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Phosphate capture by ultrathin MgAl layered double hydroxide nanoparticles

Chen Liu \textsuperscript{a,c,g}, Meiyi Zhang \textsuperscript{*a}, Gang Pan \textsuperscript{*a,b,c}, Laura Lundehøj \textsuperscript{d}, Ulla Gro Nielsen \textsuperscript{d}, Yi Shi \textsuperscript{a,e} and Hans Christian Bruun Hansen \textsuperscript{f,g}

\textsuperscript{a} Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
\textsuperscript{b} Center of Integrated Water-Energy-Food studies (iWEF), Nottingham Trent University, Nottinghamshire, NG25 0QF, UK
\textsuperscript{c} University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{d} Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark
\textsuperscript{e} Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China
\textsuperscript{f} Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark
\textsuperscript{g} Sino-Danish Center for Education and Research (SDC), China

\textsuperscript{*} Corresponding author: gpan@rcees.ac.cn (GP), myzhang@rcees.ac.cn
Abstract

Capture of phosphorus from runoff and wastewater is of high priority in order to reclaim phosphorus for food security and to prevent water pollution. Here we report an environmentally friendly method to synthesize ultrathin MgAl layered double hydroxide (LDH) nanoparticles for phosphorus adsorption. Fast co-precipitation of magnesium and aluminum at 25-80 °C in the presence of urea resulted in the desired LDH with variable admixtures of amorphous aluminum hydroxide (16-38%) quantified from solid state $^{27}$Al MAS NMR. Freshly synthesized particles appeared as exfoliated single layers that upon drying stacked to form particles with thickness of 3 to 5 nm (four to six LDH layers) and lateral sizes of ~30 nm, as seen by XRD, SEM, TEM, and AFM. Phosphate adsorption on LDH nanoparticles synthesized at room temperature (LDHns-U25) was very fast and reaction reached equilibrium within 15 min at pH 8.5. The freeze-dried LDHns-U25 nanoparticles exhibited phosphate sorption capacity of $98\pm15$ mg P g$^{-1}$, which is 55% higher than for conventional LDH. Phosphate was bound to LDH electrostatically and via inner-sphere surface complexation as evidenced from a combination of $^{31}$P MAS NMR spectroscopy, surface potential measurements, IR spectroscopy, and ionic strength effects on phosphate sorption. This study demonstrates that urea-facilitated synthesis of LDH nanoparticles provides high capacity phosphate sorbents with potentials for phosphate recovery from waste waters.

Key words: Phosphate removal; Hydrotalcite-like compounds; Nanosheets; Adsorption; Wastewater

1. Introduction
Phosphorus is essential for agriculture and food security for the growing world population. However, excessive anthropogenic phosphate (P) arising from fertilization, treated municipal and industrial wastewater may cause eutrophication of receiving water bodies (Conley et al. 2009, Emmanuelawati et al. 2013, Shannon et al. 2008). Phosphorus capture and recycling is crucial, as phosphorus mineral deposits are being depleted (Pan et al. 2018, Reijnders 2014). Robust and efficient methods for P reduction at low cost and energy are therefore needed to address these challenges. Various technologies have been employed for phosphate removal from wastewaters, such as chemical precipitation, biological removal, ion exchange and adsorption. Among them, adsorption is promising due to less sludge production, high uptake capacity and efficiency at low P concentrations (Emmanuelawati et al. 2013, Moharami and Jalali 2013).

Layered double hydroxides (LDH) have been studied as sorbents for P removal due to their high anion-exchange capacity and their ability to accommodate different anions in the interlayer. LDH are layered structures comprising positively charged metal hydroxide layers typically comprising two different metal ions, interchanging with anionic interlayers of charge compensating anions (Das et al. 2003, Das et al. 2007, Mohapatra and Parida 2016). Here we refer to a specific LDH by the identity of the metal cations and the anion, e.g., MgAl-SO₄, for an LDH with magnesium and aluminum in the metal hydroxide layer and SO₄²⁻ in the interlayer. Promising P adsorption has been observed for MgAl-Cl, ZnAl-Cl, and ZnAl-NO₃ LDH from both synthetic solutions and waste waters (He et al. 2010, Kuzawa et al. 2006). New
generations of nanostructured adsorbents have been developed for P removal (Fang et al. 2015, Su et al. 2013) with high surface areas and abundant active adsorption sites. For instance, Zhang et al. (2015) reported a nano-Mg(OH)$_2$ modified polystyrene material exhibiting high adsorption capacity (45.6 mg P g$^{-1}$) for phosphate. However, the application of nanomaterials for wastewater cleaning has been challenged by complex manufacturing processes and use of toxic precursors.

