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Optimization of phosphate recovery from urine by layered double hydroxides

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Abstract

Urine contains sufficient phosphorus (P) to consider P recycling form urine as an interesting strategy. In this study, the potential of MgAl or ZnAl layered double hydroxides (LDHs) to be used in such recovery was assessed. LDHs are anion exchangers with a high P selectivity, and P-loaded LDHs have demonstrated fertilizer potential. A critical factor for efficient P recycling with LDH is the stability of these materials, which can be compromised by urinary citrate, complexing aluminium (Al^{3+}) and by the low pH of fresh urine dissolving the alkaline LDHs. Different phase pure ZnAl and MgAl LDHs were synthesised by coprecipitation in scenarios of varying synthesis pH and Mg/Al or Zn/Al ratios. The obtained materials were incubated in P solutions at different pH, with or without citrate in full factorial combinations, and in fresh and stored human urine. The P sorption capacities increased for LDHs synthesised at lower pH, at increasing Al content and for sorption solutions with lower pH. These trends are explained by an increased anion exchange capacity (AEC) and by P speciation (charge) in the LDHs, an interpretation supported by XRD measurements. The P capacity reached 61 mg P/g LDH, which equals 85 % of the theoretical LDH exchange capacity. Only 1 g LDH is required to remove 90 % of P from 1 L urine and evidence is found that sorption, not struvite precipitation, is the P removal mechanism involved. The ZnAl LDHs were equally effective in P uptake compared to the MgAl LDHs, but the ZnAl materials showed more irreversible P sorption in contrast with the high desorption yields (53 mg P/g) of the MgAl LDHs. Therefore, the large potential of MgAl LDHs for P recovery from urine is supported by this study.

Keywords

Layered double hydroxide (LDH), phosphorus, adsorption, recovery, urine, X-ray diffraction (XRD)

1. Introduction

Phosphorus (P) is an essential nutrient for all living organisms, including agricultural crops. The availability of P for crops is of vital importance to maintain high productivity and secure global food production. Therefore, P fertilisers are widely used in agriculture and horticulture. The vast majority of commercial P fertilisers is derived from rock phosphate, a limited commodity (Withers et al., 2015). Irrespective the ongoing discussion on available reserves, it is clear that there is limit and that they will become scarce in the long run (Scholz et al., 2014). To ensure food production in the future, P recovery from waste streams will have to become an important pillar to maintain an adequate P supply to food crops. Recycling P from urine is one of the potential strategies.

Globally, the total emission of P via urine is estimated to be 2 Mt P/annum (Schröder et al., 2010). Technologies available for P removal during wastewater include adsorption (Schneider et al., 2017), anion exchange (O'Neal and Boyer, 2013) and biological processing (Gieseke et al., 2002). Most often, however, chemical precipitation through the addition of aluminium (Al^{3+}) or iron (Fe^{3+}) salts is used (Morse et al., 1998). This technology is primarily focussing on the removal, and not on recycling of P and is well known to result in solid by-products with a low P availability due to the formation of insoluble $AlPO_4$ and $FePO_4$ (Desmidt et al., 2015). A notable exception is the crystallization of struvite ($MgNH_4PO_4 \cdot 6H_2O$) in liquid waste streams (Doyle and Parsons, 2002; Ronteltap, 2009). Struvite can indeed be used as a P fertiliser with high agronomical potential in a multitude of soils (Cabeza et al., 2011; Massey et al., 2009; Vogel et al., 2015).

Thus far, the possibility of using layered double hydroxides (LDHs) for the recovery of P from urine has not been explored. The LDHs can be loaded with PO_4 anions for on-site concentration of P from urine and then transported to sites where gradual release is appreciated, i.e. to supply P to a growing crop..The P-loaded LDHs have recently been proven to be ecological and efficient P fertilisers with potential slow-release characteristics (Benício et al., 2016; Everaert et al., 2016). Everaert et al. (2017) recently demonstrated equal agronomic efficiency of struvite and P-loaded LDHs. The combined approach of P removal and direct application on the field could make a valuable contribution in the efforts towards a closed P cycle.

Layered double hydroxides are a class of anionic clay minerals following the general chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$ (Evans and Slade, 2006). The structure of LDHs is similar to that of brucite $[Mg(OH)_2]$. An excess of positive charge in the hydroxide layers is introduced by the presence of trivalent cations (Evans and Slade, 2006), which needs to be counterbalanced by anions in the interlayer gallery (Evans and Slade, 2006). Therefore, the anion exchange capacity (AEC) can be increased by increasing the M^{3+} content (or decreasing the M^{2+}/M^{3+} ratio). The M^{2+}/M^{3+} ratio is altered by the synthesis pH, and so is thus the AEC, because the two different metals have different pH dependent solubilities. Furthermore, the degree of oversaturation increases with pH, which decreases the LDH crystallinity (He et al., 2006).

The P uptake by LDHs can occur by three different mechanisms. Firstly, anions can intercalate electrostatically in the interlayers. Secondly, ligand exchange can lead to an extra sorption mechanism (Ashekuzzaman and Jiang, 2017; Yang et al., 2014), probably leading to irreversible sorption, which is undesirable for P recycling. Finally, also precipitation of secondary P phases might occur (Xu et al., 2016). It seems logical that the P uptake mechanism is related to the choice of the metal cations for LDH synthesis.

The P uptake efficiency of LDHs, i.e. the combination of capacity and selectivity, increases with a decreasing solution pH (Cheng et al., 2009; Das et al., 2006; Yang et al., 2014). This trend can be interpreted by the fact that less OH^- and CO_3^{2-} anions are present that compete with P for sorption. Especially LDHs with a low M^{2+}/M^{3+} content have a high selectivity for OH^- and CO_3^{2-} anions, as a result of the high charge density of these anions (Ashekuzzaman and Jiang, 2014; Das et al., 2006). Alternatively, higher P uptake at lower pH might be interpreted as more efficient use of the AEC by sorbing monovalent $H_2PO_4^-$, instead of HPO_4^{2-} or PO_4^{3-} at higher pH (Everaert et al., 2019).

Desorption of P from the materials also critically affects the recycling performance of the LDHs. Everaert et al.(2016) found different P release mechanisms from LDHs for different kinds of soils. Their results show that LDH dissolution is probably the most important P release mechanism in acidic soils. Alternatively, in calcareous soils, they found that ion exchange with CO_3^{2-} is the most important P releasing mechanism.

This study was set up to assess the potential of different LDHs for the recovery of P from urine. The strategy was to change synthesis and adsorption conditions to optimise recovery of P, assuming that it is related to the LDH layer charge, pH and citrate concentrations in the solution. The bottleneck of this strategy is the stability of the LDHs in the urine, which contains large amounts of citrate (Putnam, 1971). First, several MgAl and ZnAl LDHs were synthesized in nitrate form by varying the synthesis pH and the M^{2+}/M^{3+} ratio to obtain materials of different capacity (AECs) and crystallinity. The MgAl are used because they have been shown to be efficient P fertilizers by Everaert et al. (2017) The ZnAl were included because Yang et al. (2014) found that the removal efficiency of ZnAl LDHs was higher than that of MgAl LDHs. Furthermore, ZnAl LDHs could have potential as a dual purpose Zn-P-fertilizer in Zn deficient soils (López-Rayo et al., 2017). Second, the P uptake capacity and the structural stability of the LDHs was compared through P adsorption studies. Because citrate might influence the stability of the LDHs, the P adsorption was measured in P solutions with or without added citrate, as well as in synthetic urine. While sorption of P on LDHs is higher at lower pH, LDHs are more stable at higher pH. A pH optimum should thus be found to compromise between these contrasting trends. Therefore, the adsorption from the P and P + citrate solutions was carried out at pH 6, 8 and 10. Finally, the P loaded LDHs were subjected to a multi-step desorption using a carbonate solution at pH 10. This multifactorial screening of synthesis, adsorption and desorption procedures was used to derive the optimal LDH synthesis and sorption conditions for P recovery from urine. Validation of this screening was done with synthetic and real (human) urine sample, the latter also addressing effects of urine storage on adsorption.

