAS NMR spectra were analyzed by Quadfit\(^{52}\) whereas the \(^1\)H and \(^{31}\)P MAS NMR spectra were analyzed by MestReNova.
Results and Discussion

Characterization of the parent LDH materials prior to phosphate adsorption

Figure 2. PXRD for the three series a) M2A, b) M3A, and c) M4A at the P loadings of 0P (parent LDH), 25P, 50P, 75P, 100P, and 400P. Reflections from the aluminum background in the sample holder (#) are seen for some samples due to limited sample quantities.

The parent LDH were characterized by $^{27}$Al MAS NMR, ICP-OES, FT-IR, Raman and PXRD prior to phosphate adsorption to assess the sample composition and structure. The powder X-ray diffractograms of M2A, M3A, and M4A (Figures 2 and S1a) are characteristic of a LDH with a hexagonal lattice and rhombohedral symmetry (R-3m). Only reflections that could be assigned to the LDH is seen, i.e., no crystalline impurities are detected. The linear ($R^2 = 0.998$) increase of the M-M distance ($a$) confirms the change in Mg:Al composition of the layer while the decrease of the basal spacing ($c$) with Mg:Al indicates a partial substitution of $\text{NO}_3^-$ by $\text{CO}_3^{2-}$ (Figure S1b). FT-IR and Raman spectra (Figures 3, 4 and S2) confirm the formation of MgAl LDH and exhibit the typical infrared vibration bands of the interlayer anions with $\nu_3(\text{NO}_3)$ and $\nu_3(\text{CO}_3)$ at 1384 cm$^{-1}$ and 1361 cm$^{-1}$ (FT-IR) and at 1055 cm$^{-1}$ and 1044 cm$^{-1}$ (Raman). However, the $\nu_3(\text{NO}_3)$ band for M4A has almost no
intensity in the Raman spectrum in agreement with the lower basal spacing for M4A as compared to M2A and M3A (Figure S1b). Hence, carbonate is mainly intercalated in M4A. Moreover, the Mg(R-Al) lattice vibrations ($\nu_{(MO_6)}$ and $\delta_{(OMO)}$) are in the range 667-586 cm$^{-1}$ and 451-400 cm$^{-1}$ (FT-IR) and 545-557, 478-467 cm$^{-1}$ (Raman) and varies in agreement with the Mg:Al ratio.$^8, 13, 15, 22, 33, 35$

**Figure 3.** An expansion of the FT-IR spectra of the region within anion vibrations (900 to 1500 cm$^{-1}$) for the three series: a) M2A, b) M3A, and c) M4A at P loading of 0P (parent LDH), 25P, 50P, 75P, and 100P. The bands $\nu_3$($NO_3^-$), $\nu_3$($CO_3^{2-}$), and $\nu_3$($PO_4^{3-}$) are marked with blue lines.
Figure 4. Raman spectra for the three series: a) M2A, b) M3A, and c) M4A at P loadings of 0P (parent LDH), 25P, 50P, 75P, 100P, and 400P.

Whereas PXRD imply highly crystalline samples without crystalline impurities, analysis of the $^{27}$Al MAS NMR spectra (Figure 5a) show the presence of amorphous aluminum hydroxide (AOH),$^{33,35,42}$ which is evident as a broad signal with $\delta_{iso}(^{27}$Al) $\approx$ 10.2-11.3 ppm in the $^{27}$Al MAS NMR spectra. The AOH is also easily identified in the $^{27}$Al 3QMAS NMR spectra (Figure S3). Hence, deconvolution of the single pulse $^{27}$Al MAS NMR spectra were performed with two sites – one for the LDH with $C_Q = 1.6$ MHz and $\eta = 0$ and one for the AOH phase with $C_Q = 3.3$ and $\eta = 0.2$, as reported earlier.$^{42}$ The presence of AOH was confirmed by the Al content determined by ICP-OES for M2A (34.6 %) which is above 33 %, the maximum Al content in an LDH considering the Al-O-Al
avoidance rule.\textsuperscript{43-44} From the simulations it was determined that Al in the LDH phase constitutes approximately two thirds of the total Al content. From this and the ICP-OES results, the Mg:Al ratio of the LDH can be calculated (Table 1). Deconvolution of \textsuperscript{1}H MAS NMR spectra of M2A and M4A (Figure S4) as well confirmed the presence of AOH.\textsuperscript{44} Moreover, the Mg:Al ratio was found to 2.6(6) for M2A and 4.9(6) for M4A, which matches the Mg:Al ratio determined by \textsuperscript{27}Al MAS NMR combined with ICP-OES within the experimental uncertainty (Table 1). See Table S3 and Figure S4 for further details.
Figure 5. a) Simulation of the $^{27}\text{Al}$ MAS NMR spectrum of M2A, b) Relative intensity of the LDH resonance for the three series: M2A, M3A, and M4A at the different P loadings, and c) $\delta_{\text{iso}}(^{27}\text{Al})$ for the LDH resonance for the three series: M2A, M3A, and M4A at the different P loadings.

