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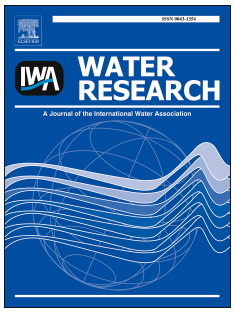


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# Layered Double Hydroxides for phosphorus recovery from acidified and non-acidified dewatered sludge

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## Abstract

Phosphate, which contains the essential element phosphorous (P), is a necessary fertilizer for agriculture, but the current phosphate deposits are running out and alternative sources are needed. Sludge obtained from wastewater treatment plants contains high concentrations of phosphorus and represents an alternative, sustainable source. In this study, sludge obtained from a wastewater treatment plant with biological and chemical phosphorus removal was acidified (pH = 3, 4, 5 and 6) to release orthophosphate followed by sequestration of the orthophosphate by a zinc aluminum layered double hydroxide ($Zn_2Al$-LDH). Sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$), and hydrochloric acid (HCl) was tested, which showed that only sulfate anions compete with phosphate and results in reduced phosphate recovery (25-35%). The orthophosphate concentration in the liquid phase increased from 20 % (raw sludge) to 75 % of the total phosphorus concentration at a pH of 3, which enhanced the phosphate uptake by the ZnAl-LDH from 1.7±0.2% to 60.3±0.6%. During acidification, the competing anion carbonate is degassed as $CO_2$, which further improved the phosphate uptake. PXRD showed the intercalation of carbonate in the LDH in the raw sludge at pH = 8, whereas orthophosphate was intercalated at lower pH values. $^{27}$Al MAS NMR spectroscopy and powder X-ray diffraction (PXRD) proved preservation of the LDH at all pH values. Furthermore, about a third of the Al is present as an amorphous aluminum phosphate ($AlPO_4$) upon exposure to phosphate at low pH (pH = 3 and

5) based on $^{27}Al$ MAS NMR spectroscopy. At a pH of 6 about a third of the P is present as brushite ($CaHPO_4 \cdot 2H_20$).

***Keywords:*** Layered Double Hydroxides (LDH), phosphate recovery, sludge acidification, wastewater, solid state NMR Spectroscopy, ion exchange

## 1.0 Introduction

Phosphorus in the form of phosphate is an essential fertilizer in the agriculture and its supply in adequate quantities is vital (Cordell et al., 2009; Shu et al., 2006). However, phosphate rock, a main source of phosphate for fertilizers, is a critical resource (European Commission, 2018). Hence, research in alternative phosphate sources, such as recovery of phosphate from wastewater, is demanded. The majority of the phosphate at wastewater treatment plants is present in the sludge, mainly in the microbial mass or as insoluble inorganic salts due to the biological and chemical removal of phosphate from the liquid phase, respectively. Biological and/or chemical treatment procedures are necessary to meet the discharge limit set by political regulations (de-Bashan and Bashan, 2004). Phosphate recovery/recycling by controlled precipitation of struvite and calcium phosphate precipitation, which remove phosphate from the liquid phase after sludge dewatering, do not exploit the full potential for phosphate recovery (Liu and Qu, 2017; Song et al., 2006; Vasenko and Qu, 2017). Thus, the sludge contains valuable phosphate, but the direct application of sludge to fields is problematic as toxins such as heavy metals, microplastic, and pathogens may be present in critical quantities. Therefore, application of sludge on farmland has been banned in several European countries (Milieu Ltd., 2010; Tarayrea et al., 2016). Incineration of sludge is an alternative, however the bioavailability of the phosphorus is low and impurities from heavy metals is problematic for more than half the ashes (Herzel et al., 2016). Furthermore, the method for heavy metal removal is expensive and the sustainability of phosphorus recovery from ashes has been questioned (Vaneeckhaute et al., 2017).

Recent studies have shown that the amount of phosphate in the liquid sludge phase is increased by acidification due to dissolution of the inorganic phosphates in the sludge (Latif et al., 2015; Sun et al., 2012;

Wu et al., 2009). Antakyali et al. reported 75 % dissolution of phosphate from digested sewage sludge by sludge acidification (Antakyali et al., 2013). Moreover, acidification improves the dewaterability of sludge (Chen et al., 2001). Incineration after acidification is the best option, which simultaneously produces energy (Lundin et al., 2004) as many European countries have banned the use of sludge in agriculture (Tarayrea et al., 2016). However, sludge acidification also dissolves other metal salts and thereby releases heavy metals bound in the sludge (Quist-Jensen et al., 2018; Wozniak and Huang, 1982). Thus, a selective phosphate adsorbent for collecting of the released phosphate is needed.

Layered double hydroxides (LDHs) are considered promising adsorbents due to their high affinity for orthophosphate (Cheng et al., 2009; Das et al., 2006; Yang et al., 2014), which are already manufactured on an industrial scale. LDHs are anion exchange materials composed of positively charged layers of divalent and trivalent cations octahedrally coordinated to edge sharing hydroxyl groups with anions (A) and water intercalated between the layers in order to obtain a neutral charge (Figure 1). The general formula for an LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot yH_2O$, where M represents cations. A variety of anions, A, can be intercalated and be exchanged for other anions in aqueous solutions giving LDHs their unique anion exchange properties (Evans and Slade, 2006).

Phosphate adsorption by LDHs has been extensively tested in e.g. aqueous solutions (Ashekuzzaman and Jiang, 2014; Das et al., 2006; He et al., 2010; Kuzawa et al., 2006; Yang et al., 2014), sewage sludge filtrate (Cheng et al., 2009), seawater (Chitrakar et al., 2005), and waste water (Drenkova-Tuhtan et al., 2013). In addition, the recyclability of the LDH by desorption of phosphate by a basic NaOH solution and subsequent regeneration by calcination has been performed for MgFe and ZnAl LDHs for six to seven cycles (Ashekuzzaman and Jiang, 2017; Cheng et al., 2009).

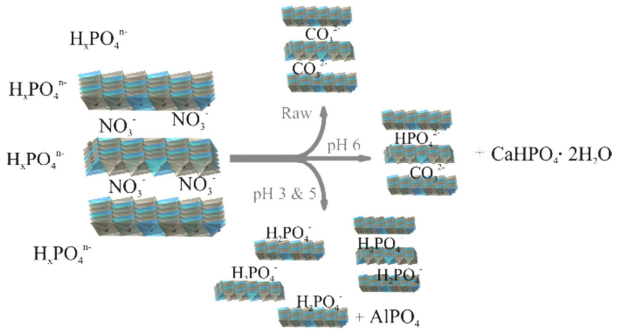
Alternatively, the phosphate incorporated in the LDH can be directly used a as a fertilizer (Bernardo et al., 2018; Everaert et al., 2016) or recovered by desorption (Chitrakar et al., 2005; He et al., 2010; Zhang et al., 2016) followed by precipitation of as a calcium phosphate and regeneration of the LDH (Kuzawa et al., 2006). The phosphate adsorption by ZnAl LDHs was nearly unchanged after five cycles (He et al., 2010).

Different implementations methods for LDHs based sorbents at wastewater treatment plants have been investigated. Direct addition of the solid LDHs provides a large surface area and is simple, but it is difficult to separate the LDH later (Goh et al., 2008). This can be circumvented by coating the LDH on magnetic materials and thereby perform magnetic separation after phosphate capture (Drenkova-Tuhtan et al., 2013) or by anchoring the LDH on a filter material or in membranes (Jia et al., 2018; Zhang et al., 2016).

Two of the major challenges for the design of the most efficient LDH sorbent are to understand how the LDHs capture P and the effect of competing anions. The most commonly studied LDH are MgAl, MgFe, CaAl, CaFe, and ZnAl LDH due to their limited toxicity and easy preparation. It is known that the hydrocalumites (CaAl and CaFe LDH), which have a slightly different crystal structure (Taylor, 1973), are destroyed upon phosphate exposure and calcium phosphates are formed (Radha et al., 2005; Xu et al., 2010).

Phosphate capture by the hydrotalcite LDHs including MgFe, ZnAl, and MgAl may proceed by both precipitation of phosphates (dissolution of the LDH) (Bernardo et al., 2016; Du et al., 2009; Radha et al., 2005) as well as intercalation, surface complexation and the pH dependence (Bernardo et al., 2016; Du et al., 2009; He et al., 2010; Radha et al., 2005; Yang et al., 2014).

Given the high affinity of LDH for especially phosphate and carbonate (Goh et al., 2008) both the pH dependent orthophosphate and the carbonate equilibria (Eqs. 1 to 6) are expected to affect the phosphate adsorption under variable pH conditions. At low pH, carbonate is degassed as $CO_2$ and will not compete with phosphate (Eqs 1-3). Above this pH carbonate is present mainly as $HCO_3^-$ and competition is likely. Thus, an increase in the phosphate adsorption by the LDH is expected at low pH. The protonation of phosphate, which increases with pH, also affects the capacity.