2. Materials and methods

All glassware and plastic bottles used in the experiments were acid washed to ensure an absolute removal of P contaminations. Solutions were prepared using ultrapure water (18.2 MΩ). The optimisation of synthesis and sorption conditions was done with 12 LDH materials in full factorial combinations of ten P adsorption conditions.

2.1 LDH synthesis

Six different MgAl LDHs and six different ZnAl LDHs were synthesized using the coprecipitation method (He et al., 2006). Each metal precursor solution was prepared by dissolving either $Mg(NO_3)_2 \cdot 6H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ with $Al(NO_3)_3 \cdot 9H_2O$. The total metal cation concentration in the precursor solution was 3 M and the M^{2+}/M^{3+} ratio in the solution was changed to be either 2, 3 or 4. At 20 °C, 50 mL of this metal solution was added dropwise to 400 mL of ultrapure water in a continuously stirred reaction vessel over 5 hours using a perfusor pump (Braum Perfusor Space). The reaction vessel was continuously flushed with N_2 gas before, during and after the precipitation reaction to remove atmospheric CO_2 from the reaction vessel, thereby minimising CO_3^{2-} in solution. During precipitation, the pH of the reaction solution was kept constant by controlled addition of a 3 M NaOH solution using a titrator (Metrohm 702SM Titrino). For the MgAl LDHs, synthesis was performed either at constant pH 12 or 10; for the ZnAl LDHs at constant pH 10 or 8. The MgAl LDHs are synthesised at different pHs than the ZnAl LDHs because of the different pH dependent solubility of Mg compared to Zn. After 5 h, the suspension was ‘aged’ for 16 h at 20 °C whilst stirring. Afterwards, the material was recovered through centrifugation (10000 g, 20 min), washed twice by resuspension in ultrapure water and dried at 60 °C. The abbreviations used for the 12 different LDHs are listed in Table 1.

2.2 Characterisation of LDHs

The crystallographic properties of the as-synthesized LDHs were examined by X-ray diffraction (XRD) using a STOE COMBI P diffractometer with monochromated CuKα1-radiation. The M^{2+} and M^{3+} metal content of the as-synthesized LDHs was determined by Induced Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific iCAP 7000 series) after dissolving the LDHs in nitric acid. The NO_3^- content of the as-synthesised Mg samples was measured by the sulfonilamide colorimetric method using a SKALAR SA-40 after dissolution in chloric acid.

2.3 P adsorption by LDH

The P adsorption isotherms were determined for the 12 LDH minerals in seven different synthetic solutions and three real urine solutions. First, stock solutions containing 2.8 g/L

KH_2PO_4 (20.5 mM P) or 2.8 g/L KH_2PO_4 and 0.65 g/L sodium citrate dihydrate (2.3 mM citrate) were prepared, and their pH adjusted to either 6, 8 or 10 using a 1 M NaOH solution. Also, a synthetic urine was prepared according to Griffith et al. (1976) (Table 2). The pH of the synthetic urine was adjusted to pH = 6.0 using a 1 M NaOH solution. Different amounts of as-synthesized LDH material were added to 5 mL of the different solutions: the ratio of mole P to mole charge in the LDH was 25 %, 50 %, 66.6 %, 100 % or 200 %. This approach was preferred over the traditional approach of varying the sorbate concentration at constant solid-liquid (S/L) ratio to mimic the technology to remove P from urine. The experiment was performed using three replicates per treatment. The suspensions were shaken end-over-end during 24 h. Preliminary results indicated that equilibrium has been reached after this time. Furthermore, preliminary results also showed that the release of cations from MgAl LDHs is acceptable, with low Al release after 24 hours and a maximum of 12 % of Mg released from the LDHs. After shaking, the suspensions were centrifuged (10000 g, 20 min). The P concentration in the supernatants was measured by ICP-OES, and the recovered materials were dried at 60 °C.

The urine experiments were performed using only the Mg_2Al10 materials. Urine samples were collected from students. Each sample was subjected to three treatments, i.e. fresh, NH_4NO_3 amended or stored urine: For the fresh urine, the pH (5.8-6.3) was adjusted to pH = 6.0 using a 1 M NaOH or HCl solution. To investigate the effect of ammonium (NH_4^+), 1.0 g of NH_4NO_3 was added to 75 mL of the fresh urine. The addition of NH_4^+ simulated the effect of urea hydrolysis. This concentration of ammonia can be expected after urea hydrolysis, assuming ammonia can volatilize as it would at the high pH of stored urine. After NH_4NO_3 addition, the pH of the solution was adjusted to 6.0. Finally, subsamples of fresh urine were stored at 20 °C for 1 week, the pH of these samples increased to 8.0-9.0 and was also adjusted to pH= 6.0. All samples were equilibrated with LDH to obtain the adsorption isotherms.

The XRD characterzation was performed on material recovered from one replicate of the highest and lowest S/L ratio of each adsorption isotherm. The obtained Langmuir adsorption isotherms were fitted using JMP Pro 13 to obtain the parameters (Q_{max} and K) of the Langmuir equation (Langmuir, 1918):

$$Q = Q_{max} \frac{K\,.C}{1 + K\,.C} \qquad \text{(Eq. 1)}$$

with Q the amount adsorbed P (g/g), Q_{max} the maximum capacity of P (g/g), K the sorption constant (L/g) and C the P concentration in solution (g/L). The required mass of LDH to remove 90 % of the P in solution was calculated from the parameter values as:

$$R_m = \frac{C_S.K\,.V + K\,.m\,.Q + V - \sqrt{(C_S\,.K\,.V + K\,.m\,.Q + V)^2 - 4\,.C_S.K^2\,.m\,.Q\,.V}}{2\,.C_S.*\,K\,.V} \qquad \text{(Eq. 2)}$$

R_m is the proportion of P removed, C_s is the initial P concentration in solution (g/L), V is the volume of the solution (L) and m is the added amount of LDH (g). After the parameters of this equation were obtained, inverse prediction was used to estimate the required mass of LDH for 90 % P removal and its statistical uncertainty.

2.4 P desorption efficiency

The desorption of P from the materials was examined for the samples loaded in a solution containing the lowest S/L ratio. Of each of these P-loaded LDH, 20 mg was weighed in a tubular shaped dialysis membrane (Medicell Membranes Ltd, MWCO of 12-14 kDa). A desorption solution of 5 mM $NaHCO_3$ was prepared and adjusted to pH 10 using a 1 M NaOH solution, and 5 mL of this solution was added in the membrane. The membranes were then closed, and inserted in a 50 ml tube containing another 45 mL of the same 5 mM $NaHCO_3$ solution (pH 10). The tubes were shaken end-over-end. At specific moments (after 2 hours and 40 minutes, 8 hours, 1 day, 3 days, 1 week and 2 weeks), the P concentration of the outer solution in each tube was determined (ICP-OES) and the outer solution renewed. After 3 weeks of incubating the samples, the P concentration in the last solution was measured. To determine the remaining P in the LDHs after these desorption steps, the membranes were transferred to 10 mL of nitric acid and shaken end-over-end during 24 h. Complete dissolution of the LDHs and the membranes was confirmed, and the P concentration of this acid solution was determined (ICP-OES). The P content measurement (ICP-OES) after destruction of a pure dialysis membrane confirmed the P content in the membranes to be negligible. The total amount of desorbed P was divided by the amount of P loaded onto the LDHs to obtain the percentage of desorbed P.