The $^{25}\text{Mg}$ MAS NMR spectra M2A, M3A, and M4A (Figure 6) match earlier reported $^{25}\text{Mg}$ MAS NMR spectra of MgAl-LDH.$^{43-44}$ An ideal MgAl-LDH contains only a single $^{25}\text{Mg}$ resonance: a
$^{25}\text{Mg}$ with three Mg and three Al in the first metal ion coordination sphere ($\text{Mg(OAl)}_3(\text{OMg})_3$).\textsuperscript{44} However, the $^{25}\text{Mg}$ MAS NMR spectrum of M2A cannot be satisfyingly simulated with a single $^{25}\text{Mg}$ site (Figure S5) implying a lower Al content (Mg:Al > 2) in the LDH.\textsuperscript{44} This is in good agreement with the Mg:Al of 2.6(6) (Table 1) obtained from deconvolution of the $^1\text{H}$ MAS NMR spectrum (Figure S4).

Simulations of the $^{25}\text{Mg}$ MAS NMR spectra of M3A and M4A were not attempted, but visual inspection shows that the two samples have less Al than the M2A sample seen as the high frequency brucite like Mg(OMg)$_6$ site observed at approximately 0 ppm.\textsuperscript{44} This site is most intense for M4A implying that the Al content in the LDH phase is M2A > M3A > M4A, in agreement with the Mg:Al ratio of the synthesis solutions.
Figure 6. $^{25}\text{Mg}$ MAS NMR spectra for M2A0P (parent LDH, spinning speed = 8 kHz), M2A100P (spinning speed = 8 kHz), M3A0P (parent LDH, spinning speed = 7 kHz), M3A100P (spinning speed = 9 kHz), M4A0P (parent LDH, spinning speed = 9 kHz), and M4A100P (spinning speed = 9 kHz). * and # marks spinning side band and MgO from the rotor, respectively.

**Phosphate adsorption capacity**

The TAC for a Mg$_n$Al-LDH with nitrate in the interlayer under the assumption of anion exchange as the only mechanism for phosphate adsorption, is directly proportional to the aluminum content in the LDH. It also depends on the pH-controlled speciation of the orthophosphate anions (H$_2$PO$_4$\(^-\)/HPO$_4^{2-}$ /PO$_4^{3-}$, Table S2). For example, the exchange reaction for intercalation of HPO$_4^{2-}$ species from a solution at pH = 9.79 ((pKa$_2$+pKa$_3$)/2) is:
\[ Mg_{1-x}Al_x(OH)_2(NO_3)_2 \cdot 2xH_2O + \frac{x}{2} HPO_4^{2-} \rightarrow Mg_{1-x}Al_x(OH)_2(HPO_4)_x \cdot 2xH_2O + x \cdot NO_3^- \]

(2)

For each Al half a monohydrogen phosphate ion, HPO_4^{2-}, can theoretically be intercalated and one nitrate is then expelled. The TACs were estimated under the assumption of two water molecules per Al. However, the experimental adsorption capacity (EAC) should be lower than TAC if carbonate is partly intercalated, since carbonate will not be completely replaced by phosphate due to the higher affinity of LDH for carbonate.\(^8\) How the degree of protonation of the phosphate ion (PO_4^{3-}, HPO_4^{2-}, or H_2PO_4^+)\(^,\) which affects the TAC is reported in Tables S2 and S4. For example, twice as much H_2PO_4^- can be intercalated as HPO_4^{2-}.