Exfoliated LDH (here called LDH nanosheets) are interesting candidates as high capacity P adsorbents because they possess a permanent positive layer charge and a high specific surface area (Hibino and Jones 2001). A typical approach for formation of LDH nanosheets is to exfoliate pre-synthesized LDH layered compounds, usually by intercalation of large anionic solutes to weaken the interlayer interaction, followed by delamination of the modified products in organic solvents (Ma et al. 2006). However, the synthesis processes are time consuming and make use of costly (and toxic) organic solvents and reagents similar to other nano-adsorbents, which is a limitation for broader application.

In order to prevent stacking of the LDH nanosheets, one strategy is to introduce a stabilizer with high ability to form hydrogen bonds with hydroxyl groups as it may break the integrated bonding network among the hydroxyl groups of the metal hydroxide layers, the interlayer water molecules and anions (Wei et al. 2014). Formamide has been a classical agent for exfoliating LDH layers (Yu et al. 2015), but unfortunately makes synthesis unsustainable. Urea may represent a non-toxic alternative. The urea molecule has a high proportion of strongly electronegative
elements, one oxygen and two nitrogen atoms, implying a high capability of forming hydrogen bonds (Ma et al. 2006). Although homogeneous precipitation by thermal hydrolysis of urea - the so called ‘urea method’ (Costantino et al. 1998), results in formation of LDH but with admixtures of amorphous Al-(hydr)oxide phases (Pushparaj et al. 2015), this method is frequently used for preparation of well-crystallized, large sized (2-20 µm) LDH under hydrothermal conditions (Adachi-Pagano et al. 2003, Hibino and Ohya 2009, Ogawa and Kaiho 2002). Progressive hydrolysis of urea usually produces hydroxide and carbonate ions, which are main components of the metal hydroxide layers and interlayers of LDH, and thus results in homogenous nucleation and crystallization of carbonate LDH (Hibino and Ohya 2009, Ogawa and Kaiho 2002) as well as formation of other layered phases (Staal et al. 2017). We hypothesize that a low reaction temperature may prevent urea hydrolysis, and thus that urea hydrates accumulate at the surface of LDH sheets, stabilizing the colloidal suspension, and causing the LDH layers to grow in-plane only and thus to produce LDH nanosheets.

In this study, we report a new route for direct synthesis of MgAl-NO\(_3\) LDH nanosheet materials in urea solution. The P adsorption properties of this new material were studied with emphasis on adsorption kinetics, capacity and affinity as well as effects of solution pH and ionic strength. Solid state nuclear magnetic resonance (NMR) spectroscopy, zeta potential measurements, and Fourier transform infrared spectroscopy (FTIR) was used for characterization of the nanoparticles and P bonding.

2. Experimental

2.1 Materials
Magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O), aluminium nitrate (Al(NO$_3$)$_3$·9H$_2$O), urea (CO(NH$_2$)$_2$), formamide (CH$_3$NO), concentrated nitric acid (HNO$_3$, 68 %), sodium hydroxide (NaOH, 98 %) and potassium dihydrogen phosphate (KH$_2$PO$_4$) were supplied by Sinopharm Chemical Reagent Co. (Beijing, China). All chemicals were of analytic grade (or higher), and was used without further purification. Deionized water was purged with high grade nitrogen (99.99%) for 30 min prior to use in order to remove carbon dioxide.