3. Results and discussion

3.1 Characteristics of as-synthesised LDHs

The crystallinity of the as-synthesised LDHs is an important characteristic for the given technology. Highly crystalline materials are expected to have higher P sorption capacities and increased desorption yields (Goh et al., 2008). The XRD patterns of the materials suggest that the as-synthesised MgAl materials are almost phase pure LDH materials (Figure 1a). A small reflection at 29° 2θ can be seen in the XRD patterns of Mg_2Al12 and the MgAl10 LDHs. This reflection is characteristic for boehmite (AlO(OH)). Another characteristic reflection of boehmite at 28° 2θ is also visible in the XRD patters of the Mg_2Al10 and the Mg_4Al10 LDHs, further indicating that indeed a small amount of boehmite precipitated during synthesis of these materials. The strong (003) reflections in the patterns indicate a consistent stacking of nitrate anions in the interlayer galleries (Evans and Slade, 2006; Kuang et al., 2010). The interlayer spacing was calculated from the positions of the (003) reflections assuming a constant hydroxide layer thickness of 4.8 Å (Shimamura et al., 2012). Furthermore, the orientation of intercalated nitrate anions relative to the basal plane can be calculated, given that the diameter of nitrate is 5.54 Å (Everaert et al., 2016). The interlayer spacing increases with decreasing M^{2+}/M^{3+} (increasing Al content) for the Mg10 LDHs (Table 1). Due to the increase of the layer charge density as Al content increases, a denser packing of the nitrate anion population is required, leading to a more vertical orientation (Witzke et al., 2012). This is attributed to a shift in nitrate orientation: this is 50° for the Mg_2Al10 LDH, 41° for the Mg_3Al10 LDH and 37° for the Mg_4Al10 LDH; angles relative to the basal plane. For the Mg12 LDHs and the Zn8 LDHs (Figure 1b), the differences in d-spacing are limited between materials with varying M^{2+}/M^{3+} ratio. The amount of NO_3^- in the materials was measured (Table 1). The LDH synthesized at pH 12 have a lower NO_3^- content compared to those prepared at pH 10, which is likely related to the larger intercalation of OH^- at the higher pH (Everaert et al., 2019). In addition, some of the charge deficit in these materials is compensated by electrostatic interaction on the outside of the LDHs.

Clear structural differences in ZnAl LDHs between the materials synthesised at pH 10 and those synthesised at pH 8 are visible in the XRD patterns (Figure 1 b). The XRD patterns of the materials synthesised at pH 8 suggest that phase pure LDHs are synthesised, which is not the case for the materials synthesised at pH 10. This difference can be explained by the solubility characteristics of Zn and Al (discussed below). In addition, the Zn10 LDHs materials have three clear reflections between 30 and 40 2Ɵ, identifying as a zincite phase (Islam et al., 2013). More zincite was precipitated in the Zn_4Al10 material than in the Zn_3Al10 and Zn_2Al10 materials. This is likely the result of the Zn concentration in the metal solution, which was the highest for Zn_2Al10. The d-spacings of the Zn8 LDHs with different M^{2+}/M^{3+} ratio are not significantly different. In contrast, large changes in the d-spacing between the Zn10 LDHs containing different M^{2+}/M^{3+} ratio are found. However, as these materials are no phase pure LDH materials, large differences are expected.

The measured M^{2+}/M^{3+} ratio (Table 1) determines the AEC of phase pure LDH materials. High AEC materials are likely to have increased P adsorption capacities compared to low AEC LDHs. Interestingly, while the M^{2+}/M^{3+} ratio in the LDHs is consistently lower than the M^{2+}/M^{3+} in the precursor solution for the ZnAl LDHs, the M^{2+}/M^{3+} ratio in the LDHs is consistently higher than in the precursor solution for MgAl LDHs. This is explained by the pH dependency of the solubility characteristics of the metals. Mg solubility steadily decreases with an increasing pH. Conversely, both Al and Zn have amphoteric characteristics. In alkaline conditions Al precipitates less with increasing pH, and therefore more Al stays in solution during the synthesises at pH 12 than at pH 10. This results in a higher M^{2+}/M^{3+} ratio in the LDHs synthesised at pH 12 compared to those prepared at pH 10. Zn also has amphoteric properties. Therefore, the synthesis pH has a more limited effect on the M^{2+}/M^{3+} ratios of the ZnAl LDHs than on the MgAl LDHs. The AEC of the MgAl LDHs is inversely related to M^{2+}/M^{3+} ratio, however, this may not be the case for ZnAl LDHs due to the large presence of the secondary zincite phase.

3.2 P adsorption by LDH

In general, the Langmuir model fitted the adsorption data well (Figure 2). The capacity of the Langmuir isotherm (Table 3 and S1) is an important parameter to differentiate between LDHs. The largest P uptake was found in the Mg_2Al10 material and reached 61 mg P/g material. This is close to the theoretical adsorption P sorption capacity of a MgAl LDH with a M^{2+}/M^{3+} ratio of 2. The theoretical P sorption capacity of LDHs can be calculated using the general chemical formula of the LDHs: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$. The P sorption capacity of LDHs thus depends on the metals present in the material and the M^{2+}/M^{3+} ratio. For a completely dried MgAl LDH with a Mg/Al ratio of 2, and assuming P sorbs only as a divalent anion, the formula becomes $Mg_4Al_2(OH)_{12}HPO_4$. The total molar mass of this material is 451.2 g/mole. The maximum capacity of P (31 g/mole) is then 31/451.2 or 68.7 mg P/g LDH. The same method can be used to derive the theoretical P sorption capacity of other LDHs with other M^{2+}/M^{3+} ratios or metals. On a molar basis, the theoretical capacity of ZnAl LDHs is the same as that of MgAl LDHs. However, because Zn is heavier than Mg, the capacity is lower on a mass basis. For a ZnAl LDH with a Zn/Al ratio of 2, the theoretical capacity is 50 mg P/g LDH (Harland, 1994).