The HPO_4^{2-} adsorption isotherms of the three LDH samples (M2A, M3A, and M4A; Figure S6) correspond to a H type isotherms according to Giles classification\(^54\) with a strong adsorption at low HPO_4^{2-} concentration followed by a continuous increase of adsorption at medium and high concentration indicating several mechanisms of adsorption. The phosphate adsorption isotherms did not completely reach a plateau even at high phosphate loading implying two (or more) adsorption mechanisms, which are hard to model with either the Langmuir or the Freundlich model. We ascribe this phenomenon in part to the presence of AOH in the samples. Thus, the adsorption capacities corresponding to the anion exchange reaction were estimated as the kink of the isotherms (Figure S6) and are summarized in Table 1 (EAC). As already mentioned by Everaert et al. for similar Mg\(_r\)Al-NO_3 phases, LDH with Mg:Al ratio equal to 2 and 3 display similar adsorption behavior and capacities toward HPO_4^{2-} anions while Mg_4Al has a much lower efficiency to remove HPO_4^{2-}.\(^55\) The adsorption capacities for our three LDH are in the same range as earlier reported adsorption capacities for LDH.\(^8, 11, 21, 31-32\) Furthermore, the EAC for M2A and M3A but not M4A match the TACs (Table
S4): 50 mg P/g, 40 mg P/g, and 34 mgP/g for a Mg_2.6Al-NO_3, Mg_3.9Al-NO_3, and Mg_5.2Al-NO_3 LDH, respectively. However, taking into account the presence of 30% and 33% AOH in M2A, M3A and M4A (Table 1), the corresponding TACs for the LDH are reduced to 35 mgP/g, 28 mgP/g, and 23 mgP/g, respectively. Hence, EAC for M2A and M3A are greater than the expected TAC (134 % and 164 % respectively), indicating that anion exchange may not be the only phosphate uptake phenomenon and/or that the identified AOH contributes. The adsorption capacity for M4A is 74 % of the TAC due to the presence of mainly carbonate in the parent M4A LDH.

**Characterization of the phosphate loaded LDH samples**

The phosphate loaded samples were characterized by a combination of ICP-OES, PXRD, FT-IR and Raman spectroscopy as well as ^1^H, ^25^Mg, ^27^Al, and ^31^P MAS NMR to determine the phosphate adsorption mechanism.

**Phosphate content in the LDH samples:**

The Mg:Al ratio (ICP-OES) and LDH content in the bulk samples (^27^Al MAS NMR) showed no significant changes upon phosphate exposure, c.f., Table S5 and Figure 5b, respectively. Moreover, the (110) reflection, which reflects the Mg content in the cation layer, is not shifted implying that the Mg:Al ratio of the LDH is also unchanged (Figure 2). Thus, there is no indication of dissolution or chemical transformation of the LDH upon phosphate exposure even at a P loading of 400 % for 62 h. The phosphate concentration at the different loadings for the three series is given in Figure 7. Generally, the phosphate content in the solid phase increases with the phosphate concentration in the solution for the three series. The phosphate content for the three series at the two highest phosphate loadings (100P and 400P) matches very well the adsorption capacity determined from the phosphate
adsorption isotherms given in Table 1 except for M4A400P (39 mgP/g), which is more than twice the 
EAC (17 mgP/g) due to the high phosphate concentration and exposure time (62 h).

Figure 7. The amount of adsorbed P of for the three series: M2A, M3A, and M4A determined by 
ICP-OES. The 25P, 50P, 75P, 100P were exposed to phosphate for 5 h. The 400P samples were 
exposed for 62 h. The experiments were performed under alkaline conditions (pH \approx 9-10).