2.2 Synthesis of ultrathin LDH nanoparticles

Four different syntheses of MgAl-NO$_3$ LDH were performed in presence of urea at room temperature (LDHns-U25) and at 80°C (LDHns-U80), in formamide (LDHns-F), and by a conventional co-precipitation method (LDH-Ref), respectively. A 1 L solution containing NaNO$_3$ (0.01 M) and urea (6 M) was prepared in thermostatic water bath with pH adjusted to pH of 10.0 ± 0.5 using 0.5 M NaOH. A 200 mL mixed solution composed of 0.04 M Al(NO$_3$)$_3$·9H$_2$O and 0.08 M Mg(NO$_3$)$_2$·6H$_2$O was added dropwise ($\approx$10-15 mL min$^{-1}$) to the beaker. Simultaneously, a solution of 0.5 M NaOH was added dropwise to maintain pH at 10.0 ± 0.5 under magnetic stirring (400 rpm) and N$_2$ flushing to avoid the entrance of CO$_2$ (30 mL min$^{-1}$) (Table 1). The pH was monitored using a Mettler Toledo combination pH electrode to ensure proper rate of NaOH addition. The resulting precipitate was collected by centrifugation for 15 min at 12840 g, washed twice with anhydrous ethanol and once with CO$_2$-free deionized water in sealed containers, and finally freeze-dried at -46°C for 24 h.
For comparison, LDHns-F was synthesized by modification of the method by Yu et al. (2015) using the same metal salt concentrations and the same reaction time as described above, except formamide was instead of urea (Table 1). For reference, a conventional layered LDH-Ref was prepared using co-precipitation at constant pH similar to the method of Yun et al. (1995) (Table 1). The precipitate was stirred for 1 h and aged in water bath under stirring at 70°C for 24 h. All the other conditions were the same except formamide and urea was not added. The product was freeze-dried as described above.

Table 1. Composition of the solution, temperature and reaction time used for the synthesis of LDH.

2.3 Solid state characterization

The Mg and Al contents of the LDH samples were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) after dissolution of the samples in HCl solution. The crystallinity, morphology and specific surface area of the LDHs synthesized were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electronic microscopy (TEM), atomic force microscopy (AFM), and Brunauer-Emmett-Teller N₂ adsorption (BET). A Zetasizer Nano ZS potential analyzer was used to measure the zeta potential of LDH particles in suspension before and after P adsorption. To study the phosphate speciation and bonding in the LDH, ³¹P MAS NMR spectra and Transmission Fourier transform infrared spectroscopy (FTIR) were used. ²⁷Al magic angle spinning (MAS) NMR spectroscopy was used to detect the presence of non-LDH impurities in the
products, and to record LDH transformation when exposed to phosphate. Detailed description of the measurements above can be found in the Supporting Information.

2.4 Phosphate adsorption

Phosphate adsorption kinetics was studied in batch experiments. Prior to use, the suspensions with a certain amount of freeze-dried LDH adsorbent dispersed in NaNO\textsubscript{3} electrolyte in polypropylene centrifuge tubes, were placed in an ultrasonic bath (80 kHz) for 30 min to minimize aggregation of LDH nanoparticles. Subsequently, various volumes of KH\textsubscript{2}PO\textsubscript{4} solutions were added to the suspensions to yield a mixture volume of 30 mL, with LDH concentration of 1 g L\textsuperscript{-1} in 0.01 mol L\textsuperscript{-1} NaNO\textsubscript{3} background and initial phosphate concentrations of 50 mg P L\textsuperscript{-1} and 80 mg P L\textsuperscript{-1}, respectively. The tubes were then shaken at 170 rpm for 8 h at 25±1°C, and the solution pH was kept constant at 8.5±0.1 using adjustment with 0.1 mol L\textsuperscript{-1} HNO\textsubscript{3}/NaOH. The supernatant was separated by centrifugation from 0~1440 mins at 12840 g for 5 min to determine the solution P concentration. The supernatants were filtered through a 0.22 μm polypropylene syringe filter and then analyzed for phosphate concentration using the molybdate colorimetric method at a wavelength of 880 nm using a spectrophotometer (UV-756 PC, Shanghai Sunny Hengping Scientific Instrument CO. LTD, China).

Adsorption isotherms were determined at pH 8.5±0.1 with the initial phosphate concentration ranging from 10 to 120 mg P L\textsuperscript{-1} in presence of 1 g L\textsuperscript{-1} LDH and 0.01 mol L\textsuperscript{-1} NaNO\textsubscript{3} electrolyte. The suspensions were constantly agitated for 24 h in a thermostatic shaker (25±1°C). After completion, suspensions were centrifuged, the supernatant sampled and the pellet re-dispersed in water to determine desorption of
phosphate with all experimental conditions maintained the same as during adsorption. Phosphate concentration was determined as described above. Adsorption data were fitted by the Langmuir isotherm model using non-linear regression in OriginPro 2016.