The adsorption capacities can be related to the five factors that were tested: the type of LDH metals (MgAl or ZnAl), the charge, i.e. M^{2+}/M^{3+} ratio (2, 3 or 4), the synthesis pH (high or low), the solution type (P, P + citrate or synthetic urine) and the adsorption solution pH (6, 8 or 10). A least square model was fitted showing that the M^{2+}/M^{3+} ratio, the solution pH and the synthesis pH significantly ($p<0.01$) affect the P adsorption capacity. The M^{2+}/M^{3+} ratio logically explains the LDH AEC and thus its potential for P uptake. The effect of a lower P uptake at increasing solution pH confirms the results of Cheng et al. (2009); Das et al. (2006) and Yang et al. (2014). The effect can be attributed to i) a more pronounced competition between PO_4 anions and OH^- ions (Das et al., 2006), ii) a higher concentration of CO_3^{2-}, causing more competition for sorption of P (Ashekuzzaman and Jiang, 2014; Das et al., 2006) and iii) a change in P speciation of the P solution, and as a result also the speciation of P sorbed on the LDH (Everaert et al., 2019). At a pH below 7.2, P will be present mostly in the monovalent species ($H_2PO_4^-$), whereas at the higher pH values, the divalent HPO_4^{2-} will be prevalent (Cheng et al., 2009; Das et al., 2006). More monovalent P than divalent P is required to compensate the AEC. Lastly, there is significantly more P sorption when LDHs are synthesised at lower pH. This effect can be explained by the higher crystallinity in these LDHs as discussed in the previous section. Furthermore, the LDHs synthesised at a higher pH contain less NO_3^-, and thus more OH^-. Hydroxide anions are less easily replaced by ion exchange than NO_3^- because of their higher charge density. The presence of citrate or other urine components has no significant effect on maximum P uptake. This result shows the high selectivity of LDHs towards P compared to larger organic anions such as citrate. Furthermore, the choice of divalent cation in the LDH material (Zn or Mg) does not significantly affect the maximum P capacity. This result is in contrast with the results reported by Yang et al. (2014), who found that ZnAl LDHs have higher P uptake efficiencies than MgAl LDHs. However, that study was performed using CO_3^{2-}-exchanged LDHs. The difference in P uptake can in this study thus be explained by a higher selectivity towards P by ZnAl LDHs compared to MgAl LDHs. There is indeed a difference between the P selectivities of the different LDHs (see below)

The P adsorption capacity of 61 mg P/g LDH is comparable to other results found in P sorption studies on LDHs such as Das et al. (2006) who obtained a maximum capacity of 44.4 mg P/g and Khitous et al. (2015) who found a maximum P capacity of 64.10 mg P/L. Compared to oxides used for P removal, LDHs have higher capacities. MgO was reported to have a capacity of 24.5 mg P/g. Hydroxides are reported to have higher P capacities that oxides. Ferrihydrite removed P with a capacity of 57.6 mg P/g by inner-sphere complexation and Al hydroxide has a higher capacity at 105.3 mg P/g, removing P by precipitation of Al phosphate (Wendling et al., 2013)

The fresh urine samples contained a total P concentration of 490-550 mg P/L. These concentrations are well within expected P concentrations in fresh human urine (Rose et al., 2015) and are relatively close to the P concentration used in the synthetic urine (635 mg P/L) according to Griffith et al. (1976). The data of the three different urine samples were pooled and Langmuir isotherms were fitted for each of the different treatments, i.e. fresh urine, fresh urine supplemented with NH_4NO_3 and stored urine. The P sorption capacities were 62 mg P/g LDH for fresh urine, 64 mg P/g LDH for fresh urine with NH_4NO_3 addition and 48 mg P/g LDH for stored urine. The sorption capacities for fresh urine are almost identical to that of synthetic urine. The Langmuir model was extended with dummy variables to differentiate differences in sorption capacities among the treatments. This analysis indicate that there is no significant effect of NH_4NO_3 addition. While storage reduced the sorption capacity, this effect is borderline significant ($0.01<P<0.05$) and not very large. The addition of NH_4^+ was included to test potential removal of P as struvite ($MgNH_4PO_4$). Struvite precipitation here is unlikely because no differences in maximal removal due to enhanced NH_4^+ were found. This result is further evidenced by speciation modelling via VMinteq using the solubility product reported by Ohlinger et al., (2000). The saturation indexes of all the replicates were below zero, which indicates struvite precipitation is not thermodynamically favoured.

The required amount of LDH (m, equation 2) to remove 90 % of P from solution (Table 4 for P and synthetic urine; Table S3 for P + citrate) depends on its maximum capacity and its selectivity (K parameter in the Langmuir equation). The m was, again, related to the five experimental factors showing that the M^{2+}/M^{3+} ratio, the metal cation (Zn or Mg) in the LDH and the solution pH significantly ($P<0.01$) affected m with synthesis pH having a weaker effect ($P < 0.05$). These factors are primarily related to differences in capacity, m decreases as maximum capacity increases. Less LDH is needed to remove 90 % of P from solution with ZnAl

LDHs than with MgAl LDHs and that difference is due to larger sorption constant (K) in the ZnAl LDHs. A possible explanation might be the higher sorption strength of P anions on $Zn(OH)_2$ compared to that on secondary Mg hydroxide phases. For fresh real urine samples, only between 1.0 and 1.3 g LDH/L was needed for 90 % removal of P (details not shown).

The adsorption data show that high P removal efficiencies are obtained when using highly crystalline (thus, synthesised at a low pH) LDHs with a high Al content in an adsorption solution at pH 6. Higher P removal efficiencies are found when using ZnAl LDHs compared to MgAl LDHs at lower solution P concentrations, or the sorption isotherm is steeper at lower P concentrations for ZnAl LDHs than for MgAl LDHs. The levels of significance (P-values) of the different variables used in the models can be found in Table S2 and S4.

3.3 LDH stability and intercalation properties

The XRD patterns are important in assessing the LDH stability. It is expected that highly crystalline materials will release more of their adsorbed P compared to more amorphous materials. The latter bind more P via ligand exchange, which is less reversible interaction in comparison with anion exchange. Not all XRD patterns are presented here, but the general trend is that the material crystallinity decreases when decreasing the S/L ratio, which is associated with higher P uptake (Figure 3a). This is likely related to the formation of amorphous Al phosphates at high P uptake. This effect is more pronounced at pH 6 than at higher solution pH, indicating that MgAl LDHs are less stable in more acid conditions. These effects are also more pronounced in the ZnAl LDHs (Figure 4a.) than in the MgAl LDHs. The greater loss of structure of ZnAl LDHs compared to MgAl LDHs could be explained by the formation of amorphous $Zn_3(PO_4)_2$, of which the formation is more thermodynamically favourable than the formation of $Mg_3(PO_4)_2$. An incomplete shift of the (003) reflection can be seen at low S/L ratios. The left tail of the reflection indicates basal spacing expansion by P intercalation in some of the LDH layers. This can be explained by the difference in position between the intercalated anions. Planar NO_3 can flatten between the layers, while tetrahedral P cannot. Thus intercalation of P results in interlayer expansion of the LDHs. However, the small shift in the maximum of the reflection suggests that electrostatic interaction and ligand binding on the outside of the LDHs might be important sorption mechanisms for P uptake.

The XRD patterns of Mg10 materials before and after P uptake from a P + citrate solution at pH 6 (Figure 3b) show that LDHs with a lower Al content are more stable. Complexation of Al by P is assumed to be an important mechanism of LDH dissolution and structure loss. Al in LDHs with a lower Al content will form less complexes. Furthermore, LDHs with lower Al content are intrinsically more stable. This is because at high Al content, Al-O-Al bonds can form. These local structural deficits in the hydroxide layers are probably causing instability due to charge repulsion, according to the cation avoidance rule (Evans and Slade, 2006). Interestingly, when citrate is present in the solution and LDHs with higher Al content are used, a partial or complete shift of the (003) reflection is shown. This proves that citrate can intercalate in these materials if positioning in the interlayer is optimised. This does not happen in materials with a low Al content as the charge density of these materials is not high enough to favour intercalation of trivalent citrate anions.