Identification and quantification of the phosphate species by $^{31}$P MAS NMR: The $^{31}$P MAS NMR 
spectra contains up to four different local environments (resonances): A ($\delta_{\text{iso}}(^{31}\text{P}) = 8.3-8.7$ ppm), B 
($\delta_{\text{iso}}(^{31}\text{P}) = 2.3-3.4$ ppm), C ($\delta_{\text{iso}}(^{31}\text{P}) = -1.9$ to -0.7 ppm), and D ($\delta_{\text{iso}}(^{31}\text{P}) = -7.0$ to -5.1 ppm), as 
illustrated in Figure 8. The $\delta_{\text{iso}}(^{31}\text{P})$ for all sites decreases with the Mg:Al ratio (lower Al%) (Table 
2). The relative intensity depends on the P loading and the Mg:Al ratio of the parent LDH, as 
illustrated in Figures 8 and 9. The remaining $^{31}$P MAS NMR spectra (50P and 75P loading) are 
presented in Figure S7. A fifth resonance with $\delta_{\text{iso}}(^{31}\text{P}) \approx 6$ ppm from K-struvite,\textsuperscript{37} which constitutes 
less than 5 % of the total intensity may be present, but cannot be unambiguously confirmed as it 
overlaps with the A and B sites. The potassium could originate from the K$_2$HPO$_4$ stock solution. The 
$\delta_{\text{iso}}(^{31}\text{P})$ and the relative intensity of the four resonances obtained from deconvolution of the $^{31}$P MAS 
NMR spectra are reported in Table 2 and Figure 9, respectively. A chemical exchange between
carbonate and bicarbonate has been reported for LDH. Thus, $^{31}$P-$^{31}$P EXSY MAS NMR spectra were recorded for M2A100P and M4A100P to probe dynamic exchange, e.g., between two phosphate species in the interlayer, but no sign of exchange were observed (Figure S8).

**Figure 8.** $^{31}$P MAS spectra for the three series; M2A, M3A, and M4A with P loadings of 25, 100 and 400. The sites A, B, C, and D are marked. The top line is the experimental data, the second is the simulated and the bottom line is the residual.

**Assignment of site A:** Site A is only present for the M2A (11-29 %) and M3A (0-17%) series and not M4A series. Thus, site A must be due to a distinct difference between M4A and the other two. A comparison of the PXRD, FT-IR, and Raman as well as the $^{25}$Mg and $^{27}$Al MAS NMR data for the
three series reveal that phosphate intercalates in the M2A and M3A LDH, but not in the M4A LDH as explained below.

**Table 2.** $\delta_{\text{iso}}^{(31P)}$ for A, B, C, and D obtained from deconvolution of the $^{31P}$ MAS NMR spectra and assignment of the P-species.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\delta_{\text{iso}}^{(31P)}$ [ppm]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M2A</td>
<td>M3A</td>
</tr>
<tr>
<td>A</td>
<td>8.5-8.7</td>
<td>8.3-8.6</td>
</tr>
<tr>
<td>B</td>
<td>3.0-3.4</td>
<td>2.6-3.2</td>
</tr>
<tr>
<td>C</td>
<td>-1.3 to -0.7</td>
<td>-1.4 to -0.9</td>
</tr>
<tr>
<td>D</td>
<td>-5.9 to -5.1</td>
<td>-6.1 to -5.3</td>
</tr>
</tbody>
</table>

The basal spacing of the LDH and thereby the intercalated anion can be examined from the position of the (003) reflection in the powder X-ray diffractograms. Previous PXRD studies suggest that both H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$ can be intercalated in MgAl- and ZnAl-LDH depending on the pH conditions.$^{13, 15-16, 36, 50}$ In addition, the drying temperature of the sample affect the position of the (003) reflection, which complicates a comparison with earlier studies, as details about sample drying is often missing. For example, a decrease of the interlayer distance from $d_{003} = 10.9 \AA$ to $d_{003} = 8.2 \AA$ was seen for ZnAl-HPO$_4^{2-}$ LDH when drying temperature was raised from 20 to 60 °C.$^{16}$

Upon phosphate exposure the (003) reflection for M2A and M3A shifts from $2\theta = 10.2^\circ$ (8.7 Å) to $11.1^\circ$ (8.0 Å) and $2\theta = 10.5^\circ$ (8.5 Å) to $2\theta = 11.2^\circ$ (7.9 Å), respectively, corresponding to the exchange of nitrate by carbonate in the parent sample (Figures 2a and 2b).$^{57-58}$ At a higher phosphate loadings the (003) reflection for M2A first broadens (50P) and subsequently split in two reflections at $2\theta = 8.8^\circ$ (10.0 Å) and $11.1^\circ$ (8.0 Å), which are assigned to monohydrogen phosphate (HPO$_4^{2-}$)
and carbonate intercalated in the LDH interlayer, respectively.\textsuperscript{15, 58} For M3A, the (003) reflection only broadens and in agreement with that the content of site A in the $^{31}$P MAS NMR spectra is lower than for M2A, c.f. (Figure 2b and 9). The shoulder at $2\theta = 8.8^\circ$ (10.0 Å) at the higher P loading as well implies intercalation of some HPO$_4^{2-}$ into the LDH,\textsuperscript{15} but carbonate remains the predominant interlayer anion based on PXRD (Figure 2b). M4A contains only carbonate in the interlayer based on the location of the (003) reflection at $2\theta = 11.2^\circ$ (7.9 Å; Figure 2c)\textsuperscript{58} and a unique band at 1044 cm$^{-1}$ in the Raman spectrum (Figure 4) from carbonate.\textsuperscript{33, 35} The position of the (003) reflection is unchanged upon exposure to phosphate implying no intercalation of phosphate at any P loading.

