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Stability of magnetic LDH composites used for phosphate recovery

Changyong Lu*, Tae-Hyun Kim¹, Jesper Bendix¹, Mustapha Abdelmoula†, Christian Ruby†, Ulla Gro Nielsen¹, Hans Chr. Bruun Hansen*§

§ University of Copenhagen, Faculty of Science, Department of Plant and Environmental Sciences, Thorvaldsensvej 40, 1871, Frederiksberg C, Denmark

ǁ Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

ǂ Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark

† Université de Lorraine, CNRS, LCPME, 54600 Nancy, France

* Corresponding Author (Changyong Lu): clu@plen.ku.dk
Abstract

Layered double hydroxides (LDH) and their magnetic composites have been intensively investigated as recyclable high-capacity phosphate (P) sorbents but with little attention to their stability as function of pH and phosphate concentration. The stability of a Fe₃O₄@SiO₂-Mg₃Fe LDH P sorbent as function of pH (5-11) and orthophosphate (Pᵢ) concentration (1-300 mg P/L) was investigated. The composite has high adsorption capacity (approx. 80 mg P/g) at pH 5 but with fast dissolution of the LDH component resulting in formation of ferrihydrite evidenced by Mössbauer spectroscopy. At pH 7 more than 60 % of the LDH dissolves within 60 min, while at alkaline pH, the LDH is more stable but with less than 40 % adsorption capacity as compared to pH 5. The high Pᵢ sorption at acid to neutral pH is attributed to Pᵢ bonding to the residual ferrihydrite. Under alkaline conditions Pᵢ is sorbed to LDH at low Pᵢ concentration while magnesium phosphates form at higher Pᵢ concentration evidenced by solid-state ³¹P MAS NMR, powder X-ray diffraction and chemical analyses. Sorption as function of pH and Pᵢ concentration has been fitted by a Rational 2D function allowing for estimation of Pᵢ sorption and precipitation. In conclusion, the instability of the LDH component limits its application in wastewater treatment from acid to alkaline pH. Future use of magnetic LDH composites requires substantial stabilisation of the LDH component.

Key words: phosphate removal, pH effect, phosphate concentration, LDH dissolution, ferrihydrite, precipitation.
1. Introduction

Phosphorus (P) in the form of orthophosphate is a limited resource which is mainly used as fertilizer and critical for feeding the world population [1-3]. Phosphorus use is highly unsustainable with substantial parts of phosphorus wasted and going out of circulation [4], and at the same time phosphorus overuse and poor control via waste streams have caused widespread eutrophication. The presence of trace amounts of phosphate in discharged wastewater triggers eutrophication, leading to poor water quality, algal blooms including production of toxic cyanopeptides, and ecosystem destabilization [5, 6]. Thus, reduction of phosphorus emission and management is one of the UN sustainability clean water and sanitation goals [7]. The EU Water Framework defines a cut-off total P concentration for lake eutrophication at 0.1 mg P/L, while WHO set this threshold concentration at 0.05 mg P/L (here the phosphate concentration is given in terms of mass of P in phosphate per liter of solution) [8, 9]. Thus, development of a phosphorus capture and recovery technology has high priority.

Phosphate removal from wastewater by adsorption is an alternative to chemical precipitation and biological treatment methods. Adsorption processes are often easier to control, faster, cheaper and scalable compared with often more complex precipitation and biological methods [10-15]. Layered double hydroxide (LDH) with the general formula of 
\[ [M_{a}^{II}]_{1-x}[M_{b}^{III}]_{x}(OH)_{2}]^{x+}[A_{x/n·yH_{2}O}]^{x-} \]

where \( M_{a}^{II} \), \( M_{b}^{III} \) and \( A_{n-} \) are di- and trivalent metal cations and \( n \)-valent anion respectively [16], have been intensively investigated as Pi sorbents because of their anion exchange property, high sorption capacity and fast sorption kinetics [17-19]. In general, Pi sorption to LDH mainly takes part via electrostatic interactions, interlayer anion exchange, and surface complex formation [20-24]. Whereas the
hydrocalumite type LDH (CaFe and CaAl) are destroyed upon P\textsubscript{i} exposed leading to the formation of calcium phosphate precipitation [21]. LDH and its composites have high P\textsubscript{i} sorption capacity, ranging from 50 mg P/g to 100 mg P/g, at weak acid (pH 6) to intermediate pH (pH 7~8) [25]. On the contrary, they have low P\textsubscript{i} sorption capacity at high pH (pH 9 ~ 10), typically lower than 5 mg P/g (Table S1). Moreover, the type of interlayer ion may affect the sorption capacity. For example carbonate and sulfate decrease the adsorption capacity compared with nitrate and chloride due to competitive ion-exchange [26]. The lamellar structure and the sub- to micrometer size of LDH particles make them difficult to be used in packed filter columns and even to collect by filtration or sedimentation [21]. However, by attaching the LDHs to magnetic nanoparticles such as magnetite, the magnetic composites can be separated in a magnetic field and thus be regenerated after P\textsubscript{i} sorption [27]. Examples of such magnetic LDH P sorbents comprise magnetic nanoparticle decorated ZnFeZr LDH [27], MgAl LDH [28] and MgFeZr LDH [29] composites (Table S1).