Preliminary tests show a very small release of Al and a maximum of 12% of Mg release from LDHs. More Mg than Al is present in the as-synthesised LDHs, which is a first explanation why more Mg dissolves during adsorption than Al. This phenomenon can be further explained by the differences in solubilities of secondary Al phases (such as Al-oxyhydroxides and Al-phosphates) and secondary Mg phases (such as Mg-hydroxides and Mg-phosphates).

Secondary phases containing Al are more thermodynamically stable than secondary phases containing Mg. The combination of the loss of crystallinity indicated by the XRD data and VMinteq modelling suggest that some of these secondary phases have formed during P adsorption and it is likely that a large fraction of these precipitates contain Al, explaining why much more Mg than Al is in solution after 24 h (Gustafsson, 2016).

The structural loss in the ZnAl LDHs during P sorption is more pronounced than in the MgAl LDHs (Figure 4a). Note that the Zn_2Al8 material maintains more of its high intensity reflections after P uptake than the Zn_2Al10 material. This confirms that LDHs are more stable when synthesised at lower pH. The other materials follow the same trend.

There is no large effect of the addition of citrate or urine on structural loss (Figure 4b). This is surprising because complexation of Al by citrate was expected to result in a loss of crystallinity of the LDH and subsequent precipitation of amorphous phases. However, this does not appear to be the case. A possible explanation might be that the complexation of Al by citrate retains the Al in solution, which prevents it from precipitating. A slight loss in crystallinity can be observed in the synthetic urine treatments. The higher ionic strength of these solutions could induce more dissolution of the material, resulting in loss of structure.

Thus, in general, there is more structure loss in the LDHs that take up large amounts of P. There is more structure loss in ZnAl LDHs than in MgAl LDHs and there is more structure loss in LDHs containing more Al. Finally, when adsorption is performed at lower pH, structure loss increases. The combination of these results suggest that high capacity materials adsorb at least a fraction of the P by mechanisms other than electrostatic interaction, e.g. precipitation and ligand exchange.

3.4 P desorption efficiency

After adsorption, the P should be present in an exchangeable form in the material for it to be useful as a fertiliser. An example of the stepwise desorption of P from P loaded Mg_2Al10 LDH is presented in Figure 5 (other P desorption data follow similar trends). The total amount of P desorbed from the high loaded treatments are given in Table 5. Carbonate, an anion present in relatively large concentrations in soils, is used as a competing anion to replace P. LDH materials have a high selectivity of CO_3^{2-}over P due to the high charge density of CO_3^{2-}. High P desorption yields can be obtained with the multi-step desorption method because i) the large excess of CO_3^{2-}added and ii) the equilibrium is disturbed after each step. While this desorption does not indicate whether or not the desorption can be classified as a slow-release or a fast-release desorption, other studies indicate that P loaded LDHs act as a slow-release fertiliser in soils (Benício et al., 2016; Everaert et al., 2016). The statistical analysis shows that P desorption (in mg/g) is significantly affected ($P < 0.01$) by the M^{2+}/M^{3+} ratio and by the pH of the adsorption. These parameters also relate strongly to the maximum capacity for the LDHs, i.e. the desorbed P mainly depends on the adsorbed amount. A large difference in desorption yield was found between ZnAl LDHs and the MgAl LDHs. Only very small amounts of P were desorbed from ZnAl LDHs. As the XRD patterns (Figure 4a) show a high loss of structure in the ZnAl LDHs, it is suspected that the P in these materials is retained in amorphous phases, while a larger proportion of adsorbed P on MgAl LDHs is bound by electrostatic interactions. The levels of significance (P-values) of the different variables used in the models can be found in Table S3.

The desorption of P, expressed relative to the P content of the LDHs after adsorption, is given in Tables 6. For ZnAl LDHs, this fraction was well below that of MgAl LDHs. Surprisingly, LDHs with a M^{2+}/M^{3+} ratio of 2 desorbed more P than those with less Al, despite loss of crystallinity (Figure 3b). Layered double hydroxides have a high affinity for high charge density anions such as CO_3^{2-}. This effect increases for LDHs with a higher charge density, or more Al, explaining why these materials desorbed more P.

The data suggest that structure loss does not necessarily imply irreversible P binding. Much P could be desorbed even from materials showing loss of crystallinity (high Al content, low adsorption pH). The very pronounced loss of structure in P loaded ZnAl LDHs, however, yields very low amounts of desorbable P.

Taken together, this study proves the high potential of MgAl LDHs for P recovery from urine. The largest uptake 61 mg P/g is equivalent to 28 % P_2O_5, the common formula used to express P-content in fertilisers. This P_2O_5 content is smaller than that of struvite (57 % P_2O_5). The desorption yield of the materials reached up to 84 % of the adsorbed amount suggesting a high fertilizer potential. The long-term fertiliser potential of LDH-P merits further investigation as slow-release of P may increase plant P uptake.

4. Conclusion

In this study the feasibility of LDHs for P recycling (recovery and release) from urine was assessed. Although ZnAl LDHs proved to be efficient P adsorbents, they have a very low desorption potential, making MgAl LDHs the preferred candidates. A lower synthesis pH yields materials with higher adsorption capacities, likely a combination of higher crystallinity and less intercalation of OH^-. Urine solutions might be exposed to LDH at their native (weakly acid) pH as this increases P uptake, even though it decreases LDH crystallinity. This study showed that the addition of citrate or other urine compounds does not affect the P adsorption capacities of LDHs. In short, MgAl LDHs synthesised at pH 10 with a high Al content should be used in solutions at pH 6 to maximize P uptake and subsequent P desorption. Given that fresh urine has a median pH of 6.2, and that the pH of urine increases while stocked, it is important to use the urine as fresh as possible. This could be feasible by using source-separating toilets and adsorption columns in places where many people use the toilet, such as office buildings, highway gas stations and festivals. This study confirms the potential of MgAl LDHs for P recovery from urine and its possible recycling.

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Figure 1: (a) XRD patterns of as-synthesid NO_3^--MgAl LDHs prepared at pH 10 and 12, and with high, medium or low AEC (M^{2+}/M^{3+} ratio's of 2, 3 and 4). (b) XRD patterns of as-synthesid NO_3^- -ZnAl LDHs prepared at pH 8 and 10, and with high, medium or low AEC (M^{2+}/M^{3+} ratio's of 2, 3 and 4). The interlayer spacing is given for each material (Å).

Figure 2: The phosphate adsorption isotherm on LDH Mg_2Al10 from a P solution at pH 6, a synthetic urine solution and real urine with the X-axis the equilibrium P concentration in solution. The lines represent the fitted Langmuir adsorption isotherm.

Figure 3: (a) XRD pattens showing the effect of solution pH and P loading on LDH stability during exchange. The bottom pattern presents the pattern of the as-synthesised material; other patterns are from material recovered after P sorption. Low loading stands for sorption in a P solution containing P equal to 25% of the total sorption capacity of the material. High loading patterns were taken after sorption from a solution containing P equal to 200 % of the maximum capacity of the LDHs. (b) XRD patterns showing the effect of M^{2+}/M^{3+} ratio on LDH stability after incubation in a P + citrate solution. The interlayer spacing is given for each material (Å).

Figure 4: (a) XRD patterns showing the effect of synthesis pH during P sorption on LDH stability after incubation in P solution. (b) XRD patterns showing the effect of anions in solution on LDH stability. The as synthesised materials are shown as reference. The interlayer spacing is given for each material (Å).

Figure 5: Stepwise desorption of P from LDH Mg_2Al10. The LDH was loaded with P in a P solution at pH 6 and a low S/L ratio. The dotted line merely shows the trend of the desorption.