In addition, a kinetic study of HPO$_4^{2-}$ adsorption by M2A by in-situ PXRD (Figure S9) clearly shows the progressive exchange of the nitrate by HPO$_4^{2-}$. Exchanged M2A-HPO$_4^{2-}$ LDH display (003), (006) and (009) diffractions lines with $d_{hkl}$ respectively at $2\theta = 8.17^\circ$, 16.39 $^\circ$, and 24.52 $^\circ$, respectively resulting in a basal spacing of 10.84 Å.

The $v_d$ band for phosphate at $\sim 1070$ cm$^{-1}$ in the FT-IR spectra (Figure 3) and 1062 cm$^{-1}$ Raman spectra (Figure 4) is observed for the three series after phosphate exposure with the $v_I$ band at 982 – 987 cm$^{-1}$ assigned to HPO$_4^{2-}$ species with C$_{3v}$ symmetry (Raman).\textsuperscript{59} However, a broadening of the $v$(OH) vibration at $\sim 3000$ cm$^{-1}$ in the FT-IR spectra (Figure S10), which earlier has been assigned to hydrogen bonding between the water in the interlayer and the intercalated phosphate\textsuperscript{15, 22} is only observed for M2A and M3A and not for M4A. In addition, for the M2A and M3A series (Figures 3a and 3b), the intensity of the phosphate band increases with the P loading and the intensity of the nitrate band simultaneously decreases. Whereas only a small increase in the $v_d$(HPO$_4^{2-}$) band is observed as the P loading is increased for the carbonate containing M4A LDH (Figures 3c and 4c), indicating less phosphate adsorption in agreement with the adsorption isotherms (Figure S6). Hence, mainly nitrate and not carbonate is exchanged with phosphate upon phosphate adsorption.
Furthermore, the $^{25}\text{Mg}$ and $^{27}\text{Al}$ MAS NMR spectra imply that phosphate is intercalated in the M2A and M3A LDH and not in the M4A LDH. No changes are seen in the $^{25}\text{Mg}$ MAS NMR spectra of M4A upon phosphate exposure (100P), whereas the line shapes in the $^{25}\text{Mg}$ MAS NMR spectra of M2A and M3A series broaden (Figure 6). The $\delta_{\text{iso}}(^{25}\text{Mg})$ depends on the intercalated anion. Consequently, the broadening of the signal is assumed to be caused by a distribution in $\delta_{\text{iso}}(^{25}\text{Mg})$ due to the intercalation of phosphate and/or the loss of crystallinity (vide infra) and therefore only observed for the M2A and M3A series. Similarly, the $\delta_{\text{iso}}(^{27}\text{Al})$ shifts from 11.7 ppm (parent LDH) to 10.5 ppm (400P) for the M2A series and from 11.0 ppm to 10.6 ppm for the M3A series, whereas no change is seen for M4A (Figure 5c). $\delta_{\text{iso}}(^{27}\text{Al})$ for MgAl-LDH also depends on both the intercalated anion as well as metal ratio. The change in $\delta_{\text{iso}}(^{27}\text{Al})$ for the M2A (1.2 ppm) and M3A (0.4 ppm) series is therefore assigned to the exchange of nitrate with phosphate in agreement with PXRD, FT-IR, and Raman data.

Thus, the difference between the M2A, M3A, and M4A series is that phosphate only intercalates in M2A and M3A and not M4A. Hence, site A, which is only present for M2A and M3A, is assigned to phosphate intercalated in the LDH interlayer. Intercalation is not the dominating mechanism for the phosphate adsorption, as site A constitute 0-30 % of the total intensity.