In order to investigate how adsorption was affected by solution pH and ionic strength, 0.03 g freeze-dried LDH was added to 30 ml of 75 mg P L\(^{-1}\) solutions at three different electrolyte concentrations of 0.001, 0.01, or 0.1 mol L\(^{-1}\) NaNO\(_3\), respectively. The pH of the solution was adjusted from 7 to 11 using 0.1 mol L\(^{-1}\) HNO\(_3\)/NaOH. The equilibrium pH was measured after 24 h and the supernatants were filtered through 0.22 μm membrane for phosphate analysis.

3. Results and Discussion

3.1 Chemical and structural characterization of LDH nanoparticles

The phase composition of the synthesized freeze dried and gel-like fresh LDH was examined by powder-XRD (Fig. 1). When the freshly synthesized gel-like LDH product was examined, the basal reflections ((003) and (006)) were barely detectable (Fig. 1a), manifesting the lack of long-range order along the c-axis (Wang and O'Hare 2012, Yu et al. 2015). When samples were run as freeze-dried powder samples on a glass sample holder, a broad and intense basal reflection at 10.75° (0.82 nm) was observed demonstrating re-stacking of the colloidal LDH nanoparticles with nitrate in the interlayer (Fig. 1b) (Wu et al. 2005). The gel-like samples showed no signs of basal reflections, but the characteristic (110) reflection was observed (Fig. 1a insert). The cell parameter \(a\) (average metal-metal distance) calculated from the (110) reflection (X'Pert HighScore Plus) for dried LDHns-U25, LDHns-U80, LDHns-F, and LDH-Ref samples
were 3.054 Å, 3.048 Å, 3.048 Å, and 3.045 Å, respectively. An $a$ distance of 3.04 Å and 3.06 Å for Mg$_2$Al-NO$_3$ and Mg$_3$Al-NO$_3$ LDH, respectively have been observed by Hu and O'Hare (2005) and Wu et al. (2005), suggesting a Mg:Al ratio between 2:1 and 3:1 in our samples. Among the four samples, LDHns-U25 was synthesized at the lowest temperature, resulting in lowest intensity and broadest diffraction peaks (Fig. 1b). It can be concluded that direct synthesis in urea or formamide affords LDH nanoparticles with less crystallinity than that of traditional co-precipitation method.

The purity of LDH preparations was further probed by $^{27}$Al MAS NMR spectroscopy (Fig. 2). The asymmetric line shape of the isotropic resonance is characteristic for MgAl-LDH with impurities of amorphous aluminum hydroxides (AOH), see Pushparaj et al. (2015) and Staal et al. (2017) for a detailed discussion. Deconvolution of the $^{27}$Al MAS NMR spectra allowed for an estimate of the relative concentration of the AOH phase admixture in the samples ranging between 16 and 38% (Fig. 2, Table S2). The admixture of AOH phases was expected given the fast metal salt addition, very short aging and absence of post synthesis treatment (Pushparaj et al. 2015). The relative AOH content was lower (16%) for the samples synthesized at 80°C than for the samples prepared at 25°C (38%); hence the formation of AOH is temperature dependent, as observed earlier for co-precipitation (Pushparaj et al. 2015). In addition, all the samples contain less than 5% of tetrahedrally coordinated Al as seen
from shifts at approx. 64 and 74 ppm, which most likely originates from a colloidal 
aluminum hydroxide gel (Staal et al. 2017).

The physiochemical properties of the three LDH nanoparticle samples and the 
LDH-Ref are summarized in Table 2. The bulk Mg:Al ratios of LDHns-F, LDHns-U25, 
LDHns-U80, and LDH-Ref samples were 1.97, 1.90, 2.10, and 1.91, respectively 
(calculated from ICP-OES), which are close to the Mg:Al ratios in the synthesis mixture. 
However, the actual Mg:Al ratios in LDH is higher (Table 2) because only 75±5 to 
84±5 % of the total Al is in the LDH phase based on $^{27}$Al SSNMR (Table S2), i.e., the 
LDH is depleted in Al as compared to the bulk composition (Staal et al. 2017) (see 
above). The N$_2$-adsorption/desorption isotherms of the LDH samples were analyzed to 
determine their specific surface areas and porosity (Fig. S2). The hysteresis loops 
display no limiting adsorption at high P/P$_0$, which is common for plate-like particles 
with slit-shaped pores (Zhan et al. 2016). All specific surface areas of the LDH 
nanoparticles (83-97 m$^2$ g$^{-1}$) were higher than that of LDH-Ref (52 m$^2$ g$^{-1}$, Table 2). The 
LDH samples display a distinct H3-type hysteresis loop (P/P$_0$ > 0.4), implying the 
presence of mesopores (2-50 nm). The average pore diameters of all the samples are 
small with a narrow distribution below 20 nm, indicating a mesoporous structure.