Table 1: Overview of the different LDH synthesis conditions and the measured molar M^{2+}/M^{3+} ratio of the MgAl or ZnAl LDHs prior to P adsorption. The AEC=anion exchange capacity scored from the synthesis M^{2+}/M^{3+} ratio and the measured M^{2+}/M^{3+} ratio, d spacing and NO_3^- content; note that the interlayer is occupied by OH^- and NO_3^- anions.

LDH	**Synthesis pH**	**Molar M^{2+}/M^{3+} ratio**	**Interlayer spacing (Å)**	**NO_3^- content (mmol/g)**
			MgAl	
Mg_2Al12	12	2.83	7.76	1.08
Mg_3Al12	12	3.35	7.86	1.13
Mg_4Al12	12	4.42	8.03	1.92
Mg_2Al10	10	2.09	9.04	2.68
Mg_3Al10	10	3.24	8.42	3.11
Mg_4Al10	10	4.33	8.10	3.11
			ZnAl	
Zn_2Al10	10	1.81	7.68	n.d.*
Zn_3Al10	10	2.60	8.93	n.d.
Zn_4Al10	10	3.71	9.96	n.d.
				n.d.
Zn_2Al8	8	1.97	9.01	n.d.
Zn_3Al8	8	2.87	9.04	n.d.
Zn_4Al8	8	3.87	9.07	n.d.

*n.d.=not determined

Table 2: Synthetic urine components following Griffith et al. (1976). The sodium oxalate used by Griffith et al. (1976) is replaced by oxalic acid dehydrate on an equal molar base of oxalate.

Compound	Concentration (g/L)
$CaCl_2{\cdot}2H_2O$	0.65
$MgCl_2{\cdot}6H_2O$	0.651
NaCl	4.6
Na_2SO_4	2.3
Na_3citrate$\cdot 2H_2O$	0.65
Oxalic acid$\cdot 2H_2O$	0.02
KH_2PO_4	2.8
KCl	1.6
NH_4Cl	1.0
Urea	25.0
Creatinine	1.1

Table 3: The P sorption capacities of different LDHs (mg P/g LDH ± 95% confidence interval) exposed to P at different pH values as fitted by the Langmuir adsorption isotherms. The highest capacity (in bold) is reached for LDHs with high Al content that are synthesised at low pH and that are loaded in P solutions at low pH.

LDH	**P adsorption solution**			**Synthetic urine**
	pH 6	**pH 8**	**pH 10**	**pH 6**
			MgAl	
Mg_2Al12	53 ± 8	30 ± 2	30 ± 2	38 ± 8
Mg_3Al12	47 ± 15	18 ± 1	18 ± 1	40 ± 3
Mg_4Al12	32 ± 4	16 ± 3	12 ± 1	n.d.*
Mg_2Al10	**61 ± 12**	54 ± 9	47 ± 5	64 ± 8
Mg_3Al10	56 ± 6	37 ± 3	34 ± 2	51 ± 4
Mg_4Al10	51 ± 16	23 ± 3	21 ± 2	47 ± 4
			ZnAl	
Zn_2Al10	34 ± 5	30 ± 8	32 ± 3	26 ± 2
Zn_3Al10	39 ± 7	20 ± 2	25 ± 3	13 ± 1
Zn_4Al10	n.d.	23 ± 5	24 ± 6	49 ± 7
Zn_2Al8	57 ± 12	38 ± 8	34 ± 5	32 ± 2
Zn_3Al8	29 ± 8	22 ± 4	26 ± 4	8 ± 1
Zn_4Al8	18 ± 3	15 ± 1	21 ± 7	n.d.

*n.d.=not determined

Table 4: The required LDH dose (g LDH/L ± 95% confidence interval) to remove 90% of the P from solution. The lowest amount of LDH (in bold) is required for ZnAl-LDHs with larger AEC synthesised at low pH and exposed to low pH P solution.

LDH	**P adsorption solution**			**Synthetic Urine**
	pH 6	**pH 8**	**pH 10**	**pH 6**
		MgAl		
Mg$_2$Al12	1.6 ± 0.3	2.3 ± 0.2	2.4 ± 0.3	1.7 ± 0.2
Mg$_3$Al12	3.0 ± 0.7	3.9 ± 0.4	3.8 ± 0.6	1.5 ± 0.1
Mg$_4$Al12	3.0 ± 0.5	6.2 ± 1.0	5.8 ± 0.6	n.d. *
Mg$_2$Al10	1.1 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.0 ± 0.1
Mg$_3$Al10	1.5 ± 0.1	2.2 ± 0.2	2.5 ± 0.1	1.5 ± 0.1
Mg$_4$Al10	5.5 ± 1.2	6.4 ± 1.4	6.7 ± 0.8	1.8 ± 0.1
		ZnAl		
Zn$_2$Al10	2.1 ± 0.2	1.7 ± 0.1	1.7 ± 0.1	3.2 ± 0.4
Zn$_3$Al10	1.5 ± 0.1	3.1 ± 0.2	2.3 ± 0.1	4.6 ± 0.5
Zn$_4$Al10	n.d.	2.3 ± 0.1	2.4 ± 0.1	1.5 ± 0.0
Zn$_2$Al8	**0.9 ± 0.1**	1.4. ± 0.1	1.6 ± 2.7	2.0 ± 0.2
Zn$_3$Al8	1.8 ± 0.1	2.4 ± 0.2	2.1 ± 0.1	6.7 ± 0.9
Zn$_4$Al8	3.2 ± 0.3	3.8 ± 0.3	5.0 ± 4.3	n.d.

*n.d.=not determined

Table 5: The P desorption yields (mg P/g LDH ± 95% confidence interval) of P loaded LDHs subjected to repeated wash of a carbonate solution at pH 10. The highest desorption yield (in bold) is found in the same LDH that has the highest capacity.

LDH	**P adsorption solution**			**Synthetic urine**
	pH 6	**pH 8**	**pH 10**	**pH 6**
		MgAl		
Mg_2Al12	47 ± 13	28 ± 1	22 ± 16	12 ± 23
Mg_3Al12	30 ± 28	13 ± 6	15 ± 1	20 ± 6
Mg_4Al12	30 ± 1	20 ± 19	12 ± 1	n.d.*
Mg_2Al10	**53 ± 2**	35 ± 1	n.d.	37 ± 1
Mg_3Al10	31 ± 16	23 ± 2	24 ± 2	33 ± 36
Mg_4Al10	29 ± 7	21 ± 5	13 ± 5	22 ± 20
		ZnAl		
Zn_2Al10	11 ± 4	11 ± 4	9 ± 3	9 ± 5
Zn_3Al10	5 ± 2	4 ± 3	4 ± 3	3 ± 1
Zn_4Al10	n.d.	3 ± 1	3 ± 3	9 ± 1
Zn_2Al8	22 ± 20	6 ± 1	10 ± 3	13 ± 28
Zn_3Al8	4 ± 1	4 ± 3	3 ± 3	3 ± 2
Zn_4Al8	3 ± 2	4 ± 3	1 ± 1	n.d.

*n.d.=not determined

Table 6: Desorption yield as a fraction of adsorbed P (% ±95% confidence interval). The highest desorption yield (in bold) is found in the same LDH that has the highest capacity.