LDHs are known to buffer pH due to dissolution in water with release of hydroxide (and metal) ions [30]:

\[
[M_{a1-x}^{III}M_{bx}^{II}(OH)_2]^{x+} [A_n^{n-} \cdot yH_2O]^{x-} (s) \rightleftharpoons (1-x)M_{a}^{2+} (aq) + xM_{b}^{3+} (aq) + \frac{x}{n} A^{n-} + 2OH^- + yH_2O \quad \text{Equation 1}
\]

Note, that the trivalent metal ions which are produced would form (hydr)oxide precipitates due to the negligible solubility of M\textsubscript{b}\textsuperscript{III} hydroxides/oxides. The extent and rate of dissolution of the LDH is controlled by the nature of the divalent metal cations and the interlayer anions [31-33]. For example, the LDHs are strongly thermodynamically favored over the separate
Ma hydroxides in the order \( \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Co}^{2+} \approx \text{Ni}^{2+} < \text{Zn}^{2+} \), when \( \text{Cl}^- \) is the interlayer anion [32].

Environmentally benign materials are required for water cleaning. This limits the suitable LDH candidates for wastewater treatment to MgAl, MgFe, CaAl, CaFe and Fe(II)Fe(III) LDHs [34]. Despite a vast number of publications on LDH Pi sorbents, the stability of LDHs for practical applications has not been evaluated. Most waste waters have pH in the range from 6.5 to 8.5 [35], which clearly would challenge the use of LDH as recyclable sorbents in magnetic composites due to the solubility of the LDH phase. For example, the well studied Fe\(_3\)O\(_4\)/MgAl-NO\(_3\) LDH composite showed 33\% dissolution of Mg over 6 h in a sorption study with initial pH at 7 [36]. In a study of synthetic MgAl and ZnAl LDHs for P recovery from urine, 12\% of Mg and even more Zn dissolved during sorption at constant pH 8 for 24 h [37]. Pi sorption to hydrocalumite-type CaAl and CaFe LDH showed ready dissolution of LDH and formation of Ca\(_5\)(PO\(_4\))\(_3\)OH and Ca(HPo\(_4\))\(_2\)H\(_2\)O precipitates in non-buffered solutions [24, 38]. MgFe-CO\(_3\) LDH dissolved completely with formation of MgHPO\(_4\)·3H\(_2\)O in 24h when exposed to very high Pi concentrations (> 1 M) at pH 7, demonstrating that not only the pH but also the high Pi concentration could also stimulate the dissolution of LDH [39]. For Pi sorption at pH where the LDH dissolves, residual M\(_b\) (hydr)oxides may form strong sorbents of Pi. Thus, Pi retention by LDHs not only comprise anion exchange and surface complexation by the LDH, but may also comprise Pi sorption to dissolution residues and precipitation processes, see Fig. 1.
The instability of the LDH may hamper regeneration and re-use of the LDH during Pi sorption, but to which extent is still unclear. Although Pi sorption to MgFe LDH has been extensively studied due to its high sorption capacity compared with MgAl LDH [29, 40], its stability and mode of Pi sorption at pH and Pi concentrations in wastewater needs to be critically examined. In this study, we aim to assess the stability of the potential recyclable magnetic MgFe LDH sorbent as a function of pH and Pi concentration (Fig. 1). The investigation focus on quantification of LDH dissolution as a function of pH (especially at pH neutral) and Pi sorption combined with solid-state analysis of alteration in the MgFe LDH structure and formation of new phases during sorption.

**Figure 1. Schematic illustration of the phase changes and Pi sorption processes addressed in the study.**
2. Materials and methods

2.1 Materials

All chemicals were purchased from Sigma and directly used without further purification. All sample solutions were prepared with ultrapure water (18.2 MΩ·cm) (SI 1.1).

2.2 Synthesis of Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH

The Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH composite (referred to as composite in this paper) was synthesized by previous reported methods [34, 40, 41]. For experimental details, see SI (1.2).

2.3 Phosphate sorption and Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH dissolution

Experiment 1 (Exp. 1) The kinetics of P$_i$ sorption and LDH dissolution from the composite was followed by monitoring the P$_i$ and Mg concentrations in pH buffered suspensions. The composite (1 g/L) was dispersed in an aqueous solution of 10 mM KNO$_3$ electrolyte, 11.92 g/L HEPES buffer (4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid, C$_8$H$_{18}$N$_2$O$_4$S) and 50 mg P/L added as KH$_2$PO$_4$. The pH of the solution was buffered by HEPES at pH 7.2 throughout the experiment. At various times (1, 2, 5, 10, 30 min, 1, 2, 3, 6, 12 and 24 h), 2 mL of the suspension was sampled and filtered through a 0.2 μm regenerated cellulose filter (Mikrolab Aarhus A/S) and the filtrate stored at 4 °C until determination of P$_i$ and Mg. In a separate experiment, the pH buffering effect of the composite was illustrated by preparing the same suspension as above but without adding HEPES buffer. The pH of the suspension was measured at 1, 2, 5, 10, 30 min, 1, 2, 3, 6, 12 and 24 h by using Metrohm 827 pH meter.
Experiment 2 (Exp. 2) In this experimental series dissolution and Pi sorption of the composite as function of solution Pi concentration and pH was studied. The experiments were carried out as described for Exp. 1, but with initial Pi concentrations at 1, 2, 5, 10, 20, 50, 100, 200 and 300 mg P/L. No HEPES buffer was used, but suspension pH was controlled at 5, 7, 9 and 11 by addition of HCl or NaOH solution (SI 1.3). All suspensions were placed on a shaking table at 250 rpm for 24 h once the pH had stabilized.