97 *Figure 1: Illustration of layered double hydroxide (LDH) used for phosphorus recovery.*

98

99

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad \text{eq. 1}$$

$$H_2CO_3 \xrightleftharpoons{pK_a = 6.4} H^+ + HCO_3^- \quad \text{eq. 2}$$

$$HCO_3^- \xrightleftharpoons{pK_a = 10.4} H^+ + CO_3^{2-} \quad \text{eq. 3}$$

$$H_3PO_4 \xrightleftharpoons{pK_a = 2.2} H^+ + H_2PO_4^- \quad \text{eq. 4}$$

$$H_2PO_4^- \xrightleftharpoons{pK_a = 7.2} H^+ + HPO_4^{2-} \quad \text{eq. 5}$$

100

$$HPO_4^{2-} \xrightleftharpoons{pK_a = 12.7} H^+ + PO_4^{3-} \quad \text{eq. 6}$$

101 Phosphate is mainly present as $HPO_4^{2}$ in the pH range from 7.4 to 10.4, whereas phosphate mainly exist as
102 $H_2PO_4^-$ in the region between 2.2 and 7.4. Therefore, the phosphate adsorption is expected to be larger under
103 acidic conditions due to the lower charge of phosphate anion. The objective of this study is to dissolve the
104 orthophosphate bound in the sludge and investigate how the pH, spanning from untreated sludge and sludge
105 acidified to a pH of 3, 5 and 6, respectively affects phosphate adsorption by a ZnAl LDH. Furthermore,
106 competition from other anions, e.g., carbonate in the wastewater and the anion (nitrate, chloride, and sulfate)
107 from the acid used for acidification, the stability of the LDH and the phosphate speciation after capture is
108 also studied. This was addressed by performing adsorption studies followed by collecting of the solid
109 product, which was characterized by powder X-ray diffraction (PXRD), $^{27}$Al and $^{31}$P MAS NMR
110 spectroscopy. PXRD provide information about the crystalline phases and possible phosphate intercalation in
111 the LDH, whereas $^{27}$Al and $^{31}$P MAS NMR give detailed insight into the stability of the LDH and phosphate
112 speciation, respectively.

113 The ZnAl LDH was chosen over MgFe and MgAl LDHs for this study, as it has a high affinity for phosphate
114 (He et al., 2010). MgFe LDHs are difficult to characterize by NMR due to the paramagnetic iron. For MgAl
115 LDH precise quantification of the LDH content is difficult due to overlap of the $^{27}$Al resonances from the

MgAl LDH and amorphous Al impurities (Pushparaj et al., 2015). Moreover, hydrothermal treatment of the synthesis mixture was performed to reduce the amount of aluminum hydroxide (Pushparaj et al., 2015), which is well known to bind phosphate (Emmerik et al., 2007; Li et al., 2013; Lookman et al., 1997).

## 2.0 Materials and methods

### *2.1 Sludge characteristics*

Sludge was obtained from Aalborg West wastewater treatment plant (330.000 PE), Aalborg, Denmark. This plant uses mainly biological treatment, but with potential addition of iron chloride as chemical treatment after the aeration tanks. The sludge used in this study was obtained from the thermophilic digester (operating at 55 °C), where excess sludge from the secondary treatment and primary sludge is added. The pH of the sludge was adjusted by addition of 2M $H_2SO_4$, 2M HCl, or 7M $HNO_3$, respectively to the desired pH (3, 4, 5 and 6). The orthophosphate (o-P) and total-phosphate (t-P) were measured for each pH value according to the procedure given in Danish Standards (Danish Standard, 1985a, 1985b). All analyses were performed in triplicates. The samples were centrifuged at 5000 G in 10 minutes and filtered through a 15 µm filter before o-P analysis and LDH addition. The dry matter content of the sludge was estimated by leaving around 15 g of raw sludge in a drying oven at 105 ºC for 24 hours. Afterwards, the dry matter was incinerated at 550 ºC for 2 h to determine the organic/inorganic matter. The pH and conductivity were measured using a Mettler Toledo Seven Multi with a pH electrode BlueLine 17 (SI Analytics) and an Inlab 731 conductivity electrode (Mettler Toledo). The ammonium concentration was measured by using the Berthelot method where salicylate was used as a substitute for phenol (Danish Standard, 1975; Searle, 1984).

The concentration of cations in the raw sludge was measured on a inductively coupled plasma spectrometer (ICP). First, the cations were extracted from sludge by concentrated $HNO_3$ and then the samples were filtered through a 0.45-µm filter. The concentrations of Fe, Ca, Cr, Cu, Fe, Mg, Pb, and Zn were then quantified using ICP (iCap 6300 DUO; Thermo Scientific, Waltham, MA, USA). The samples were measured in radial view. 1 ppm Yttrium was used as the internal standard. All ICP measurements were made in duplicates.

Arsenic was measured by a test kit (Hach). $NH_4^+$ and cations have only been measured once, thus these values represent the sludge at the sampling time (April 2017). A detailed composition of the sludge can be found in Table 1. Notice that the metals in Table 1 are dissolved metals or metals bound to particles smaller than 0.45 µm.

*Table 1: Chemical composition of sludge from the Aalborg West treatment plant.*

| **Composition** | | |
|---|---|---|
| **pH** | 8.14 ± 0.57 | - |
| **t-P** | 1580.4 ± 21.4 | mg/L |
| **o-P** | 347.7 ± 65.4 | mg/L |
| **$NH_4^+$** | 1520.8 | mg/L |
| **Al** | 0.986 | mg/L |
| **Ca** | 10.9 | mg/L |
| **Cr** | 0.391 | mg/L |
| **Cu** | 0.122 | mg/L |
| **Fe** | 7.28 | mg/L |
| **Mg** | 2.73 | mg/L |
| **Pb** | 0.0114 | mg/L |
| **Zn** | 0.469 | mg/L |
| **As** | < 0.2 | mg/L |
| **Dry matter** | 35.1 ± 0.7 | g/kg |
| **Organic matter** | 21.6 ± 0.5 | g/kg |
| **Inorganic matter** | 13.9 ± 0.6 | g/kg |

*2.2 LDH synthesis*

A $Zn_2Al$-LDH (ideally $Zn_{0.66}Al_{0.33}(OH)_2](NO_3)_{0.33}\cdot 2H_2O$) was utilized for phosphate recovery. The LDH was synthesized by co-precipitation at constant pH 8.5 followed by hydrothermal treatment, which gives the

highest purity LDH (Pushparaj et al., 2015). A solution with 0.67 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.33 M $Al(NO_3)_3 \cdot 9H_2O$ (Zn:Al ratio of 2:1, total metal concentration 1 M) and a 1 M NaOH solutions were prepared in decarbonated MiliQ water. The decarbonated water was produced by boiling the water and bubbling nitrogen ($N_2$) through for at least 30 min. A $N_2$ was also bubbled through the reaction mixture as well to minimize carbonate contamination. The reaction mixture was transferred to a hydrothermal bomb and placed in the oven at 120 °C for 24h. The precipitated solid was washed three times with decarbonated MiliQ water and collected by centrifugation before it was dried at 60 °C overnight. The sample was characterized by ICP-EOS, powder X-ray diffraction, and solid state $^{27}$Al MAS NMR spectroscopy. ICP-EOS showed a Zn:Al ratio of 2.16. No non-LDH reflection was observed in the PXRD diffractograms, but analysis of the $^{27}$Al MAS NMR spectrum (Figure S1) showed that 15±4 % of the Al in an amorphous aluminum hydroxide phase (AOH) (Jensen et al., 2016; Pushparaj et al., 2015). Hence, the Zn:Al ratio of the LDH phase is estimated to 2.54 based on $^{27}$Al MAS NMR.

*2.3 LDH adsorption*

LDH adsorption studies were performed at ambient temperature at different pH values and LDH dosage. The dosage of the LDH below pH of 7.2 was 0.882 g LDH/0.2 g o-P. At pH above 7.2 the dosage was doubled (1.78 g LDH/0.2 g o-P) to account for changes in protonation ($H_2PO_4^-$ vs $HPO_4^{2-}$). The LDH was dosed to 10 ml of sludge samples according to measured o-P concentration (triplicates). The samples were mixed using a rotator mixer. After a given time, LDH was separated from solution by centrifugation at 5000 G for 5 minutes. o-P was analyzed in the solution before and after LDH adsorption (Triple analysis). The samples were collected and dried at 60 °C overnight prior to PXRD and solid state NMR analyses. The adsorption capacity ($C_{\%}$) was estimated from eq. 7.

$$C_{\%} = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad \text{(eq. 7)}$$

where $C_0$ and $C_t$ are the o-P concentration in the liquid phase before and after LDH adsorption, respectively.

175

176 *2.4 LDH characterization*

177 The PXRD diffractograms were collected on a Rigaku miniflex 600 with a Cu K-α radiation, a tube voltage
178 and current at 40 kV and 15 mA, respectively. The spectra were collected with a step size of 0.02° and a
179 speed of 10°/min in the 2θ range from 5 to 70°.

180 Quantitative solid state $^{27}$Al and $^{31}$P MAS NMR spectra were recorded on a JEOL 500 MHz NMR
181 spectrometer using a 3.2 mm double resonance probe and a spinning speed of 13 kHz. The single pulse $^{27}$Al
182 MAS NMR spectra were recorded with a relaxation delay of 1 s and short 10° pulse to ensure quantitative
183 spectra. A relaxation delay of 150 s was used for the single pulse $^{31}$P MAS NMR spectra. The $^{31}$P MAS
184 NMR spectra were analyzed using MestreNova.