**Fig. 2.** Deconvolutions of the $^{27}$Al MAS NMR spectra of the MgAl-LDH nanoparticles, 
a) LDHns-F, b) LDHns-U80, c) LDHns-U25, d) LDHns-F_P, e) LDHns-U80_P and f) 
LDHns-U25_P. The experimental spectrum (Exp), simulated (Sim) and difference (Dif)
are shown for each. The results are summarized in Table S2.

Table 2. Composition, BET and pore sizes of pristine LDH and nanoparticle samples

TEM images (Fig. 3) show that the three LDH samples synthesized in presence of formamide or urea have a sheet-like structure with a lateral size of ~30 nm, and a thickness of ~5 nm, respectively. The urea synthesis products are a few nanometers thick, evidenced by the slender dark colored area (Fig. 3a-b), where some of the particles are obviously curled. Sample LDHns-U25 (Fig. 3a) consists of very small, less well defined and highly aggregated particles which probably is due to a relatively high amount of AOH in this sample compared to its counterparts that were synthesized at 80°C (Table S2). The inset in Fig. 3c displays the basal plane of an individual LDH hexagon. Representative SEM images of the samples (Figure S3, Supporting Information) also confirm the formation of ultrathin sheet-like morphology.

Fig. 3. TEM images of LDH nanoparticles: a): LDHns-U25; b): LDHns-U80; c): LDHns-F; (d) AFM image and the corresponding height profile for the marked line in the image for LDHns-U25 mapped in ScanAsyst mode, height image over scanning area of 200×200 nm².

To further quantify the thickness of LDH nanoparticles, the freeze-dried materials were examined by AFM. The height profile along transects across particles are shown in Fig. 3d, which reveals a particle thickness of 3 to 5 nm. Fig. 3d displays sheet-like objects with a similar lateral size as observed by TEM (Fig. 3c). The thickness for a single metal hydroxide layer plus the interlayer is 0.8 nm as seen from XRD (Fig.1b).
Particles with thicknesses of 3 to 5 nm thus consist of approximately four to six layers (Li et al. 2005, Ma et al. 2006). These compelling evidences confirm the formation of LDH nanoparticles with a thickness of only few layers consistent with previous studies of exfoliated layered LDH (Fang et al. 2015, Hibino and Jones 2001, Ma et al. 2006). For comparison, the AFM image of LDH-Ref along with the corresponding height profile is shown in Fig. S4. The LDH-Ref particles have a diameter of 100-150 nm; the thickness > 14 nm is considerably larger than the thickness of the LDH nanoparticles confirming that the synthesis using urea or formamide leads to very thin LDH.

### 3.2 Phosphate adsorption

The kinetics of phosphate adsorption to LDHns-U25 and LDH-Ref at initial phosphate concentration of 80 mg L⁻¹ were well fitted by a pseudo second-order model (eqn. (1)) (Fig. 4a, parameters in Table S3).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1)
\]

where \(q_t\) is the adsorbed amount at a time \(t\) (mg g⁻¹), \(q_e\) is the adsorbed amount at equilibrium, and \(k_2\) (g mg⁻¹ min⁻¹) the rate constant. Phosphate adsorption on LDHns-U25 reached equilibrium within 15 min. The comparison of \(k_2\) showed that phosphate adsorption on LDH-Ref is slightly slower than that on LDHns-U25 (Table S3). Similar adsorption with equilibrium reached within 15 mins has been observed for phosphate adsorption to ultrathin \(\gamma\)-Fe₂O₃ nanosheets and to single sheet iron oxides produced from Fe²⁺-Fe³⁺-LDHs (Fang et al. 2015, Liu et al. 2016).

**Fig. 4.** a) Kinetics of phosphate adsorption to LDHns-U25 and LDH-Ref; b) Adsorption
isotherms for phosphate adsorption to pristine LDH and LDH nanoparticles and the corresponding Langmuir fits (error bars represent the standard deviation of duplicates).

Table 3. Langmuir isotherm parameters for phosphate adsorption to LDH.