Experiment 3 (Exp. 3) This experiment was similar to Exp. 2 but only Pi concentrations of 10 mg P/L was tested to avoid side reactions due to high Pi concentrations and to operate with Pi concentrations typical for wastewater influents [7]. In addition equilibration time was reduced to 1 h to have short contact time for real waste water treatment [42]. The pH of the suspensions was controlled at pH 5, 6, 7, 8, 9, 10 or 11 (± 0.1) by addition of HCl or NaOH solution (SI 1.3).

The solid phases were collected by an NdFeB magnet (Size 50 mm x 15 mm x 15 mm, magnetic strength approx. 324 N) after Pi sorption and dried at 60°C overnight, while the solutions were filtered through 0.2 μm regenerated cellulose filter (Mikrolab Aarhus A/S) and stored at 4°C. Pi and Mg concentrations were determined in all the filtrates. Pi concentrations in solution were measured by the Molybdenum-Blue method using a ultraviolet–visible spectroscopy (UV-Vis) and Mg was determined by atomic absorption spectroscopy (AAS). The content of Mg in the solids after sorption was determined with ICP. For further information about solid state characterization techniques, see SI 1.5.

2.4 Solubility calculations
Visual MINTEQ equilibrium speciation software ver 3.1 [43] was used to estimate supersaturation of solutions with respect to magnesium phosphates, such as Mg$_3$(PO$_4$)$_2$, MgHPO$_4$, Mg(H$_2$PO$_4$)$_2$. The thermodynamic database supplied with the software was used (SI 1.6).

2.5 P$_i$ sorption and phase distribution versus pH and P$_i$ concentration.

All sorption data from Exp. 2 were fitted to produce a "sorption surface" with sorbed P$_i$ versus pH and equilibrium P$_i$ concentration using the nonlinear surface fit function in Origin 9.6 software using a Rational 2D Function [44]. The model was used for analysis and demonstration of the continuous change in P$_i$ sorption as function of solution P$_i$ concentration and pH. Fitting parameters are listed in Table S8.

The extent of P$_i$ sorption in form of magnesium phosphate precipitates was estimated based on estimations of mass of LDH derived from PXRD traces of samples taken after P$_i$ sorption. First, Rietveld profile-fitting in X’pert Highscore Plus software [45] with the Pseudo Voigt profile function was used to analyse the PXRD data (SI 1.5.3) to determine the amount of LDH and Fe$_3$O$_4$ in crystalline phases after P$_i$ sorption (Exp. 2). Next, the theoretical concentration of Mg released was calculated (SI 5, Eq. S10), assuming that the Mg release is proportional to the amount of dissolved LDH. Last, the theoretical Mg release was compared with the observed Mg concentration after P$_i$ sorption, and the difference between these two values was then allocated to Mg in magnesium phosphate precipitates (Details in SI5). Estimates of the fraction of P$_i$ in magnesium precipitates (Eq. S11) was added to the "sorption surface" using OriginPro 2019 software.

3. Results and discussion
In this study, the Fe₃O₄@SiO₂-Mg₃Fe LDH composite was first synthesized and characterized in detail (SI 2), followed by Pᵢ sorption and dissolution experiments at controlled pH, ranging from 5 to 11, with exposure to various solution Pᵢ concentrations (1–300 mg P/L). Different solid state characterization techniques, such as PXRD, TEM, ⁵⁷Fe Mössbauer spectroscopy and ³¹P MAS NMR were used to characterize the composite before and after Pᵢ sorption. LDH dissolution in terms of Mg release and Pᵢ sorption was correlated with solid phase analysis to conclude on dissolution, Pᵢ phase distribution and modes of Pᵢ sorption versus pH and Pᵢ concentration.

3.1 Phosphate sorption to Fe₃O₄@SiO₂-Mg₃Fe LDH

Figure 2. (a) Kinetics of Pᵢ sorption (qᵣ) to Fe₃O₄@SiO₂-Mg₃Fe LDH and the corresponding fit by pseudo second-order kinetics (Eq. S4) (sorbent concentration 1 g/L; 50 mg P/L; pH 7.2, 25 °C). (b) Isotherms for Pᵢ sorption (qₑ) versus solution Pᵢ concentration (Cₑ) at different pH values (sorbent concentration 1 g/L, contact time 24 h, Exp. 2).
After mixing with the pH buffered Pᵢ solution (Exp. 1), the Pᵢ sorption kinetic was well fitted by pseudo second-order kinetics (Eq. S4, \( R^2 0.999 \)) with a rate constant of \( 5.4 \times 10^{-3} \text{ g/mg P min}^{-1} \). Equilibrium was reached within 120 min (Fig. 2a), demonstrating relatively fast Pᵢ removal. Sorption isotherms (Exp. 2) showed that Pᵢ bonding to the composite was of the Freundlich type (Eq. S5, \( R^2 0.979-0.999 \) Table S2) with no clear sorption maxima (Fig. 2b). The Pᵢ sorption capacity decreased remarkably with increasing pH from 5 to 11, with 3 to 8 times less sorption at pH 11 than pH 5 depending on the solution Pᵢ concentration (Fig. 2b and 3b) which is similar with other observations in previous studies on LDHs Pᵢ sorbents [46-48].