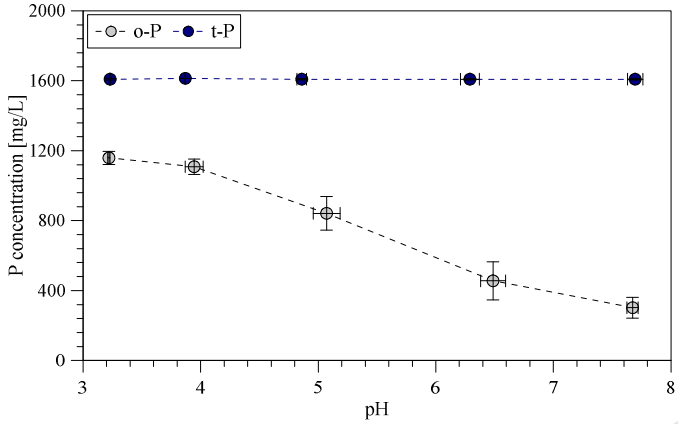
185

186 **3.0 Results**

187 The phosphate release during acidification and phosphate adsorption by LDH using different acids are
188 discussed in the following section. Finally, LDH has been characterized after phosphorus adsorption to
189 determine how phosphorus adsorbs to LDH and if the LDH can sustain at a low pH.

190 *3.1 Acidification of sludge*

191 The sludge was acidified and the concentration of t-P and o-P were measured before and after centrifugation,
192 respectively (Figure 2). The pH was increased slightly after centrifugation due to removal of carbon dioxide,
193 but the maximum increase was 0.5 (pH 6). The concentration of o-P increased from about 300 mg/L (raw
194 sludge) to about 1200 mg/L (at pH 3) due to solution of inorganic phosphates, i.e., a fourfold increase in the
195 o-P concentration. 1200 mg/L corresponds to 75% to the total amount of phosphorus in the sludge, as
196 reported earlier (Antakyali et al., 2013).




197

198 *Figure 2: o-P and t-P concentration as a function of the sludge pH. Acidification was done by addition of 2M $H_2SO_4$*

199

200 *3.2 LDH uptake kinetics*

201 The efficiency of o-P adsorption by of the ZnAl LDH was studied through the uptake kinetics. The LDH
202 used in this study has incorporated $NO_3^-$ as the negative ion and therefore, the sludge was only acidified with
203 $HNO_3$ in the kinetic studies to avoid competition with other anions.

204 Around 90% of the o-P in the liquid phase is adsorbed in sludge acidified to pH 3 and only around 20 % in
205 the raw sludge (pH 7.79). At the highest pH, the adsorption kinetics stabilizes after 20 minutes, whereas for a
206 pH of 3 the amount of o-P adsorbed increased from 57.9±0.6 % at 20 minutes to 80.2±2.2 % after 4 hours
207 (Figure 3). The reason for the poor adsorption at higher pH was most probably due to competition with
208 carbonate at near neutral pH, whereas less carbonate is present at low pH due to $CO_2$ degassing (vide infra).
209 The $CO_2$ degassing is also observed from the buffer capacity of the sludge (c.f., Figure S2 in supplementary
210 information including the experimental method to obtain the buffer capacity). The phosphate equilibrium
211 was taken into account in the kinetics studies, as described in section 2.3.

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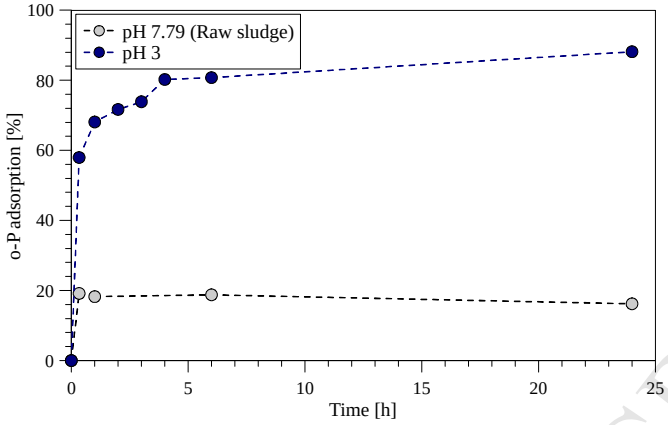



*Figure 3: Kinetics of phosphate adsorption at different pH. $[o\text{-}P]_{initial}$=229.3±11.9 mg/L at pH 7.79 and $[o\text{-}P]_{initial}$=1157.1±25.2 mg/L at pH 3.*

The zinc concentrations in the aqueous phases were measured by ICP before and after adsorption probe if the LDH is partiallty dissolved, as illustrated in Table 2 for the kinetic studies using nitric acid. The LDH is maintained in the raw sludge since the Zn concentration corresponds to less than one percent. However, about 8-10 % of the Zn is dissolved at a pH of 3 . To further test the conservation of LDH at low pH, analysis of the solid phase LDHs are reported in section 3.4.

*Table 2: Zn concentration in solution after LDH dosage.*

| Time [h] | Raw sludge | | pH 3 | |
|---|---|---|---|---|
| | Zn [mg/L] after adsorption | Zn released [%] | Zn [mg/L] after adsorption | Zn released [%] |
| 1 | 8.23 | 0.291 | 230 | 8.13 |
| 6 | 10.3 | 0.371 | 245 | 8.82 |
| 24 | 6.96 | 0.249 | 303 | 10.8 |

### *3.3 Phosphate adsorption at different pH*

Phosphate adsorption was evaluated at five different pH values (pH = 3, 4, 5, 6, 7.79 (raw sludge)), where the pH was adjusted by addition of $HNO_3$ prior to addition of different amounts of LDH (Figure 4). A small increase in the pH of approx. 0.5±0.2 was always observed immediately after addition of LDH due to its

basic nature. Similarly, the adsorption increased when the pH was lower, but it is evident that there is a gap between pH 5 and pH 6, c.f., Figure 4. The phosphate adsorption increases from 10.2±1.6 % to 44.9±3.3 % at dosage of 4-6g LDH/g o-P due to the favorable shift in the carbonate equilibrium as $CO_2$ is degassing during acidification (vide supra). It was also noted that higher LDH amount results in an improved phosphate adsorption. However, the increase at high pH (from 8-10% to 16-24%) was limited compared to the lower pH (from 40-50% to 72-80%). Therefore, addition of more LDH was more favorable at low pH.

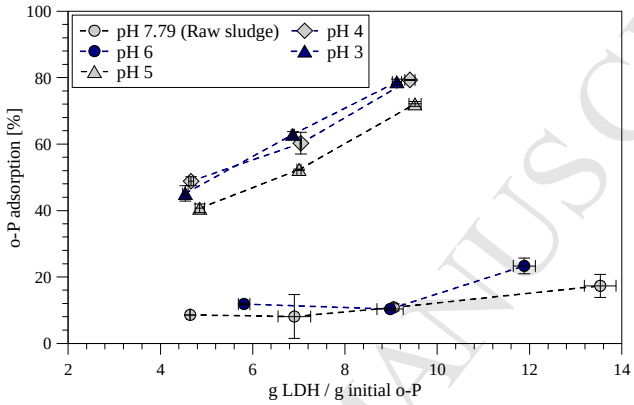
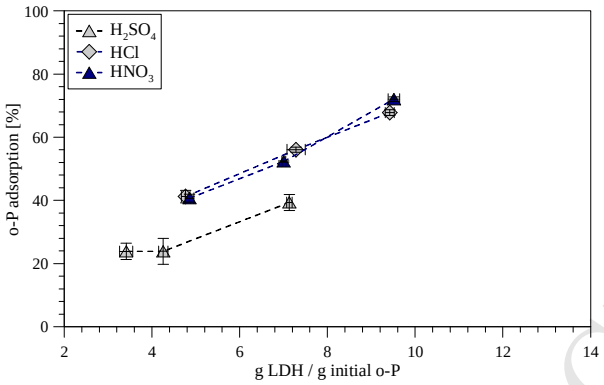



*Figure 4: Adsorption of o-P using $HNO_3$. Adsorption time: 2h. $[o\text{-}P]_{initial}$* was 1229.1, 1086.6, 743.0, 360.1, 254.1 mg/L for pH 3, 4, 5, 6 and 7.79, respectively

Three different acids (HCl, $HNO_3$ and $H_2SO_4$) were used to acidify the digested sludge to pH 5 and 3. Subsequently, the phosphate adsorption was measured after addition of various amounts of LDH (Figure 5). Similar amount of o-P was adsorbed for sludge acidified with HCl and $HNO_3$ indicating that $Cl^-$ and $NO_3^-$ did not influence the adsorption significantly. However, a significant reduction of the phosphate adsorption was seen for sulfate. For example, only 39.4±2.5 % of the phosphate was adsorbed on the LDH at a pH of 5 when sulfuric acid was used as compared to 55.2±0.9 % for nitric and hydrochloric acid at 7.2 g LDH/g o-P. This indicates that sulfate ions compete with phosphate to bind in LDH, as also observed in other studies on phosphate adsorption (Das et al., 2006; Halajnia et al., 2013). The o-P concentration in the liquid phase increased from about 20 % in the raw sludge to 75 % at pH 3 with respect to the t-P concentration. Thus the total phosphorus recovery increases significantly by acidification. For example, acidification by $HNO_3$ results in total phosphorus recovery of 60.3±0.6% at a pH of 3, which was much higher than obtained for the

raw sludge (1.7±0.2%). This illustrates that high o-P concentrations, which may be achieved by acidification or other techniques, may be required for an efficient recovery by LDH.