Furthermore, it is observed that the intercalation results in a broadening and significant decreases in the relative intensity of the (003) reflection for M2A and M3A (especially M2A) compared to the (110) reflection. Thus, the crystallinity of the LDH is lowered along the $c$-axis implying a high degree of stacking faults of the LDH layers and/or thinner LDH particles upon phosphate intercalation, which suggests strong structural disorder of the HPO$_4^{2-}$ anions in the interlayer galleries, in agreement with the increased distribution in the $^{25}\text{Mg}$ MAS NMR spectra.
Figure 9. Relative integrals for A, B, C, and D obtained from deconvolution of the $^{31}$P MAS NMR spectra for the three series; M2A, M3A, and M4A at the different P loadings.

Assignment of site D: Site D is observed in all $^{31}$P MAS NMR spectra with relative concentration of 13-27 % for M2A, 8-28 % for M3A and 12-39 % for M4A. It is assigned to phosphate adsorbed to AOH based on its $\delta_{iso}(^{31}P)$. The samples contain approx. 30 % AOH based on $^{27}$Al MAS NMR, c.f., Table 1. Moreover, two weak reflections at 2θ = 18.5 ° and 20.4 ° from gibbsite (Al(OH$_3$), ICSD 240781) are present for the M2A series (Figure 2a). This $^{31}$P resonance was also seen for a Zn$_{2.5}$Al-
LDH with the same AOH phase exposed to phosphate rich acidified sludge.\textsuperscript{36} Hence, AOH contributes to 8-39\% of the total P adsorption capacity in our samples (Figure 9). The relative concentration of site D is largest at the highest P loading (400P) for all three LDH series, indicating that LDH has higher affinity for phosphate than AOH.

\textit{Assignment of site B and C:} The two remaining sites, B and C must then be HPO\textsubscript{4}\textsuperscript{2-} and/or PO\textsubscript{4}\textsuperscript{3-} phosphate adsorbed to the surface and/or edges of the LDH particles or alternatively, poorly defined magnesium phosphate precipitates. However, there is no indication of dissolution of the LDH (\textit{vide supra}). The \textsuperscript{27}Al 3QMAS NMR spectra for M2A and M3A slightly changes upon phosphate exposure (100P), which are probably caused by the low crystallinity and change in $\delta_{\text{iso}}$(\textsuperscript{27}Al) (Figure S3). Two sites are still present and simulations of the single pulse \textsuperscript{27}Al MAS NMR spectra show that the LDH content is identical within the experimental uncertainties for all samples (Figure 5b) and no significant changes is observed in the Mg:Al ratio upon phosphate exposure (Table S5). The single pulse \textsuperscript{27}Al MAS NMR spectra for the parent LDH, 25P, and 400P for the three series are given in Figure S11. In addition, the $\delta_{\text{iso}}$(\textsuperscript{31}P) does not match common magnesium phosphates, e.g., newberyite ($\delta_{\text{iso}}$(\textsuperscript{31}P) = -7.2 to -8.0 ppm), bobierite ($\delta_{\text{iso}}$(\textsuperscript{31}P) = 4-4.7 ppm), farringonite (Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, $\delta_{\text{iso}}$(\textsuperscript{31}P) = -0.5 ppm), or cattiite (Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}.22H\textsubscript{2}O, $\delta_{\text{iso}}$(\textsuperscript{31}P) = 1.1 ppm)\textsuperscript{27, 61-63} Hence, dissolution of LDH and reprecipitation of magnesium phosphates can be excluded.

To identify B and C we instead focus on the M4A series. No significant loss in the intensity for the (003) and (006) reflection for the M4A series is seen upon phosphate exposure. Consequently, no exfoliation occurs for this series and neither B nor C is phosphate adsorbed to exfoliated single sheets. Similarly, as earlier mentioned no change is seen in the \textsuperscript{25}Mg and \textsuperscript{27}Al MAS NMR spectra. Thus, B and C are not associated with changes in the overall structure (Mg:Al ratio, stacking, crystallinity etc.) or in the local environment around Mg or Al in the bulk LDH. \textsuperscript{1}H MAS NMR spectra of M4A100P and M4A were recorded to investigate changes in the local environment around the protons.
(Figure S3). The same five resonances as for M4A with $\delta_{\text{iso}}(^1\text{H}) = 0.7$ ppm (Mg$_3$OH), 2.1 ppm (Mg$_2$AlOH), 3.1 ppm, 4.6 (H$_2$O) ppm, and 6.10 ppm are observed. Deconvolution of the $^1$H NMR spectra showed no change in the Mg:Al ratio of the LDH in agreement with PXRD. However, comparison of the spectra show an increased intensity in the region $\delta_{\text{iso}}(^1\text{H}) \approx 5-10$ ppm region, where resonances from protonated phosphate is expected. The $^1$H MAS NMR spectrum for M2A100P exhibit a larger intensity increase in this region indicating a higher concentration of protonated phosphate than in M4A100P in agreement with the higher EAC for M2A (Table 1). However, the $^1$H MAS NMR spectra do not provide more information on the binding mode of phosphate for sites B, C, or D.