### 3.2 Dissolution of Fe₃O₄@SiO₂-MgFe LDH during Pᵢ sorption
Figure 3. (a) Kinetics of Fe₃O₄@SiO₂-Mg₃Fe LDH dissolution measured in terms of the concentration of Mg in the solution during Pᵢ sorption (Exp. 1). (b) Pᵢ adsorbed and Mg released from the Fe₃O₄@SiO₂-Mg₃Fe LDH at different pH values (Exp. 3). (c) PXRD patterns of the solids after sorption at different pH and the corresponding TEM images of the solids after Exp. 3 at pH 5, 8 and 11. The red circles indicate the presence of an amorphous phase in samples at pH 5 and 8 and in the LDH phase at pH 11.
In Exp. 1, when the composite was dispersed in water, pH increased from 7.0 to 9.3 within 3 h (Fig. S6) due to the buffering effect of LDH. This is attributed to release of hydroxide ions during dissolution of the LDH (Eq. 1) [31, 49-51]. However, when pH is kept constant at pH 7.2 in HEPES buffered solution, substantial parts of the Mg$_3$Fe LDH in the composite dissolves as more than 60 % of the total Mg dissolves within 60 min (Fig. 3a). The kinetics of Mg$^{2+}$ release was well fitted by pseudo second-order kinetic resulting in a kinetic constant of 2.6×10$^{-3}$ L/mg min$^{-1}$ (Eq. S6; $R^2$ 0.999), demonstrating fast dissolution at pH 7.2. This is in line with our previous study of Zn doped MgFe LDH, which showed a similar fast dissolution kinetics ($k = 2.53 \times 10^{-3}$ L/mg min$^{-1}$) at pH 7 [50]. The PXRD data show a dramatic decrease in intensity of the Mg$_3$Fe LDH reflections, compared with the LDH kept at pH 9.3 (Fig. S8). In conclusion, both the solubility and the structural degradation of the LDH confirms that the composite is unstable at pH 7.2 and dissolves rapidly.

In Exp. 3, the Mg$_3$Fe LDH stability was investigated in non-buffered solutions as function of constant pH ranging between 5 and 11 at a constant initial P$_i$ concentration of 10 mg P/L which is within the range of P$_i$ concentration of municipal wastewater [52, 53]. Fig 3b shows a dramatic decrease of P$_i$ sorption with increasing pH. At pH 5, almost 100 % of the P$_i$ added is removed, while at pH 11 sorption is down to 20 %. In addition, the P$_i$ sorption is followed by a concurrent release of Mg depending on pH. More than 50 % of total Mg was released at pH 5 but less than 3 % Mg released at pH 11 within 1 h. PXRD of the composite after P$_i$ sorption at pH > 8 (Fig. 3c) showed that the LDH basal (003) reflection has a relative intensity of 96 % compared with the pristine composite (Fig. S2a), demonstrating that the composite is stable at pH > 8 at low P$_i$ concentration (10 mg P/L), in agreement with our recent study [34]. However, at lower pH of 7, 6 and 5 the relative intensity of the basal reflections dropped
to 37%, 20% and 0% of the initial values, respectively (Fig. 3c). TEM images of the sorbents after P_i sorption (Fig. 3c) reveal a full destruction of the platelike LDH and formation of amorphous material at pH 5, while at pH 8 more LDH remained, but still with some amorphous material present compared with the pristine LDH (Fig. S2). At pH 11, the intact Mg_3Fe LDH is present. In addition, the LDH platelet thickness estimated from the width of the (003) reflections was in the range 6.9-7.1 nm for pH > 8, and decreased to 5.3 nm, 4.6 nm and 0 nm when P_i had sorbed at pH 7, 6 and 5, respectively (Table S3), due to dissolution. Thus, Mg_3Fe LDH dissolves at acidic to intermediate pH, while it is stable at high pH.

The combined effect of pH and P_i sorption on LDH dissolution is depicted in Fig. S10, showing that about 90, 80 and 40% of total Mg has dissolved at the highest P_i sorption at pH 5, 7 and 9, respectively. PXRD of the residual solids after P_i sorption (Fig. S11 and Fig. S12) showed a dramatic decrease in intensity of the LDH reflections in the samples from pH 5 and 7 (Fig. S11a, b; Fig. S2a), confirming the instability of the LDH structure at acid and neutral pH [34, 50]. Furthermore, the (003) and (110) reflections of the Mg_3Fe LDH phases weakened or disappeared when initial P_i concentrations exceeded 50 mg/L at higher pH, such as pH 9 and 11, revealing that exposure to relative high P_i concentrations also stimulated LDH dissolution (Fig. S11c, d and Fig. S12) [34, 39]. Finally, magnetization data shows that the fraction of magnetic materials decreases from 66 to 45 wt% in the composite after P_i sorption at pH 5 (Fig. S13a and b, Eq. S9).

3.3 Residual phase formed at pH 5
Figure 4. Mössbauer spectra of (a) Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH before P$_i$ sorption measured at 140K, (b) solids after P$_i$ sorption (Exp. 3, at pH 5 with initial P$_i$ concentration at 10 mg P/L for 1h) measured at 125K and (c) 25K (Full lines correspond to fitting, parameters listed in Table S4).