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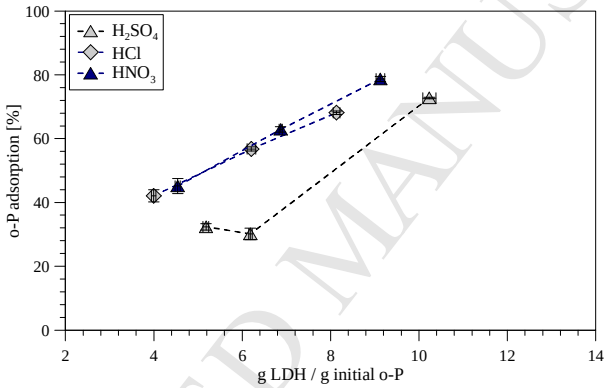


*(b)*

*Figure 5: Adsorption of o-P at (a) pH 5 ($[o\text{-}P]_{initial}$ was 825.8, 812.6 and 743.0 mg/L for $H_2SO_4$, HCl and $HNO_3$, respectively), and (b) pH 3 ($[o\text{-}P]_{initial}$ was 1258.0, 1235.7 and 1229.0 mg/L for $H_2SO_4$, HCl and $HNO_3$, respectively). Adsorption time: 2h.*

### *3.4 Characterization of the solid phases after adsorption*

The solid phase was collected after exposure of the LDH to the different sludge samples and subsequently characterization by a combination of PXRD, $^{27}Al$ and $^{31}P$ MAS NMR spectroscopy, which provided information about both the crystalline and amorphous samples as well as the stability of the LDH at the different pH values.

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*3.4.1 PXRD*

For LDH, the basal (003) and (006) reflections in the PXRD diffractograms (Figure 6) are related to the interlayer distances and are consequently a signature of the intercalated anion. The (003) reflection as well as the predominant reflections from non-LDH phases are summarized in Table 2. A ZnAl-LDH phase is observed for all samples, but there are significant changes in the intercalated anion and crystallinity of the LDH. A substantial decrease in the crystallinity of the LDH after exposure to sludge is evident as a broadening of the reflections and their decreased intensity. However, the characteristic (110) reflection from the LDH is present in all the samples. It is related to *a* (*a* = 2d(110)) of the unit cell for the LDH and thereby the metal-metal distance in the layers. Thus, the LDH structure is preserved even at a pH of 3.

For the raw sludge sample (pH = 8.14) the position of the basal reflections corresponds to the intercalation of carbonate (Liu and Yang, 2016), which shift to lower 2θ values (larger interlayer spacing) at a pH of 6 matching those reported for LDH intercalated with $HPO_4^{2-}$ (Costantino et al., 1997). The (003) reflection at this pH is very broad and span values for carbonate and hydrogen phosphates as well as overlaps with a reflection from brushite ($CaHPO_4 \cdot 2H_2O$) (Figure 6c). Thus, LDH intercalated with $HPO_4^{2-}$ and $CO_3^{2-}$ may coexist at a pH of 6. The basal reflections shift to even lower 2θ values at pH of 5 corresponds to the intercalation of $H_2PO_4^-$, which also results in a third reflection at 2θ = 22.4°, as reported earlier (Costantino et al., 1997) (Figure 6d). The increased phosphate uptake at the lower pH values is favored by a combination of the phosphate protonation and degassing of carbonate (Eqs. 1-6).

The PXRD diffractograms of the pH of 5 and 3 samples contain three similar reflections in the 5-30° range (Figures 6d and 6e). The reflection with the lowest 2θ value (8.9° at pH of 5 and 9.1° at of pH 3) does not match the interlayer spacing of an LDH intercalated with a common, small inorganic anion such as $NO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$, or $HPO_4^{2-}$ (Costantino et al., 1997; Liu and Yang, 2016; Tang et al., 2008). However, it is close to the reported value for the (003) reflection for ZnAl-LDH intercalated with formate ($HCOO^-$) (Costantino et al., 1997), pyrophosphate ($P_2O_7^{4-}$) and triphosphate ($P_3O_{10}^{5-}$) (Badreddine et al., 1999). Nevertheless, the expected (006) reflection is not observed (Figure 6d and 6e). Hence, intercalation of formate, pyrophosphate, or triphosphate does not seem likely. The possible lack of the (00*l*) reflections

290 indicate that the layers must be disrupted. The two others partially match iron dihydrogen phosphate
291 ($Fe(H_2PO_4)_3$) (ICSD 162423) and vivianite ($Fe_2(PO_4)_3 \cdot 8H_2O$) (ICSD 30645) in agreement with the high Fe
292 content in the sludge (7.28 mg/L), c.f., Table 1, but further analysis was not possible. The pH = 6 sample
293 contains brushite ($CaHPO_4 \cdot 2H_2O$) and two weak reflections of unknown origin are observed for the raw
294 sample (Table 3 and Figure 6b). Thus, the increase in the phosphate uptake as compared to the raw sample is
295 caused by a combination of $HPO_4^{2-}$ intercalation and the precipitation of brushite (Figure 6). A minor
296 reflection from brushite is visible in the diffractogram for the samples with a pH of 5 and 3 as well, but no
297 resonance for brushite is observed in the $^{31}P$ MAS NMR spectra of these samples. Hence, if present the
298 concentration is most likely less than 5 % of the total P. Precipitation of brushite and its solubility is
299 dependent on temperature, concentration and pH (Ferreira et al., 2003; Lundager Madsen and Thorvardarson,
300 1984).

301 *Table 3. The position of the interlayer reflections, (003) and from the LDH with the predominant intercalated anion in the crystalline*
302 *phases listed. Furthermore, the most intense reflections from other phases and their assignment, when possible, is given.*

| **Sample** | **(003)** | **LDH Anion** | **Other reflections** | **Assignment** |
|---|---|---|---|---|
| **Precursor** | 10.0° | $NO_3^-$ | | |
| **Raw** | 11.6° | $CO_3^{2-}$ | 28.2° and 31.2° | Unknown |
| **pH 6** | 10.8° (broad) | $HPO_4^{2-}$ and $CO_3^{2-}$ | 11.6°, 20.9°, 29.2°, | $CaHPO_4 \cdot 2H_2O$ |
| | | | 20.4°, 31.3° | |
| **pH 5** | 7.7° | $H_2PO_4^-$ | 9.1° | Unknown |
| | | | 13.4° and 22.4° | Unknown |
| **pH 3** | | | 8.9° | Unknown |
| | | | 13.4° and 22.4° | Unknown |

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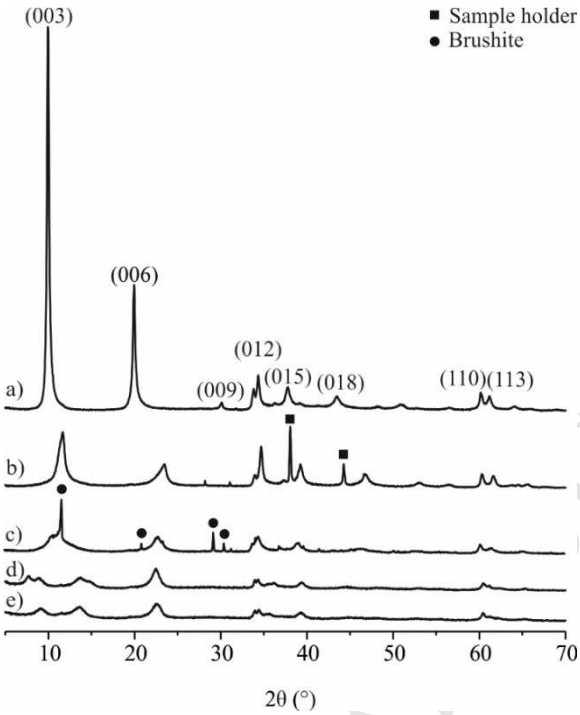


*Figure 6. PXRD for a) The precursor: $Zn_2Al$-$NO_3$ LDH, b) $Zn_2Al$-$NO_3$ exposed to raw sludge. Reflections from the sample holder are seen in the sample. c) $Zn_2Al$-$NO_3$ exposed to sludge at pH 6, d) $Zn_2Al$-$NO_3$ exposed to sludge at pH 5. d) $Zn_2Al$-$NO_3$ exposed to sludge at pH 3.*

### *3.4.2 $^{27}$Al MAS NMR spectroscopy*

The $^{27}$Al MAS NMR spectra (Figure 7) provided information about the stability of the LDH structure and other phases as well as information about amorphous Al containing phases. The resonance from a $Zn_2Al$-LDH is seen for all samples implying at least partial preservation of the LDH structure. However, non-LDH resonances are also present at a pH of 5 and 3 and to a minor extent at a pH of 6 indicating that some of the LDH is transformed to a new aluminum containing phase. These two new, broad $^{27}$Al resonances located in the region for tetrahedral and octahedral aluminum at $\delta(^{27}Al) \approx 44$ ppm and -5 ppm, respectively (Figures 7d and 7e). These values match those reported in studies of amorphous aluminum phosphates precipitated under similar pH conditions (pH = 3-7.5). The resonance located at 44 ppm was assigned to tetrahedrally coordinated aluminum to phosphate whereas the resonance at -5 ppm was assigned to octahedrally aluminum coordinated to phosphate or to four phosphate and two hydroxyl/water ligands (Burrell et al.,

2001; Lookman et al., 1997). Hence, it can be concluded that part of the LDH converts, e.g., by dissolution-reprecipitation, into amorphous aluminum phosphate, which constitute approx. 20-25% of the Al in the sample at a pH of 3 (Figure 6). A full dissolution of the LDH does not occur due to the basicity of LDHs. It cannot be excluded that some of aluminum hydroxide as well is converted to aluminum phosphate upon exposure to phosphate at low pH values (Lookman et al., 1997).