This leaves phosphate adsorbed to the surface of the LDH particles as the only binding site for the B and C P-species, which is not likely to change the bulk properties of the samples. Whatever their chemical composition, the surface of the MgAl-LDH particles will be positive due to a point of zero charge (PZC) at 12 or above. Our adsorption experiment were performed below the PZC implying a highly positive surface, which will favor adsorption of phosphate on the surface of the LDH particles.

B and C are two sites with different binding mode (monodentate or bidentate), different binding sites on the surface of the LDH particles, and/or different degree of protonation. Site B is the major P-species in all samples with a relative concentration of 45-52 %, 56-74 %, and 54-78 % for M2A, M3A and M4A, respectively, whereas the relative concentration of C is 5-25 %, 6-20 %, and 8-20 % for M2A, M3A and M4A, respectively. Thus, surface adsorption and not anion exchange in the interlayer is clearly the dominating pathway for phosphate adsorption. This can be explained by the particle morphology observed by SEM giving a higher surface area than a smooth surface (Figure S12). The as-prepared LDH display a homogeneous distribution of small hexagonal platelets, 15-25 nm thick and 100-150 nm large, leading to high concentration of reactive surface layers.
Comparison with earlier combined PXRD and $^{31}$P SSNMR studies

Phosphate adsorption by LDH have previously been studied by $^{31}$P SSNMR, but detailed analysis (deconvolution) of the $^{31}$P MAS NMR spectra, which is necessary for quantification and precise determination of $\delta_{\text{iso}}(^{31}\text{P})$ has only been reported in few studies. Most studies report only the $^{31}$P MAS NMR spectrum with distinct spectral features marked, which prevent a detailed comparison with our data. The formation of phosphate minerals, e.g. newbeyrite, bobierite, aluminum phosphate, calcium phosphates and iron phosphates, have been detected by $^{31}$P SSNMR and PXRD after exposure of LDH to phosphate. Magnesium phosphate minerals were the predominant phase identified from adsorption experiment with a starting pH of 7 and a final pH of 12 except for a broad resonance in the region 0-5 ppm, tentatively assigned to phosphate affiliated with the MgAl-LDH. Subsequently, a broad $^{31}$P resonance at $\delta(^{31}\text{P}) = 2.0$ ppm was assigned to phosphate strongly interacting with the commercial Mg$_3$Al-LDH, but detailed analyses of the spectra was not performed. The $\delta_{\text{iso}}(^{31}\text{P})$ is slightly lower than observed for M3A, but a fair agreement is seen. Phosphate bound to a Mg$_2$Al-LDH was reported at $\delta_{\text{iso}}(^{31}\text{P}) = 3.2$ ppm (major site) and -3.8 ppm. The first match well with site B and the latter is in between C and D. Hou at al performed phosphate adsorption at pH = 9 and 12 for a Mg$_3$Al-LDH. The maximum intensity was observed at 2.4 ppm (pH 9) and 3.7 ppm (pH 12), which was assigned to monohydrogen phosphate, whereas a small shoulder near 6 ppm in the pH = 12 samples was assigned orthophosphate ($\text{PO}_4^{3-}$). This was also supported by PXRD and chemical analyses. We note that Hou et al. only considered intercalation as the mechanism of phosphate adsorption. Guo et al. assigned the two dominating resonances at $\delta_{\text{iso}}(^{31}\text{P}) = -14.5$ and -7.5 ppm in the $^{31}$P MAS NMR spectrum to phosphate associated with the LDH. However, $\delta_{\text{iso}}(^{31}\text{P}) = -14.5$ ppm are in the same range as aluminum phosphate synthesized under acid condition and $\delta_{\text{iso}}(^{31}\text{P}) = -7.5$ ppm match newbeyite. Both minerals are also clearly identified by PXRD. The phosphate adsorption experiments were performed at pH = 4.3, which
explain the dissolution of the LDH and precipitation of phosphate minerals. For ultrathin (3-5 nm) MgAl-LDH the same four resonance with slightly different $\delta_{\text{iso}}(^{31}\text{P})$ were observed with a lower relative concentration of A (3-7 %) and a higher relative concentration of C (34-43 %) confirming the assignments of the P-species.