The $^{57}$Fe Mössbauer spectrum of the pristine composite at 140 K (Fig. 4a) shows one sharp quadrupole doublet with center shift ($\delta$) 0.42 mm/s and quadrupole splitting ($\Delta$) of 0.61 mm/s which is attributed to octahedrally coordinated Fe$^{3+}$ in the Mg$_3$Fe LDH [54]. The 125 K
spectrum of the composite after $P_i$ sorption (Fig. 4b) displays two quadrupole doublets with
the same $\delta$ of 0.45 mm/s and different $\Delta$ of 0.54 mm/s and 1.03 mm/s, respectively. The $\Delta$ of
0.54 mm/s corresponds to the presence of Mg$_3$Fe LDH, while the $\Delta$ of 1.03 mm/s corresponds
to presence of Fe$^{3+}$ in poorly crystalized ferrihydrite [55]. The 25 K spectrum (Fig. 4c)
confirms this identification with a contribution of a single-line with $\delta$ of 0.68 mm/s and a
magnetic broad sextet with $\Delta$ of 2 mm/s and very low magnetic field of 132 kOe attributed
to poorly crystalized ferrihydrite [55].

The high sorption capacity at low pH (79.5 mg P/g in Fig. 1b) is in agreement with the high
sorption capacity for ferrihydrite at low pH [56-59]. Thus, we estimate the obtained poorly
crystalized ferrihydrite has a $P_i$ sorption capacity around 344 mg P/g (details in SI 3), which
is much higher than common values (34–56 mg P/L) reported for ferrihydrite [59, 60]. We
attribute this high sorption capacity to the possible formation of amorphous strengite (FePO$_4$)
[61, 62] as the Fe:P ratio is close to 1:1. Apparently, extensive Mg dissolution causes
formation of ultra-small ferrihydrite particles, leading to a strengite type product [63].

3.4 Precipitation of magnesium phosphates at high pH

In Exp. 2, although the composite did not release more than about 40% of total Mg into
solution at pH 9 at an initial $P_i$ concentration of 300 mg P/L (Fig S10), the LDH structure
was almost destroyed as seen from the PXRD pattern (Fig. S11c). At pH 11, there was barely
any Mg release to solution (Fig. S9), while the relative intensity of the Mg$_3$Fe LDH (003) and
(110) peaks decreased to 26 % and 59 % of the intensity of the pristine composite,
respectively (Fig. S11d, Fig. S12), reflecting substantial dissolution of the LDH phase.
According to the previous studies of MgFe-CO$_3$ LDH [39], precipitation of magnesium
phosphates is therefore likely to take place. In order to test this, the solids after \( P_i \) sorption at pH 11 and initial \( P_i \) concentration of 300 mg P/L were examined by PXRD without prior washing (Fig. S14). This test confirmed the partial dissolution of the Mg\(_3\)Fe LDH phase seen from the decrease in intensity of basal reflections. Also, the size of crystallite domains of the Mg\(_3\)Fe LDH phase along the dimension \( a \) and \( c \) was 33% and 66% smaller after \( P_i \) sorption than before as determined from peak broadening (Eq. S3; SI 2). Solid-state \(^{31}\)P MAS NMR spectroscopy (Fig. S15) of the LDH after \( P_i \) sorption at pH 9 and 11 showed the presence of narrow resonance with \( \delta(^{31}\text{P}) = 2.5(2) \) ppm and 3.9(2) ppm at pH 9 and pH 11, respectively, demonstrating formation of an amorphous magnesium phosphate phase [34]. The Mg-P precipitate had a molar Mg/P ratio in the Mg-P precipitates of 1.4 (SI 5), which is in good agreement with formation of Mg\(_3\)(PO\(_4\))\(_2\). Thus, at high pH and elevated \( P_i \) concentrations LDH dissolves and magnesium phosphates precipitate.

Visual MINTEQ was used to compute supersaturation with respect to magnesium phosphates using the measured solution Mg and \( P_i \) concentrations at different pH (Fig. S17). No magnesium phosphates form at pH < 6, but when pH is increased to 7, MgHPO\(_4\)·3H\(_2\)O (Newberyite) precipitate at high Mg and \( P_i \) concentrations, while Mg\(_3\)(PO\(_4\))\(_2\) precipitate at pH > 8 at high \( P_i \) concentration. When pH is further increased to 9, Mg\(_3\)(PO\(_4\))\(_2\) precipitate at \( P_i \) concentrations above 62.5 mg P/L, which is in line with the observations in Fig. S10 and S11c. When pH increased to 11, Mg\(_3\)(PO\(_4\))\(_2\) precipitate even at low \( P_i \) concentrations (1 mg P/L). Thus, VMINTEQ calculations confirm that magnesium phosphates precipitate at high pH and high \( P_i \) concentrations with Mg\(_3\)(PO\(_4\))\(_2\)·8H\(_2\)O (Bobierrite) as a likely phase. Hence, at intermediate to high pH (pH = 9 - 11), \( P_i \) may also be retained due to the dissolution-precipitation reaction [32].
Fe(III)$_x$Mg$_{1-x}$(OH)$_2$(NO$_3$)$_x$ • 2H$_2$O (s) ⇌ $x$Fe(III)(OH)$_3$(s) + (1 − $x$)Mg$^{2+}$(aq) + 2 × OH$^-$ (aq) + $x$NO$_3^-$ + 2H$_2$O (aq) (1)

3Mg$^{2+}$(aq) + 2PO$_4^{3-}$(aq) + $x$H$_2$O (aq) → Mg$_3$(PO$_4$)$_2$ • $x$H$_2$O ↓ (s) (2)

3.5 Pi sorbed to Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH versus pH and equilibrium Pi concentration

Figure 5. Sorbed Pi (black dots) to Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH as a function of pH and Pi solution concentration (Exp. 2 and 3; SI 5) with Rational 2D fit. The colour bar denotes the estimated percentage (%) of Pi sorbed due to precipitation.