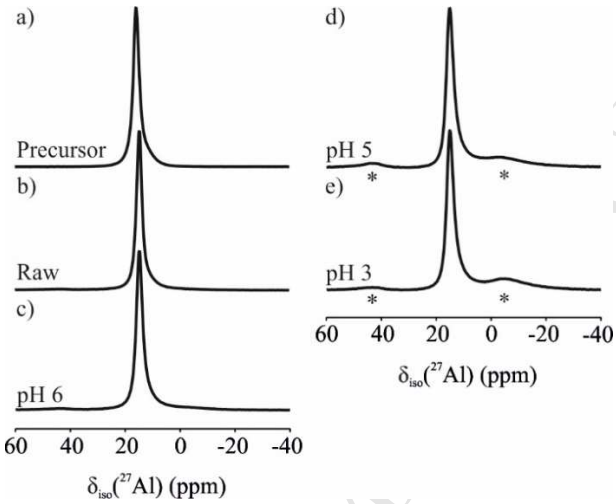


*Figure 7. $^{27}Al$ MAS NMR spectra for the a) precursor $Zn_2Al\text{-}NO_3$, $Zn_2Al\text{-}NO_3$ exposed to b) raw sludge, c) sludge at pH 6, d) sludge at pH 5, and e) sludge at pH 3. * Indicates the amorphous aluminum phosphate (see discussion in text).*

### *3.4.3 $^{31}P$ MAS NMR spectroscopy.*

$^{31}P$ MAS NMR spectra were recorded of all the samples to identify and quantify the different phosphate species present. The isotropic chemical shift ($\delta_{iso}$) and intensity obtained from deconvolution of the spectra in Figure 8 are summarized in Table 4. One signal is observed in all the spectra, accompanied by one to two weak set of spinning side band (ssb) for the raw, pH 5, and pH 3 samples and sharper ssbs for the pH 6 sample due to a narrow resonance. The three resonances at $\delta_{iso}(^{31}P)$ = 4.7(5) ppm, $\delta_{iso}(^{31}P)$ = 0.7(3) ppm and $\delta_{iso}(^{31}P)$ = -5(1) ppm are present in all the samples. PXRD and $^{27}Al$ MAS NMR show LDH and aluminum hydroxide to be the only phases present in all the samples, and hence the three resonances must therefore be from phosphate adsorbed to one of these materials. Earlier studies of phosphate adsorption on the closely related MgAl-LDH showed resonances approximately in the region 0 to 10 ppm based on visual inspection

of the $^{31}$P MAS NMR spectra (Hou et al., 2003), whereas phosphate adsorbed an aluminum hydroxides are in the region 0 to -20 ppm (Emmerik et al., 2007; Li et al., 2013, 2010; Lookman et al., 1997). Thus, the first two resonances are assigned to the LDH phase. About 20 % of the sample is AOH so we tentatively assign the -5.0(1) ppm resonance to phosphate adsorbed to the AOH phase, but some of the phosphate may be associated with the LDH.

The resonance with $\delta_{iso}(^{31}P) \approx$ -11.4 ppm is unambiguously present for the pH 5 and 3 sample, which are known to contain aluminum phosphates from $^{27}$Al MAS NMR and the $\delta_{iso}(^{31}P)$, and match those reported for amorphous aluminum phosphate (Lookman et al., 1997). Thus, $^{31}$P MAS NMR confirms the precipitation of amorphous aluminum phosphate at the low pH values possibly due to a partial dissolution of the LDH. The most intense resonance in the spectra for the sample with a pH of 6, which constitute 32±3 % of the total intensity and has a $\delta_{iso}(^{31}P)$ = 1.5(2), is assigned to brushite based on earlier reported $^{31}$P NMR data (Aue et al., 1984) and the PXRD (Figure 6). Brushite could not be unambiguously identified in the $^{31}$P MAS NMR spectra at a pH of 5 and 3 due to overlap with other resonances, but it may be present in minor quantities (< 5 %) as weak reflections from brushite are seen in the PXRD (Figure 6d and 6e). A sharp, well defined resonance with $\delta_{iso}(^{31}P)$ = 5.6(2) ppm and a relative concentration of 7±3 % most likely result of another O-P mineral, which may be related to the unknown reflections in the PXRD (Figure 6b).

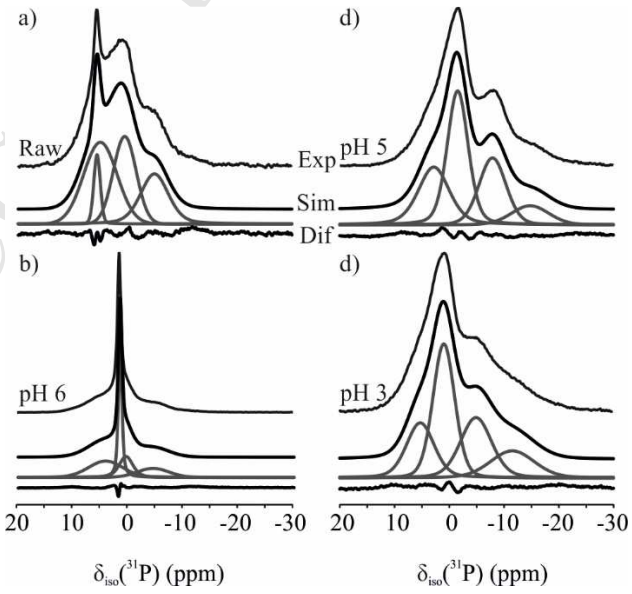


*Figure 8. $^{31}$P MAS NMR spectra of the $Zn_2Al$-$NO_3$ LDH to a) raw sludge, b) sludge at pH 6, c) sludge at pH 5 and d) sludge at pH 3.*

*Table 4. The different P species identified and quantified from deconvolutions of the $^{31}P$ MAS NMR spectra in Figure 10.*

| Sample | Assignment | $\delta_{iso}(^{31}P)$ (ppm) | I[%] |
|---|---|---|---|
| **Raw** | Unknown | 5.6±2 | 7±3 |
| | LDH-P | 5.0±4 | 41±5 |
| | LDH-P | 0.6±3 | 30±5 |
| | AOH-P | -4.9±3 | 22±5 |
| **pH 6** | LDH-P | 4.2±5 | 33±6 |
| | Brushite | 1.5±2 | 32±3 |
| | LDH-P | 0.5±5 | 18±5 |
| | AOH-P | -4.5±5 | 17±6 |
| **pH 5** | LDH-P | 4.5±5 | 26±4 |
| | LDH-P | 0.6±3 | 40±6 |
| | AOH-P | -5.1±4 | 25±6 |
| | $AlPO_4$ | -11.3±5 | 10±4 |
| **pH 3** | LDH-P | 5.2±4 | 20±4 |
| | LDH-P | 1.0±3 | 39±6 |
| | AOH-P | -4.9±5 | 25±5 |
| | $AlPO_4$ | -11.5±5 | 15±4 |

## Discussion

*Practical implementation*

Acidification is a known technology to improve dewaterability (Cai et al., 2018; Chen et al., 2001) and simultaneously dissolve orthophosphate (Antakyali et al., 2013; Quist-Jensen et al., 2018), which has been tested on both pilot and large scale applications (Antakyali et al., 2013; Cai et al., 2018). The acid consumption is higher for digested sludge compared to non-digest sludge due to the bicarbonate buffer system ($CO_2$ stripping) and an increased dissolution/release of phosphorus during acidification of the

365 digested sludge (Quist-Jensen et al., 2018). Mainly inorganic salts are being dissolved during acidification
366 (Latif et al., 2015; Sun et al., 2012; Wu et al., 2009). As a consequence, the phosphorus release depends on
367 whether phosphorus is removed biologically and/or chemically at the WWTP. In this study, acidification of
368 the sludge was performed using three different acids to investigate how this affects phosphorus adsorption by
369 LDH. Sulfate competes with phosphate leading to a reduced phosphate uptake, whereas chloride and nitrate
370 did not influence this. Other anions such as arsenate could potentially also compete with o-P, however, LDH
371 has a slightly higher affinity for phosphate than arsenate (Violante et al., 2009). Competitive intercalation
372 have been observed especially at low pH (Goh et al., 2008; Violante et al., 2009; Wang et al., 2018).
373 Nevertheless, arsenate uptake by the LDH under our conditions is not likely given the extremely low
374 concentration of arsenic (0.2 mg/L - Table 1) as compared to that of o-P (approx. 347 mg/L).