Isotherm data were well described by the Langmuir model (eqn(2)) (Fig. 4b, Table 3).

$$q_e = \frac{K_L C_e q_m}{1 + K_L C_e}$$  \hspace{1cm} \text{(2)}

where $C_e$ (mg P L$^{-1}$) is the equilibrium phosphate concentration in solution, $q_e$ (mg P g$^{-1}$) the amount of phosphate adsorbed, $q_m$ (mg P g$^{-1}$) the maximum adsorption capacity, and $K_L$ (L mg(P)$^{-1}$) the Langmuir affinity constant. The maximum phosphate adsorption capacity obtained from Langmuir fitting follows this sequence: LDHns-U25 > LDHns-F > LDHns-U80 > LDH-Ref, with $q_m$ spanning from 98 ± 15 mg P g$^{-1}$ to 64 ± 9 mg P g$^{-1}$. Desorption of phosphate from the phosphate loaded nanoparticles was evaluated after adsorption experiments by replacement of the solution with fresh electrolyte without phosphate, and controlling pH at 8.5. The extent of phosphate desorption was calculated by dividing the desorbed amount after 24 h by the initial adsorbed amount.

Phosphate desorption from LDHns-U25 and LDHns-U80 were low, with the lowest values of 0.17±0.03% and 0.82±0.04% at low P loadings, and the highest of 5.04±0.28% and 6.23±0.21% at high P loadings (Fig. 5a). Thus, desorption from LDH nanoparticles is low, hence increasing the potential of the LDH materials for water cleaning.

Fig. 5b reveals the effects of pH and ionic strength on phosphate adsorption by LDHns-U25. In the studied pH range 7-11, phosphate adsorption dropped significantly from ~73 to ~42 mg g$^{-1}$ with increasing pH. Similar pH effect on phosphate adsorption
has also been observed in another study of Mg-Al LDH (Yang et al. 2014). The protonation of the hydroxyl groups of the MgAl hydroxide layers will change with pH contributing with positive surface charge at low pH and negative surface charge at high pH (Hansen and Koch 1995; see also 3.3.2 below). At higher pH, LDH layers become increasingly deprotonated and causes electrostatic repulsion between phosphate and deprotonated surface OH groups (Chitrakar et al. 2006). Thus, the change in charge of phosphate ion, the change in charge of the LDH metal hydroxide layers and competition with OH$^-$ jointly cause adsorption to decrease with increasing pH. Furthermore, competition with carbonate is also more prevalent at high pH due to higher carbonate concentrations in equilibrium with atmospheric CO$_2$ (Lundehøj et al. 2019).

Increasing the ionic strength from 0.001 M to 0.1 M had no significant effect on adsorption (Fig. 5b). This is a strong indication that adsorption may take place via inner-sphere surface complexation (McBride 1997, Su et al. 2013, Zhang et al. 2009) which is insensitive to ionic strength as opposed to outer-sphere surface complexation and anion exchange that decreases with increasing ionic strength (Su et al. 2013). Thus, the results suggest that phosphate form inner-sphere complexes when adsorbed on LDH nanoparticles.

**Fig. 5.** (a) Phosphate desorption from LDH nanoparticles (pH 8.5±0.1, desorption time: 24 h); (b) The effect of pH and ionic strength on phosphate adsorption by LDHns-U25 (error bars represent the standard deviation of duplicates).