Our investigation shows that Pi sorption by Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH comprises at least three reactions: Pi bonding to iron hydroxides (ferrihydrite), bonding to LDH and precipitation of magnesium phosphates. By fitting the Pi sorption data with the Rational 2D function (R$^2$ = 0.99), a sorption surface (Fig. 5) can be produced to help estimate Pi sorption versus pH and equilibrium Pi concentration. The sorption surface expresses the high and low sorption capacity at low pH and high pH, respectively, and also that the sorption affinity decreases with increasing pH. The colour map shows that barely no Pi was removed by
precipitation at acid and neutral pH (Fig. 5). When pH increased to 9, at least 40 % of sorbed
$P_i$ was present in magnesium phosphates at $P_i$ concentrations > 50 mg P/L, further increasing
at higher pH and $P_i$ concentrations.

We propose a set of sorption pathways for $P_i$ bonding to the composite (Fig. 6). At acidic pH,
the LDH is readily and fully dissolved. Despite high Mg concentrations in solution (80 mg/L),
the solubility of magnesium phosphates does not exceeded saturation and hence $P_i$ is
adsorbed to the amorphous poorly crystalized ferrihydrite. At neutral pH, the LDH only
partially dissolves. Hence, $P_i$ is sorbed on the remaining LDH as well as to the poorly
crystalized ferrihydrite; at higher $P_i$ concentrations, $P_i$ is also retained due to precipitation of
magnesium phosphates. Finally, at alkaline pH where the LDH phase has its highest stability,
$Mg_3Fe$ LDH is the primary sorbent of $P_i$ at low $P_i$ concentration. However, at higher $P_i$
concentration, the $Mg_3Fe$ LDH phase is not stable and magnesium phosphates precipitate is
the main sorption pathway.
The instability of MgFe LDH we have seen is comparable to what have been observed in other studies even without constant pH control and the pH was buffered to alkaline condition. A MgAl LDH was found to release 20% of Mg within 72 h even at pH 9.12. A recent study of Pi sorption to MgFe-NO₃ LDH showed precipitation of amorphous magnesium phosphate precipitate at a solution Pi of about 100 mg P/L at pH 7.4 [34]. The solubility of LDHs decrease with the divalent cation in the order Mg²⁺ > Mn²⁺ > Co²⁺ ≈ Ni²⁺ > Zn²⁺, while for the trivalent cation the order is Fe³⁺ > Al³⁺ [32]. Hence, many Fe³⁺ containing LDHs have higher or equal solubility as the MgFe-LDH. Most stable LDHs would be of the type with Co²⁺ or Ni²⁺ as divalent cation [64]. However, these compounds are not environmentally friendly as the contain toxic metal ions. Solubility and dissolution kinetics may be decreased using larger particles and using carbonate interlayered forms rather than forms with
monovalent anions [65-67]. On the other hand, the presence of complexing agents in solution such as humic matter will increase solubility [68].

Although LDHs are seen as promising material for treatment of municipal wastewater [69], the significant dissolution of LDHs filter material during the sorption process at neutral pH limits its practical application as wastewater has pH 6.5~8.5 [35]. Vast amounts of Mg$^{2+}$ ions could be released to the environment in a scaled-up application, which would increase water hardness and block the filters and pipes due to formation of precipitates. In addition, the loss of relative expensive MgFe LDH materials would also increase the cost of wastewater treatment. Furthermore, high P$_i$ concentrations in wastewater would also stimulate the dissolution of LDHs at higher pH resulting in formation of precipitates. Thus, the widely reported LDH regeneration and P recovery strategy, where adsorbed P is extracted with alkali solution and the LDH re-used for P sorption, would be challenged [27, 70].

4. Conclusions

In this study, we demonstrate the MgFe LDH has poor stability and dissolves in the pH range of wastewater (pH 6~8). In addition to the pH controlled LDH solubility, high P$_i$ concentrations causes LDH dissolution even at high pH, by formation of magnesium precipitates. $^{57}$Fe Mössbauer spectroscopy confirms the formation of poorly crystalline ferricydrite at acidic pH while $^{31}$P MAS NMR spectroscopy demonstrate the precipitation of magnesium phosphate at high pH and high P$_i$ concentration. A combined analysis of solubility and PXRD data indicate that precipitates is the main sorption pathway at high pH and high P$_i$ concentration. The main sorption pathways are summarized as sorption by ferricydrite at acid pH, sorption by ferricydrite and LDH at neutral pH and high pH with low
Pi concentration, and precipitation of magnesium phosphates at high pH and high Pi concentration. This study demonstrates that MgFe LDHs are intrinsically unstable from pH 5 ~ 11 when used for Pi sorption which hence prevents their use as recyclable sorbents. Future application of magnetic LDHs as recyclable sorbents is only possible if the stability of the LDH component can be substantially increased.