375 Separation of the LDH from the liquid phase are not practical with the tested LDH particles. This highlights
376 the importance of developing magnetic separation of LDH (Drenkova-Tuhtan et al., 2013) or embedding
377 LDH in filter materials or membranes (Jia et al., 2018; Zhang et al., 2016).

378 *Preservation of the LDH*

379 LDHs are typically unstable below a pH of 4 (He et al., 2006), but our data clearly show that LDH is present
380 at all pH value also at pH 3. At pH = 5 and 3, $AlPO_4$ are present (approx. 20-25 % of the Al), which indicates
381 a partial dissolution of the LDH at these pH values in agreement with the increased [$Zn^{2+}$] in the solution.
382 ICP result showed a 10.8 % release of Zn, hence the Al source for the precipitated $AlPO_4$ is a both the LDH,
383 the AOH and/or sludge. Most likely, the hydroxide released by partial dissolution of the LDH increases the
384 pH preventing further dissolution of the LDH.

385 *Phosphate speciation*

386 The phosphate uptake (o-P) is pH dependent and most efficient at low pH, primarily due to the favorable
387 shift in the carbonate equilibrium towards carbon dioxide below a pH of 6.4. In addition, the lower charge (-
388 1) of the o-P at low pH allow for a higher adsorption. Precipitation of 32±3 % brushite (pH of 6) or 10-15 %
389 $AlPO_4$ (pH of 5 and 3) is seen, which is ascribed to combination of a high Ca concentration (10.9 mg/l) in the
390 sludge (Table 1) and the appropriate pH. The precipitation of $AlPO_4$ cannot account for the increased

391 phosphate adsorption from 10.2±1.6 % (pH 6) to 44.9±3.3 % (pH 5). Precipitation of iron phosphates has
392 been observed after MgFe LDH was exposed to phosphate at a pH of 5 (Du et al., 2009), but often
393 precipitation of the appropriate magnesium or zinc phosphates are seen at a pH higher than 5 (Bernardo et
394 al., 2016; Radha et al., 2005; Seftel et al., 2018). It is also found that 17-25 % of the adsorbed phosphate is
395 adsorbed to the AOH phase, an impurity in the LDH sample, which thereby is a large contributor to
396 phosphate uptake. The result indicates the presence of two different binding sites, e.g., intercalated and
397 surface adsorbed phosphate. However, further studies are needed to assign these to different LDH sites and
398 will be reported elsewhere.

399

400 **4.0 Conclusion**

401 Up to 75% of the phosphorus was extracted from digested sludge by adding nitric, hydrochloric or sulfuric
402 acid. The solid material was removed and ZnAl-LDH added to adsorp the dissolved phosphate.

403 • The ZnAl-LDH phosphate binding capacity was favored at low pH by degassing of $CO_2$ and
404 protonation of phosphate to form $H_2PO_4^-$.
405 • Sulfated reduced phosphate binding; hence acidification by sulfuric acid resulted in the lowest
406 phosphate removal.
407 • LDH was mainly preserved at pH 3, but small part of the LDH was probably dissolved and
408 precipitated as a new aluminum phase
409 • Phosphate was both intercalated in LDH by ion-exchange and adsorption.

410 Thus, ZnAl-LDH selectively removed phosphate from acidified sludge, whereby phosphorus can be
411 recovered and the iron containing liquid recycled to the active sludge process to precipitate phosphate.

412

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596

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad \text{eq. 1}$$

$$H_2CO_3 \overset{pK_a = 6.4}{\rightleftharpoons} H^+ + HCO_3^- \quad \text{eq. 2}$$

$$HCO_3^- \overset{pK_a = 10.4}{\rightleftharpoons} H^+ + CO_3^{2-} \quad \text{eq. 3}$$

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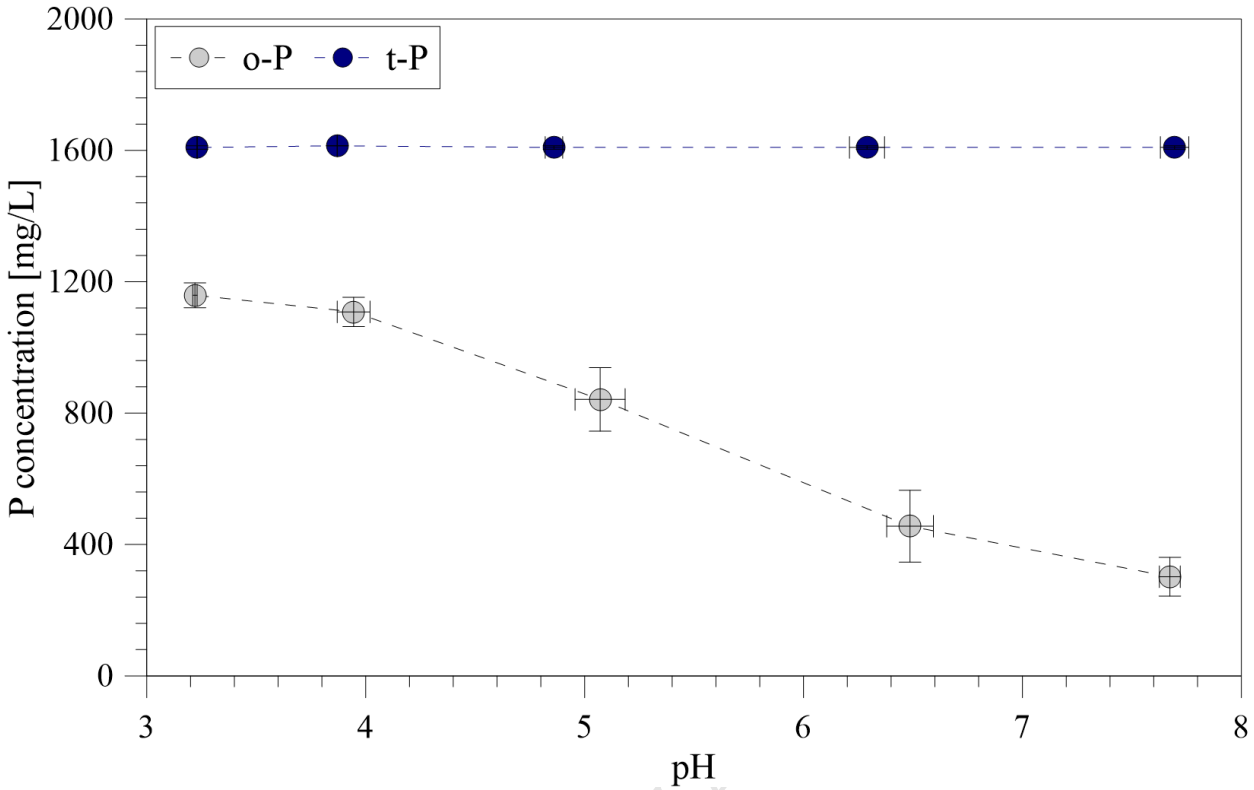


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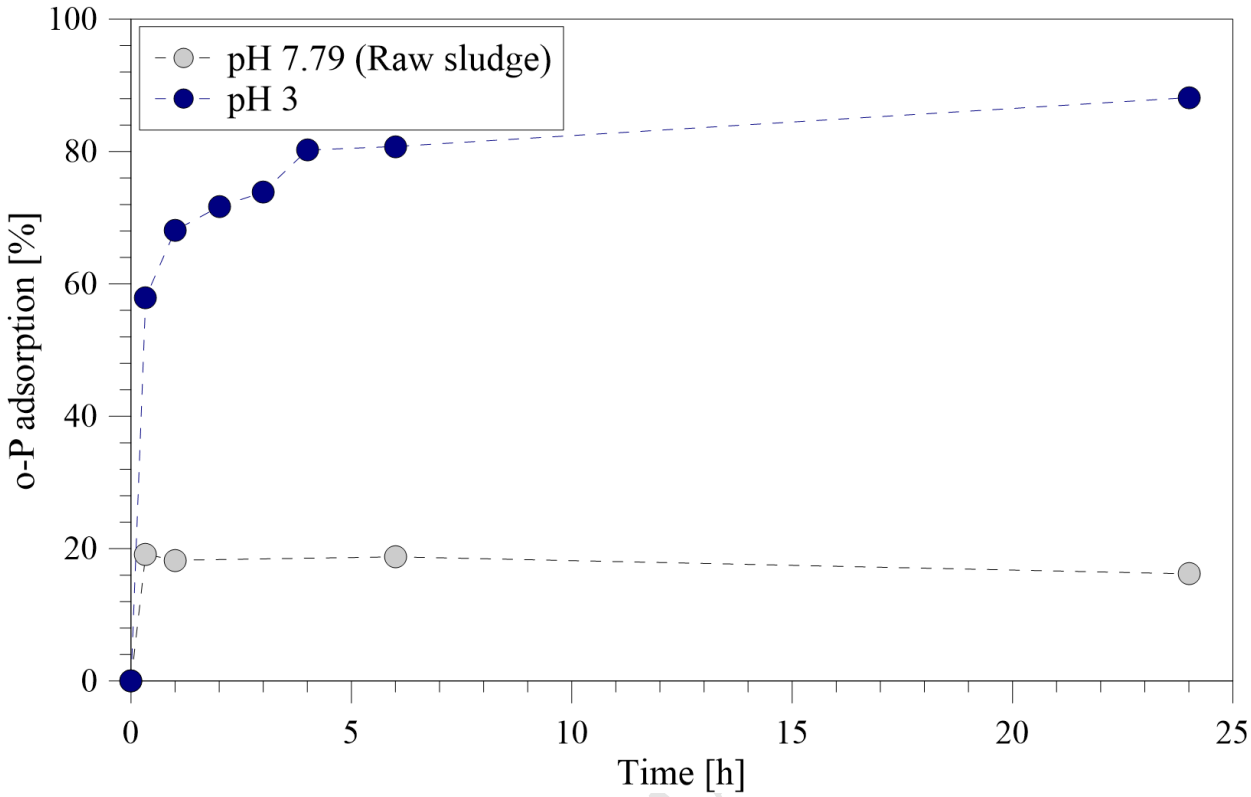