### 3.3 Phosphate bonding to LDH nanoparticles
3.3.1 Solid state NMR

$^{27}$Al MAS NMR spectra of LDH nanoparticles were recorded after exposure to phosphate. The deconvolutions of these spectra showed no significant changes in the relative concentration for the LDH component, indicating that the LDH is not dissolved or transformed when exposed to phosphate. $^{27}$Al MAS NMR spectra of the LDH nanoparticles after phosphate adsorption showed a small (0.5-0.7 ppm) change in $\delta_{\text{iso}}(^{27}\text{Al})$ indicating incorporation of phosphate in the interlayer of the LDH. $^{31}$P MAS NMR spectra were used to study phosphate speciation and bonding in the LDH. The $^{31}$P MAS NMR spectra contain one resonance, accompanied by a few weak spinning side bands (Table 4, Fig. 6). These results are in good agreement with earlier studies on MgAl-LDH (Hou et al. 2003). The presence of multiple $^{31}$P sites imply that in addition to electrostatic bonding in their interlayer, phosphate may also form surface complexes on e.g., the edges and outside of the particles. In addition, phosphate also sorbs to AOH present in the LDH nanoparticle samples according to $^{27}$Al SSNMR (Table S2). We assign the broad resonance at $\delta_{\text{iso}}(^{31}\text{P}) \approx -9$ ppm to phosphate adsorbed to AOH and possibly a small amount of an amorphous aluminum phosphate ($\text{AlPO}_4$) phase based on our recent study of phosphate adsorption on ZnAl-LDH in acidified waste water sludge (Lundehøj et al 2019). We note that the $^{27}$Al SSNMR spectra of the P-loaded samples have a small intensity ($< 5\%$) in the region 0 to -5 ppm for $\text{AlPO}_4$, but could not be determined precisely from deconvolution. This P-AOH resonance constitute 6(4) to 12(6) % of the total P c.f., Figure 6. Thus, phosphate sorbed to the AOH component is less than 15% of the total sorbed P.
Table 4. Parameters obtained from the deconvolutions of the $^{31}$P MAS NMR spectra

Fig. 6. Deconvolution of the experimental $^{31}$P MAS NMR spectra of the MgAl-LDH nanosheets exposed to phosphate. a) LDHns-F_P, b) LDHns-U80_P, and c) LDHns-U25_P. The experimental spectrum (Exp), simulated (Sim) and difference (Dif) are shown for each.

3.3.2 Surface zeta potentials

Fig. 7a shows the zeta potentials of pure LDH nanoparticles before and after exposure to 50 mg P L$^{-1}$ phosphate solution. Before the adsorption, the surface charge of LDH nanoparticles is positive in the studied pH range, but a decline is seen with increasing pH as the surface OH groups are increasingly deprotonated (Hansen and Koch 1995). After phosphate adsorption, the surface charge of LDH nanoparticles decreased significantly, and the isoelectric point of LDHns-U25 and LDHns-U80 was determined to pH 5.3 and 5.7, respectively. The marked decrease of the zeta potential after phosphate adsorption indicates that phosphate adsorbed to LDH nanosheet surfaces is bound as inner-sphere surface complexes as formation of outer-sphere surface complexes cannot shift the surface charge of this magnitude (Ren et al. 2012, Su et al. 2013, Yang et al. 2014).

Fig. 7. a) Zeta potential of LDHns-U25 and LDHns-U80 before (solid line) and after (dotted line) phosphate adsorption with initial phosphate concentration of 50 mg L$^{-1}$, adsorbent dose at 1g L$^{-1}$; b) FT-IR spectra of LDHns-U25 before (A) and after (B1-4)
phosphate adsorption at different phosphate initial concentrations: $B_1 = 20\, \text{mg P L}^{-1}$, $B_2 = 50\, \text{mg P L}^{-1}$, $B_3 = 80\, \text{mg P L}^{-1}$, $B_4 = 120\, \text{mg P L}^{-1}$.

### 3.3.3 FT-IR analysis

The FT-IR spectrum of non-treated LDHns-U25 is compared with the P-loaded sorbents at several different initial P concentrations (Fig. 7b). The strong and broad bands at 3453 cm$^{-1}$ and 1632 cm$^{-1}$ belong to the stretching and bending vibration of the hydroxyl groups (–OH) in the LDH metal hydroxide layers and water, respectively (Liu et al. 2010, Zhang et al. 2005). The bands at ca. 1384 cm$^{-1}$ are identified as $\nu_3$ mode of NO$_3^-$ (Wu et al. 2005) in the interlayer. The hydrolysis of urea proceeds in two steps, with first formation of NH$_4$CNO (2200 cm$^{-1}$) and next formation of ammonium and carbonate (Adachi-Pagano et al. 2003). However, none of these bands were observed in the IR spectra demonstrating that urea was not decomposed during synthesis (Benito et al. 2008). After reaction with phosphate solution, a new, broad band at 1059-1067 cm$^{-1}$ appeared, which can be assigned to the symmetrical stretching vibration of PO$_4^{3-}$ (Yu and Chen 2015). Its intensity increased with the phosphate concentration used indicating that the surface hydroxyl groups were replaced by the adsorbed phosphate via formation of an inner-sphere surface complex (M-O-P) between phosphate and the LDH metal hydroxide layers (Lǚ et al. 2013, Yu and Chen 2015, Zhan et al. 2016), in accordance with the results of ionic strength and zeta potential measurements. The 1384 cm$^{-1}$ peak (NO$_3^-$) decreased with increasing phosphate concentration, suggesting that competitive adsorption exists between phosphate anions and nitrate in solution.