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Appendix supplementary data

The supplementary data of this paper is available on the website at DOI:

REFERENCES


Supplementary data

Stability of magnetic LDH composites used for phosphate recovery

Changyong Lu§, Tae-Hyun Kim†, Jesper Bendixǁ, Mustapha Abdelmoula†, Christian Ruby‡, Ulla Gro Nielsenǁ, Hans Chr. Bruun Hansen*§

§ University of Copenhagen, Faculty of Science, Department of Plant and Environmental Sciences, Thorvaldsensvej 40, DK-1871, Frederiksberg C, Denmark

ǁ Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

† Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark

‡ Université de Lorraine, CNRS, LCPME, F-54600 Nancy, France

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1. Experimental Methods

1.1 Materials

Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99%), iron(II)chloride tetrahydrate (FeCl₂·4H₂O, 99%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, ≥98%), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 99%), hydrochloric acid (HCl, 36 wt%), sodium hydroxide (NaOH pellets, ≥98%), sodium nitrate (NaNO₃, ≥99%), sodium citrate monobasic (≥99.5%), ammonium molybdate tetrahydrate ((NH₄)MoO₄·4H₂O, 99.98%), potassium phosphate monobasic (KH₂PO₄, ≥99%), potassium antimony tartrate (C₄H₄O₅KSb, ≥99%), L-ascorbic acid (C₆H₈O₆, ≥99%), ammonium hydroxide solution (28 wt% NH₃ in H₂O), nitric acid (HNO₃, 65 wt% solution), sodium silicate aqueous solution (containing 2.78 M of nitric acid and 0.8 M of sodium silicate) and sulfuric acid (H₂SO₄, 99.999%) were purchased from Sigma Aldrich. All chemicals were used without further purification. Ultrapure water (resistivity of 18.2 MΩ·cm, ELGA Veolia PURELAB Chorus 1) was used for preparation of all aqueous solutions and is referred to as "water" in the following.

1.2 Synthesis of Fe₃O₄@SiO₂-Mg₃Fe LDH

First, 176 mL iron salt solution (0.159 mol/L of FeCl₂·4H₂O and 0.318 mol/L of FeCl₃·6H₂O) was added dropwise (5 mL/min) into 211 mL ammonium hydroxide solution (2.5 mol/L) and the mixture was stirred at 1000 rpm. All solutions were flushed with N₂ throughout (purity 99.9%) (55 mL/min). Subsequently, the solids were separated by a NdFeB magnet (Size 50 mm × 15 mm × 15 mm, magnetic strength approx. 324 N) then washed with 400 mL water once and dispersed in 400 mL sodium citrate solution (87 mmol/L) and kept stirring overnight. Finally, the solids were isolated by centrifugation (11630 g, 10 min) and washed with 500 mL water 2 times followed by dispersion in 200 mL water. Then 77 mL of ammonium hydroxide solution (7.77 mol/L) was added into the magnetite suspension. The mixture was heated to 70 °C under magnetic stirring (1000 rpm). 10 mL of sodium silicate aqueous solution (containing 2.78 M of nitric acid and 0.8 M of sodium silicate) was added slowly using a syringe (0.1 mL/min), and the reaction mixture was stirred (1000 rpm) additionally for 30 min at 70 °C after mixing. Subsequently, the product was magnetically removed by the NdFeB magnet (Size 50 mm × 15 mm × 15 mm, magnetic strength approx. 324 N) and washed with 3 × 200 mL water. The obtained solids were dispersed in 200 mL water and stored at 25 °C in air. The solid concentration was determined from the dry weight per volume of suspension dried at 60 °C for 24 h.

The pristine Mg₃Fe-NO₃ LDH (Mg₃Fe LDH) was prepared by coprecipitation [1, 2]. An aqueous solution of 0.094 mol/L of Mg(NO₃)₂ and 0.031 mol/L Fe(NO₃)₃ was titrated with 0.75 mol/L of NaOH containing 0.75 mol/L of NaNO₃ until pH reached ~ 9.5 (~ 97 mL). The obtained suspension
was aged for 24 h at 25 °C in a round bottomed flask under vigorous stirring and then collected by centrifugation. The product was washed three times and then dispersed in 50 mL water. The solid concentration was determined as described above. All reactions were performed using decarbonated water and under a N₂ atmosphere as described above. The decarbonated water was made by boiling ultrapure water under N₂ atmosphere for 30 min. The decarbonated water was then transferred to a clean glass bottle and cooled to room temperature under N₂ atmosphere [2].

The composite materials were synthesized via mixing the suspensions of Fe₃O₄@SiO₂ and Mg₃Fe LDH with a solid mass ratio of 1:2 between Fe₃O₄@SiO₂ and Mg₃Fe LDH. The obtained solids were separated using an external NdFeB magnet (see above) and washed with 400 mL water for 3 times. Finally, the obtained solid was dispersed in 50 mL of water (solid concentration ~6.2 g/L) and stored at 4 °C until further use. All reactions proceeded under a N₂ flow (55 mL/min).

Powder X-ray diffraction (PXRD) of above samples were carried out by drying sample suspensions on a silicon low background sample holder at 60 °C overnight (oriented samples obtained). The samples were measured using a PANalytical X’Pert Pro MPD instrument employing Co-Kα radiation (Kα₁=1.789Å, 40 kV, 40 mA) in continuous scan mode (2θ range from 5° to 90°, step size 0.02°/step and 3 s/step, PW3011/10 detector). Total Mg concentration of the 1 g/L Fe₃O₄@SiO₂-Mg₃Fe LDH suspension was determined by using 1M nitric acid to dissolve the Fe₃O₄@SiO₂-Mg₃Fe LDH composite (1 g/L) at room temperature and the Mg concentration determined in the digest using atomic absorption spectroscopy (AAS, PinAAcle 900H Perkin Elmer).