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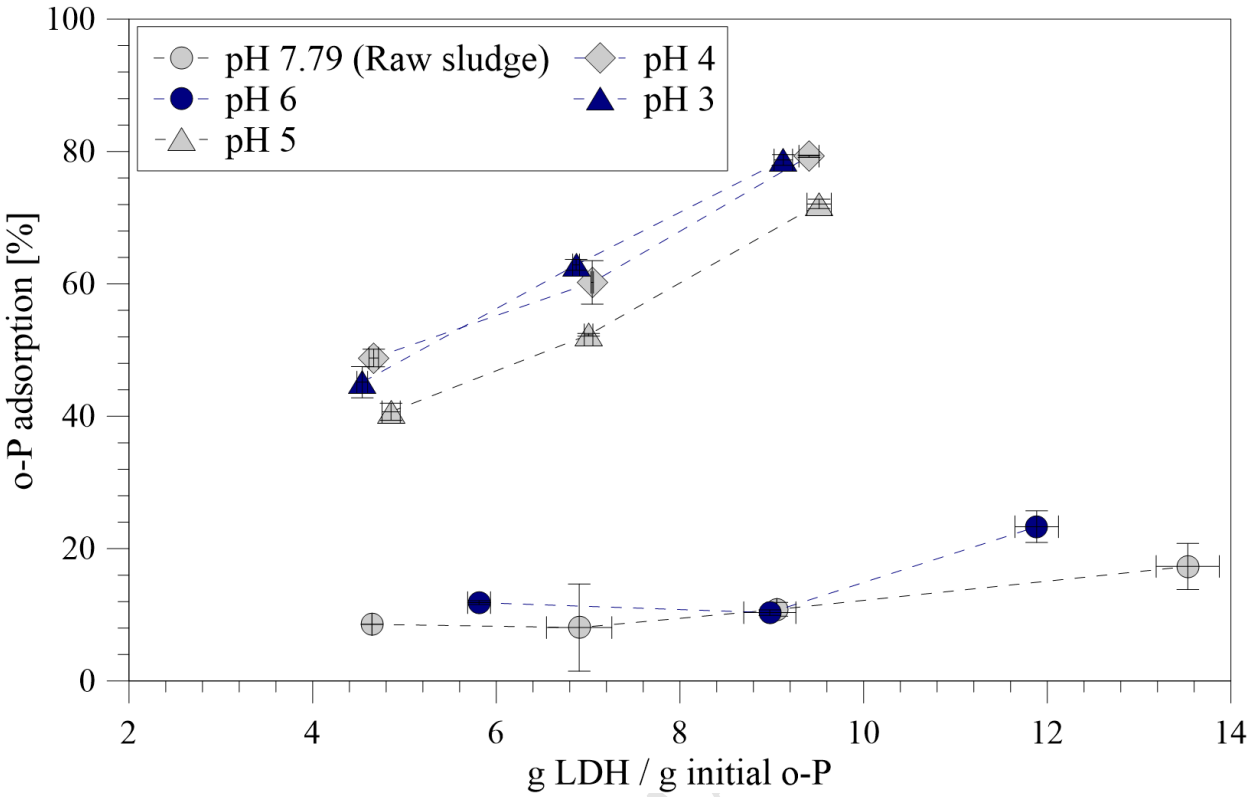


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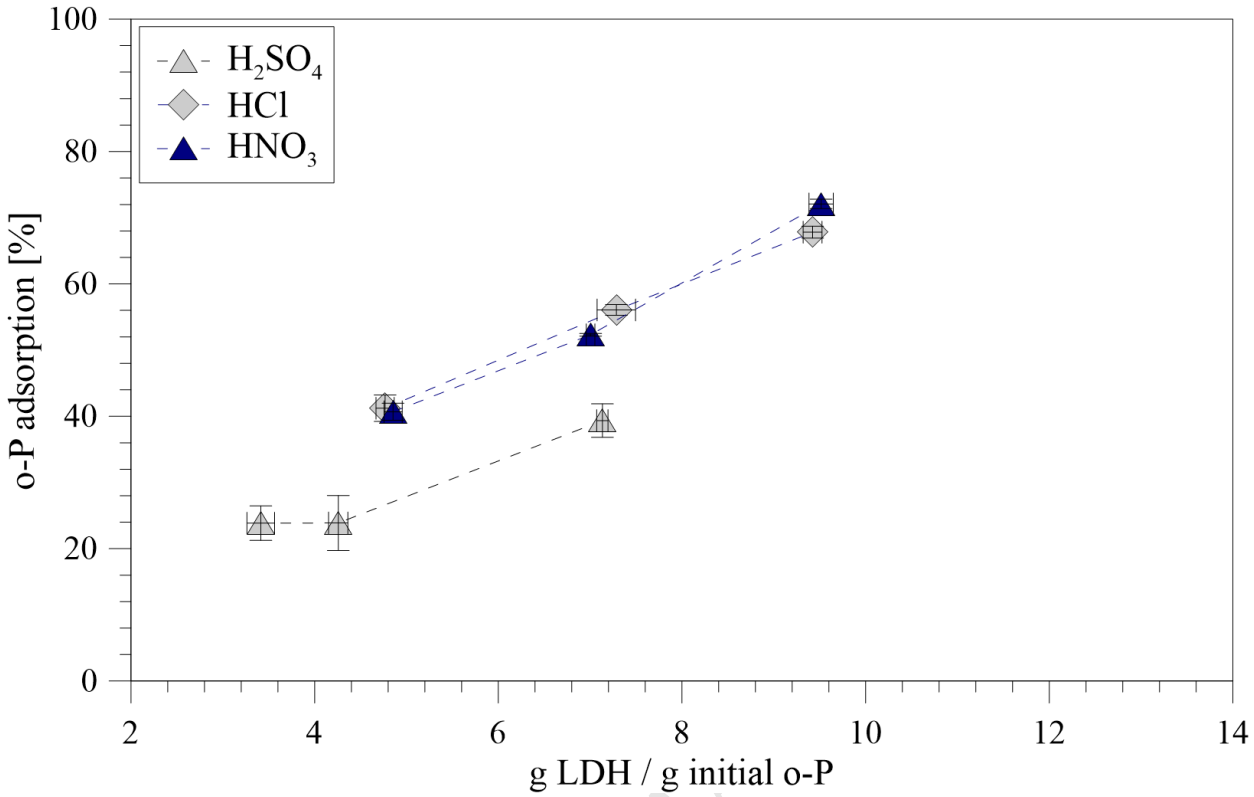