A simple calculation accounting for the charge of the LDH interlayer and the
charge of the phosphate anion provides an estimate of the maximum amount of phosphate (HPO$_4^{2-}$) that can be adsorbed due to electrostatic bonding (Supporting Information; Table 2). The estimated amounts represent 50-70% of the maximum P adsorption capacity. For LDHns-U25, LDHns-U80 and LDHns-F, the theoretical anion exchange capacities (AEC) derived adsorption capacities are 44%, 50% and 53% of the Langmuir $q_m$ values (Table S4). Other modes of adsorption than electrostatic bonding are active. The observation of four different environments in the $^{31}$P NMR spectra support the adsorption on the surface of the particles and intercalation of P in the interlayer. The latter was also confirmed by a slight increase of d-spacing after P adsorption (Fig. S1, Table S1) (Hansen 1995). The small change in interlayer spacing after intercalation is in agreement with the findings by Gillman et al. (2008), who attributes this to non-uniform distribution of phosphate/water in the interlayers. The proposed mechanism of phosphate adsorption on LDH is illustrated in Fig. 8 comprising i) there was electrostatic attraction between negatively charged phosphate species and positively charged LDH nanoparticles, ii) inner-sphere surface complexation of phosphate onto LDH metal hydroxide layers, and iii) ion exchange between phosphate anions and interlayer nitrate.

Fig. 8. Schematic illustration of the synthesis process and phosphate adsorption to LDH nanoparticles.

3.4 Perspectives for applications

Table S5 compares the maximum adsorption capacities of various adsorbents for
phosphate. It is found that the LDH nanoparticles produced in this work have a significantly higher phosphate removal capacity than many other adsorbents, e.g. granular MgAl LDH (hydrotalcite) (Kuzawa et al. 2006, Ookubo at al. 1993, Yang et al. 2014), gibbsite (Lookman et al. 1997), goethite (Kim et al. 2011), and Phoslock®, a commercial lanthanum exchanged bentonite which is used for trapping P in lake restauration (Robb et al. 2003, Ross et al. 2008, Spears et al. 2013, Dithmer et al. 2015, Xu et al. 2017). A high adsorption capacity of our LDH nanoparticles compared to other layered LDH may be attributed to the thin particles contributing a high density of adsorption sites that are not accessible in thicker LDH particles (Fang et al. 2015). The remarkably high adsorption capacity of 131 mg P g⁻¹ for CaAl LDH (hydrocalumite) is due to precipitation of calcium phosphates as the LDH dissolves (Xu et al. 2010). Amorphous aluminum hydroxide which is present in our samples (Fig. S4) has an adsorption capacity less than half of that for LDHns-U25. Many adsorbents including iron oxides (Lű et al. 2013, Zhang et al. 2009) and zirconium oxides (Su et al. 2013) often have negative surface charges at the pH of natural waters and thus sorption may be rather low even at pH 7 (Xu et al. 2017). On the contrary, LDH nanoparticles can be used even at high pH which may be encountered during eutrophication events such as cyanobacterial blooms (pH~8.5).

4. Conclusion

This study presents a facile method for the synthesis of MgAl LDH nanoparticles using urea as a dispersing agent to limit layer stacking. The mesoporous material consists of platy particles with a thickness of 3-5 nm and diameters of approximately
30 nm contributing to a specific surface area of 84 m$^2$ g$^{-1}$. The freshly synthesized and non-aged products contain variable amounts of admixed AOH (16-38%). The LDH nanoparticles show 15 min phosphate adsorption and a high phosphate adsorption capacity of close to 100 mg P g$^{-1}$ at pH 8.5. The $^{31}$P MAS NMR spectra showed that phosphate adsorption occurs by intercalation in the interlayer (ion exchange) and inner-sphere surface complexation. The latter was confirmed by ionic strength effects on adsorption, zeta-potential measurements and IR spectroscopy. NMR showed the LDH to be stable during phosphate adsorption and less than 7% of adsorbed P desorbed on 24 h desorption tests. Easy, cheap and environmentally friendly synthesis, high capacity adsorption even for high pH waters and low phosphate desorption makes the new LDH adsorbent interesting for treatment of waste waters or phosphate rich runoff.

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