For a Zn$_{2.5}$Al-LDH exposed to phosphate under neutral and acidic condition, the $^{31}$P MAS NMR spectra showed four resonances and two of these with $\delta_{\text{iso}}(^{31}\text{P}) = 4.2-5.2$ ppm and $\delta_{\text{iso}}(^{31}\text{P}) = 0.5-1.0$ were assigned to phosphate in association with the LDH. The different $\delta_{\text{iso}}(^{31}\text{P})$ for the resonances is ascribed to the presence of Zn instead of Mg. In the current study, which was performed under alkaline condition, three sites (A, B, and C) have been assigned to phosphate associated with the LDH. Hence, the number of P-species adsorbed by the LDH might depend on the pH, but further studies are needed.

**Conclusion:**

Detailed insight into the interactions between phosphate and MgAl-LDH was obtained by a powerful combination of phosphate adsorption studies along with multi-nuclear SSNMR, PXRD, FT-IR, Raman, and ICP-OES for characterization of the LDH product. Four different P-species (A, B, C, and D), were identified by analyses of the $^{31}$P MAS NMR spectra. These were assigned to phosphate intercalated in the LDH (A), phosphate adsorbed on the surface of the LDH particles (B and C), and phosphate adsorbed to an amorphous AOH (D) by combining information obtained from the different characterization techniques above. The importance of amorphous AOH formation during LDH synthesis has only recently been realized. The relative concentration of the different P-species depends on phosphate concentration, exposure time, the anion in the parent LDH, and the Mg:Al ratio. Surprisingly, surface adsorption (B+C) is the major P adsorption mechanism (52-88 %), whereas intercalation constitutes only up to 29(4) % of the total adsorbed phosphate. In addition, the
amorphous AOH phase has a significant contribution to the phosphate adsorption capacity especially at high P concentrations and long exposure times suggesting that LDH has a stronger affinity for phosphate than AOH. Thus, the mechanism for the phosphate adsorption by MgAl-LDH prepared by co-precipitation is a combination of phosphate intercalated in the interlayer (anion exchange), surface adsorption, phosphate adsorbed to the amorphous AOH with surface adsorption to the LDH being the dominating P-species. A lower crystallinity along the $c$-axis was seen after phosphate intercalation indication of strong disorder of the HPO$_4^{2-}$ anions in the interlayer. In contrast, anion exchange of carbonate with phosphate did not occur and the crystallinity is preserved along the $c$-axis. Moreover, no significant dissolution of the MgAl-LDH is seen during phosphate adsorption. The high phosphate adsorption capacities (17-47 mgP/g) make Mg$_x$Al LDH a promising phosphate adsorbent. However, for application for wastewater treatment further studies regarding the optimum particle size and morphology, as well as implication of phosphate adsorption to amorphous AOH on the recyclability of LDH have to be investigated.

**Supporting information:**

Additional information about the phosphate adsorption studies (sample preparation, theoretical adsorption capacities, adsorption isotherms, ICP-OES, FT-IR, in-situ PXRD) as well as SEM and SSNMR ($^1$H MAS NMR, $^{25}$Mg MAS NMR, $^{27}$Al 3QMAS NMR, $^{31}$P MAS NMR, and $^{31}$P-$^{31}$P EXSY NMR) data for selected samples is available in the Supporting Information.

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References:


TOC graphics

\[
\begin{align*}
\text{Al(OH)}_3 & \quad (\sim 30\% \text{ of Al}) \\
\xrightarrow{\text{HPO}_4^{2-}} \\
\text{B} & \quad \text{C} \\
\text{H}_2\text{PO}_4^{-} & \quad \text{H}_2\text{PO}_4^{-} \\
\text{A} & \quad \text{CO}_3^{2-} \\
\text{D} & + \\
\text{H}_4\text{PO}_4^{-} & \sim \text{Al(OH)}_3
\end{align*}
\]