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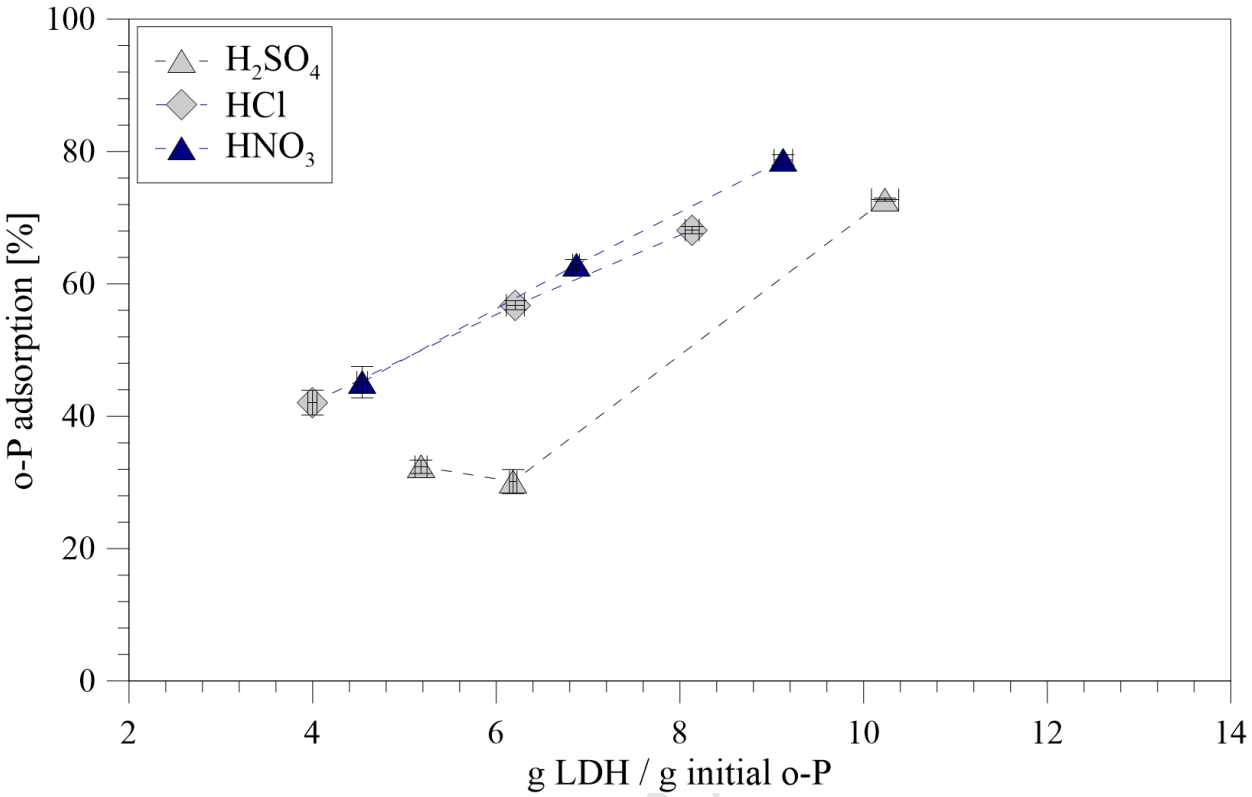


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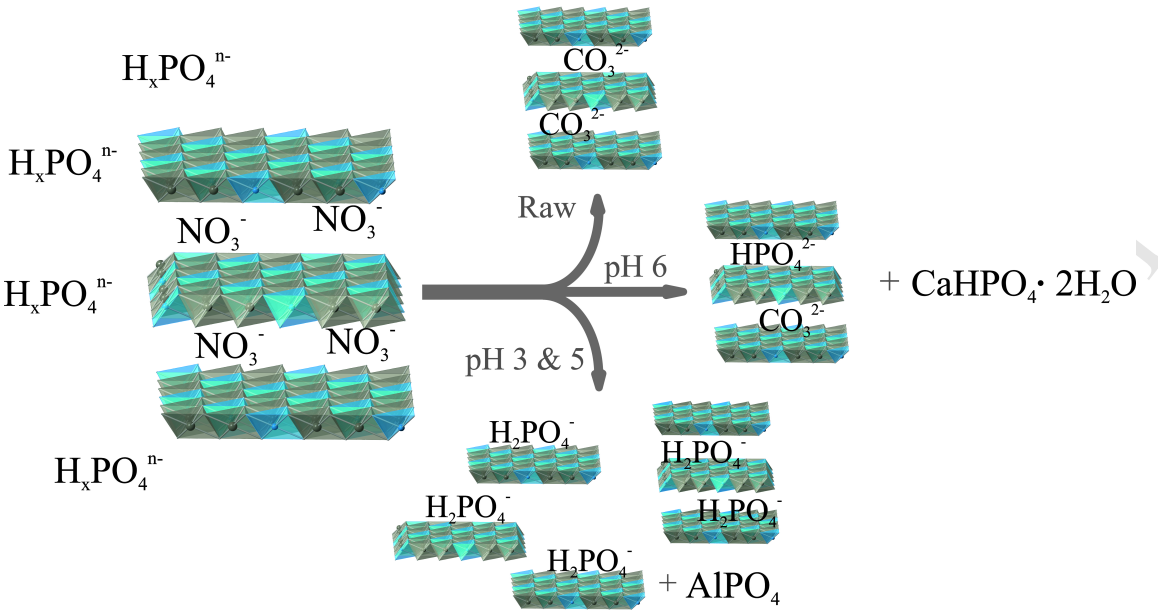


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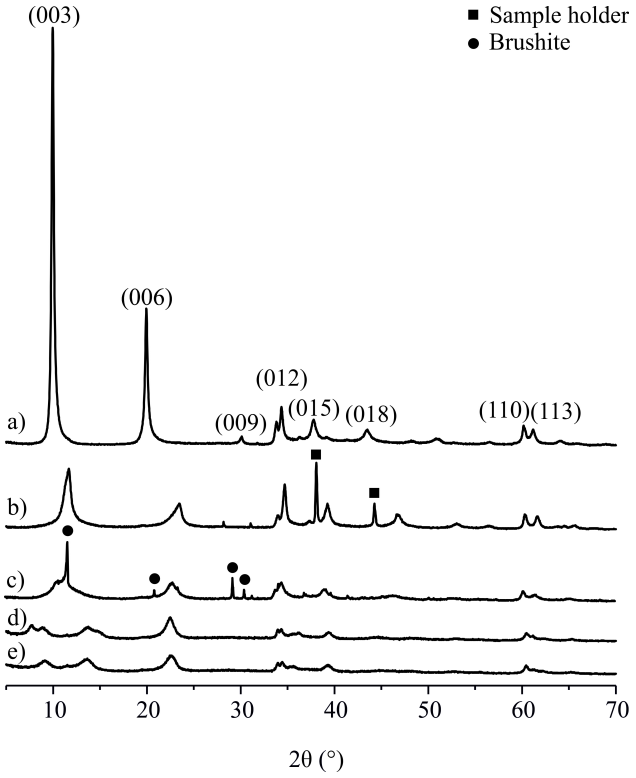


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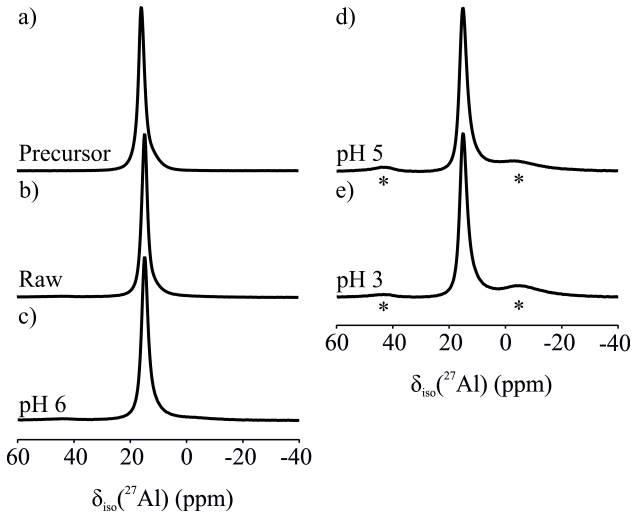


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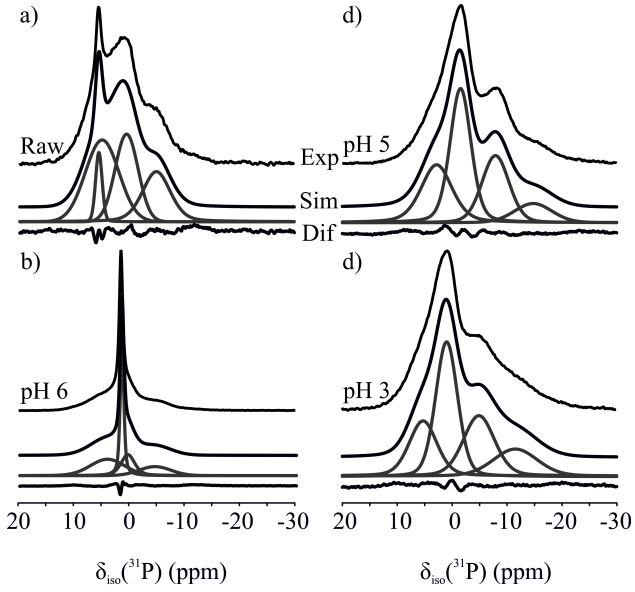


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$$H_3PO_4 \overset{pK_a = 2.2}{\rightleftharpoons} H^+ + H_2PO_4^- \quad \text{eq. 4}$$

$$H_2PO_4^- \overset{pK_a = 7.2}{\rightleftharpoons} H^+ + HPO_4^{2-} \quad \text{eq. 5}$$

$$HPO_4^{2-} \overset{pK_a = 12.7}{\rightleftharpoons} H^+ + PO_4^{3-} \quad \text{eq. 6}$$

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- Up to 75 % P is released from digested sludge by acidification
- Phosphate primarily binds to the ZnAl LDH at pH = 3, 4, 5 and 6
- Sulfate reduces phosphate binding if sulfuric acid is used for acidification
- Phosphate removal is most efficient at low pH due to less dissolved carbonate
- Solid state NMR Spectroscopy and PXRD showed preservation of LDH at all pH

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

| |
|---|
| none |

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