LDH	**P adsorption solution**			**Synthetic urine**
	pH 6	**pH 8**	**pH 10**	**pH 6**
		MgAl		
Mg_2Al12	75 ± 20	95 ± 3	82 ± 59	58 ± 119
Mg_3Al12	64 ± 61	66 ± 29	76 ± 6	62 ± 18
Mg_4Al12	78 ± 2	109 ± 105	114 ± 9	n.d.*
Mg_2Al10	**84 ± 2**	64 ± 2	n.d.	59 ± 1
Mg_3Al10	54 ± 28	58 ± 4	64 ± 0	65 ± 70
Mg_4Al10	77 ± 18	77 ± 17	56 ± 20	53 ± 49
		ZnAl		
Zn_2Al10	30 ± 11	40 ± 14	26 ± 8	31 ± 18
Zn_3Al10	11 ± 5	22 ± 17	17 ± 10	22 ± 0
Zn_4Al10	n.d.	12 ± 1	12 ± 12	21 ± 9
Zn_2Al8	35 ± 32	16 ± 1	28 ± 10	43 ± 91
Zn_3Al8	11 ± 3	17 ± 14	12 ± 10	28 ± 19
Zn_4Al8	12 ± 7	30 ± 25	6 ± 0	n.d.

*n.d.=not determined

Highlights

- P recovery from urine by LDHs was optimised.
- Synthesis and adsorption conditions greatly affect P recovery.
- ZnAl LDHs take up equal amounts of P compared to MgAl LDHs, but desorb less.

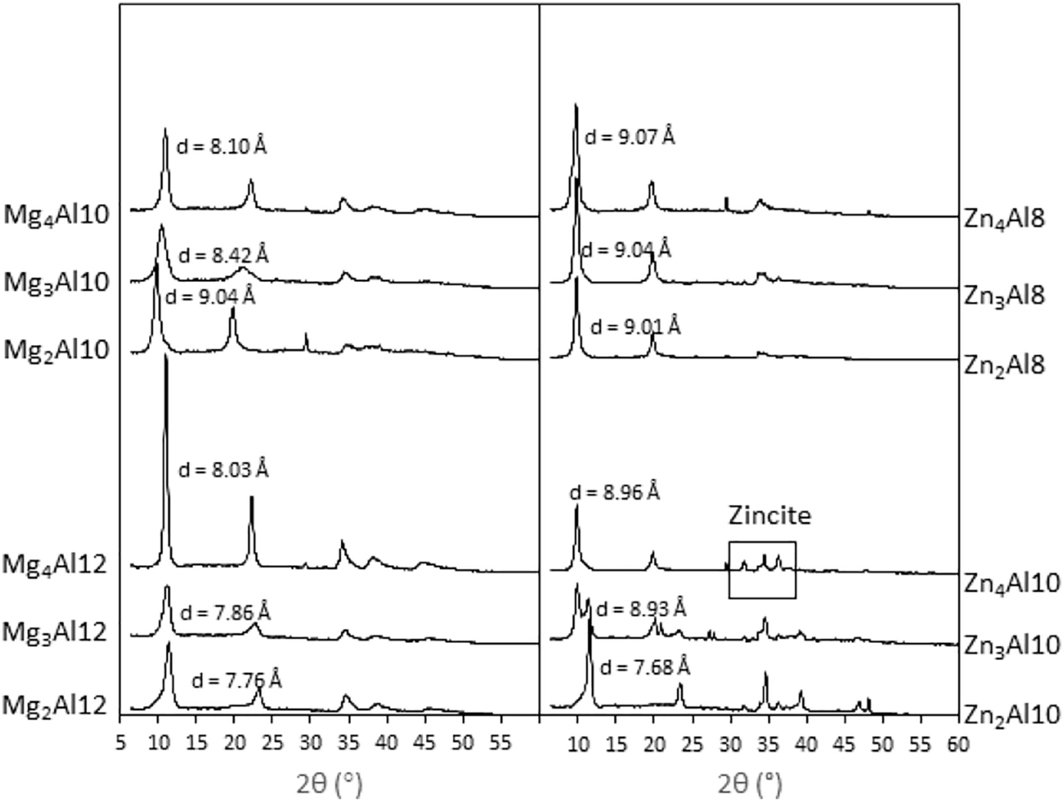
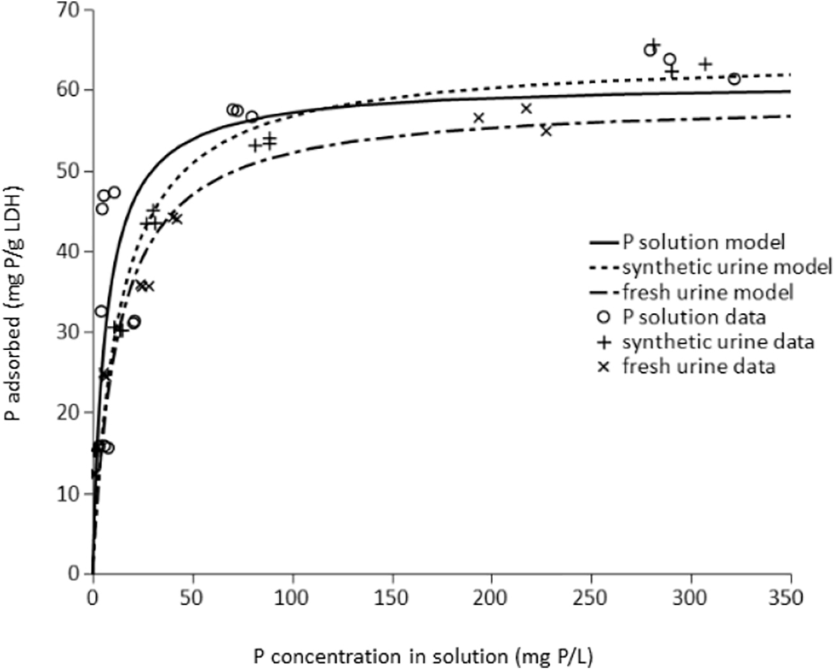

Mg$_4$Al10
d = 8.10 Å
Mg$_3$Al10
d = 8.42 Å
Mg$_2$Al10
d = 9.04 Å
d = 8.03 Å
Mg$_4$Al12
Mg$_3$Al12
d = 7.86 Å
Mg$_2$Al12
d = 7.76 Å
d = 9.07 Å
Zn$_4$Al8
d = 9.04 Å
Zn$_3$Al8
d = 9.01 Å
Zn$_2$Al8
d = 8.96 Å
Zincite
Zn$_4$Al10
d = 8.93 Å
Zn$_3$Al10
d = 7.68 Å
Zn$_2$Al10
5 10 15 20 25 30 35 40 45 50 55
10 15 20 25 30 35 40 45 50 55 60
2θ (°)
2θ (°)

Figure 1



P adsorbed (mg P/g LDH)
P concentration in solution (mg P/L)
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300
350
P solution model
synthetic urine model
fresh urine model
P solution data
synthetic urine data
fresh urine data

Figure 2

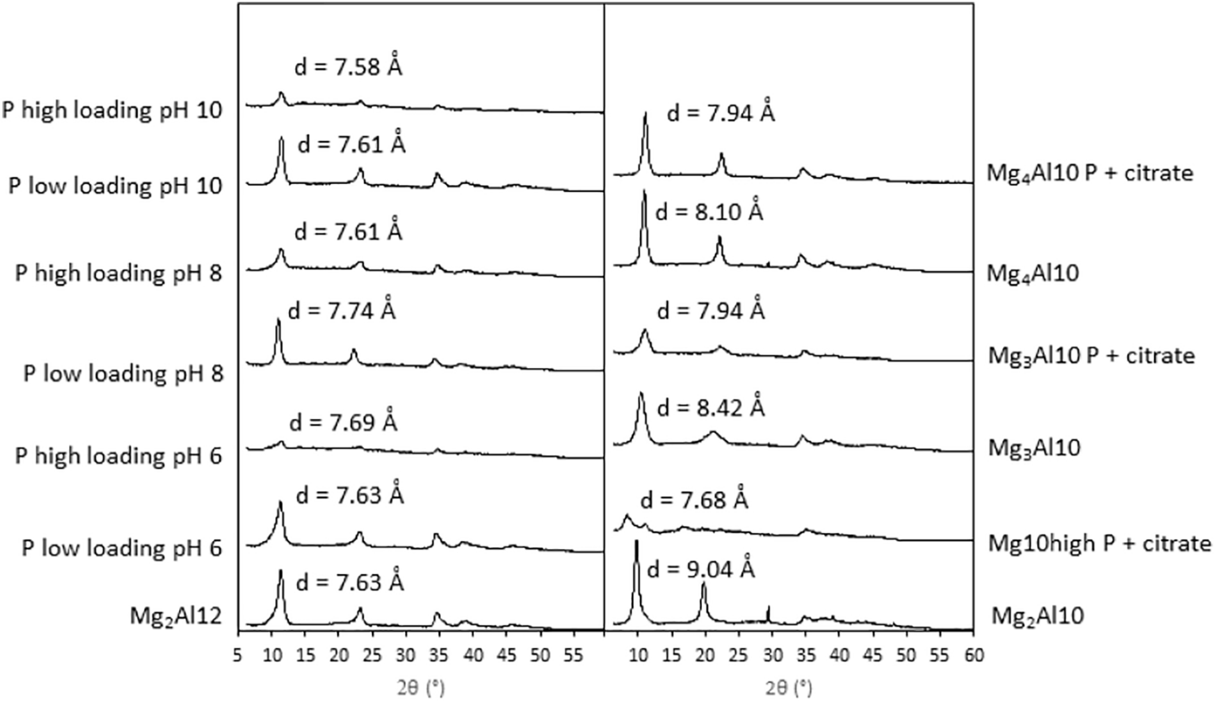

P high loading pH 10
d = 7.58 Å
P low loading pH 10
d = 7.61 Å
P high loading pH 8
d = 7.61 Å
P low loading pH 8
d = 7.74 Å
P high loading pH 6
d = 7.69 Å
P low loading pH 6
d = 7.63 Å
Mg₂Al12
d = 7.63 Å
d = 7.94 Å
Mg₄Al10 P + citrate
d = 8.10 Å
Mg₄Al10
d = 7.94 Å
Mg₃Al10 P + citrate
d = 8.42 Å
Mg₃Al10
d = 7.68 Å
Mg10high P + citrate
d = 9.04 Å
Mg₂Al10
5 10 15 20 25 30 35 40 45 50 55
10 15 20 25 30 35 40 45 50 55 60
2θ (°)
2θ (°)

Figure 3

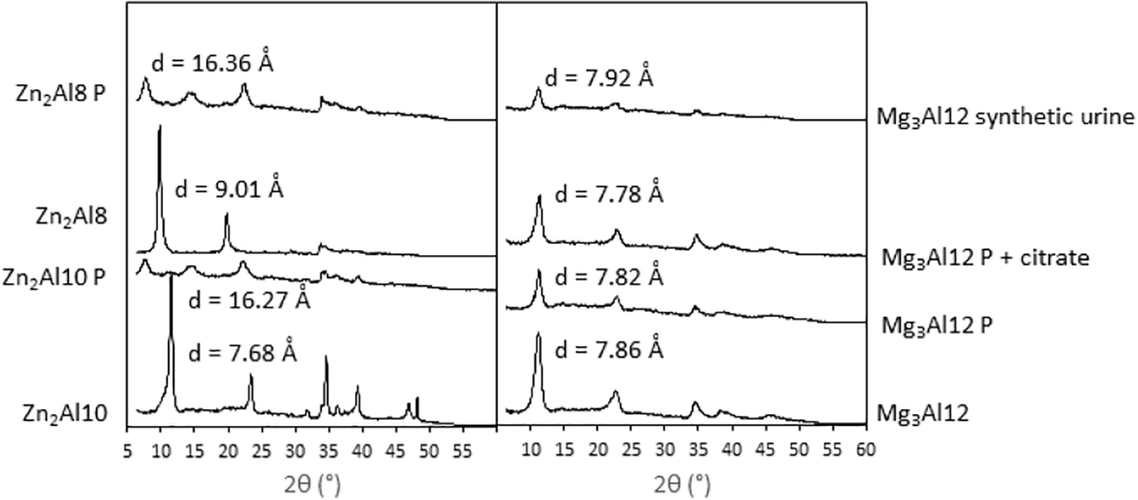

Zn$_2$Al8 P
d = 16.36 Å
Zn$_2$Al8
d = 9.01 Å
Zn$_2$Al10 P
d = 16.27 Å
d = 7.68 Å
Zn$_2$Al10
d = 7.92 Å
Mg$_3$Al12 synthetic urine
d = 7.78 Å
Mg$_3$Al12 P + citrate
d = 7.82 Å
Mg$_3$Al12 P
d = 7.86 Å
Mg$_3$Al12
5 10 15 20 25 30 35 40 45 50 55
10 15 20 25 30 35 40 45 50 55 60
2θ (°)
2θ (°)

Figure 4

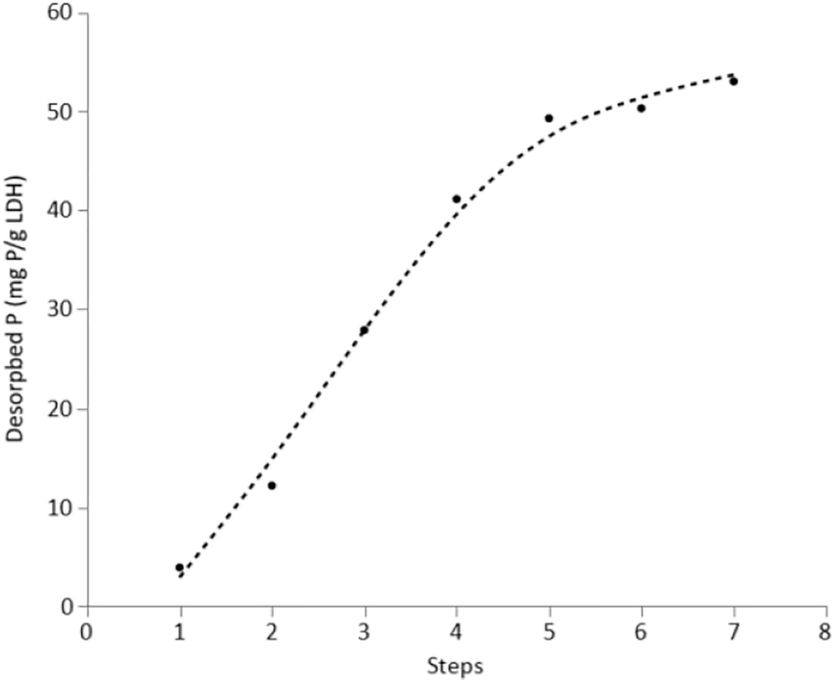


Figure 5