1.3 pH control

The pH of suspensions was controlled at a specific pH with an error ± 0.1 pH unit by addition of 1 M, 0.1 M, 10 mM and 1 mM HCl or NaOH solutions (by using Metrohm 790S Tirino pH stad). In this process, the sample solution was under magnetic stirring (300 rpm) and the pH was measured continuously. The pH was adjusted whenever the pH deviated more than 0.1 pH unit from the target pH. The concentration of the HCl and NaOH solutions used were determined by the target pH, the higher or lower the pH, the higher the concentrations. The pH control was stopped when pH was steady for 10 min at the desired pH or reaction end had been reached. Before the pH adjustment, the electrode was calibrated in pH 4.00, 7.00 and 9.00 buffers (ISO17025 Accredited Test Method INAB Ref: 264T and NIST traceable, Reagecon Diagnostics Ltd. Ireland) at 25 °C. The electrode was cleaned regularly by using 0.1 M HCl and water.

1.4 Desorption experiment

In order to estimate how much Pᵢ exists in the solids as precipitates (supposed magnesium phosphates), a desorption experiment was carried out. The solids after sorption at pH 11 with initial Pᵢ concentration of 300 mg P/L were first isolated with the NdFeB magnet and then dispersed in 50 mL
1 M NaOH aqueous solution. After stirring (300 rpm) for 24 h at room temperature, the solids were again isolated with the NdFeB magnet, and the P$_i$ concentration in the extract measured with the Molybdenum-Blue method. The desorption efficiency (%) were calculated through Eq. S1.

1.5 Characterization of solids

1.5.1 Morphological analysis

Morphological analysis of all samples were carried out by using scanning electron microscopy (SEM) (Quanta 200, FEI), field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800) and transmission electron microscopy (TEM) (FEI Tecnai T20 G2 at 200 kV). For SEM analysis, pristine Mg$_3$Fe LDH was dispersed in ethanol and a drop of the suspension was placed on a silicon wafer and then dried. After hybridization, powdered samples were attached on carbon tape. The surface of samples was sputter coated by Pt/Pd until the coating thickness reached ~10 nm; images were collected using a 20 kV accelerated electron beam.

1.5.2 Element composition analysis

The Mg/Fe ratio in Mg$_3$Fe LDH was measured by dissolving 60 mg of powdered samples in 10 mL of concentrated nitric acid (65 wt%), then treated in a microwave reactor (MarsX press, CEM Corporation, NC, U.S.A.) for 15 min. The obtained clear solution was diluted 10 times with ultrapure water for analysis by inductive coupled plasma-optical emission spectroscopy (ICP-OES, Optima 2100 DV; PerkinElmer, Waltham, MA, U.S.A.). Mg concentrations in the solution after P$_i$ sorption were measured by Atomic Absorption Spectroscopy (AAS) using a PinAAcle 900H system from Perkin Elmer. The Mg content in the remaining solids after P$_i$ sorption were determined after dissolving a known amount of the solids in 65 wt% HNO$_3$ aqueous solution and measured by Inductively coupled plasma - optical emission spectrometry (ICP-OES) using an Agilent Technologies 5100 ICP-OES. The P$_i$ concentration in solution was determined using the Molybdenum-Blue method [3] at 890 nm using a Lambda 25 UV/VIS spectrometer from Perkin Elmer (1 cm cuvettes, detection limit 0.025 mg P/L).

1.5.3 PXRD analysis

The identity and presence of crystalline substances in the solids after P$_i$ sorption was tested by PXRD. All solids after sorption were isolated with the NdFeB magnet and washed with water once and dried at 60 °C overnight. The obtained solids were grinded into fine powders and filled into the sample holder and then pressed to obtain a planar surface. All the samples were measured in continues scan mode (20 range from 5° to 90°, step size 0.02°/step and 3 s/step, PW3011/10 detector). The relative intensity of reflections was calculated by defining the intensity of the Fe$_3$O$_4$ (311) reflection as 100%. Crystal thickness along specific directions was estimated using the Scherrer equation (Eq. S3).
Rietveld profile-fitting of PXRD data of pristine Fe₃O₄@SiO₂-MgFe LDH and the samples after Pi sorption was carried out to estimate the content of remaining Mg₃Fe LDH and Fe₃O₄, using the X’pert Highscore Plus software [4] with the Pseudo Voigt profile function. The background was fit by a six parameter polynomial and refined simultaneously with the zero-point and scale factor. No correction was made for preferred orientation and peak asymmetry. Parameters characterizing the instrumental resolution function were obtained from a Si standard sample by the appropriate Rietveld analysis and kept constant during refinements. The reference pattern for the Fe₃O₄ phase was JCPDS 19-0629 and for Mg₃Fe LDH JCPDS 70-2150 (Pyroaurite) (crystal structure information is in Table S5).

1.5.4 ⁵⁷Fe Mössbauer spectroscopy and magnetization analysis

Since the Mg₃Fe LDH shows obvious dissolution at pH 5, the solids after adsorption at pH 5 were examined using ⁵⁷Fe Mössbauer spectroscopy to identify the iron rich residuals. The spectra were collected using a conventional spectrometer in transmission geometry coupled with a cold head cryostat from Advances Research Systems (USA), equipped with vibration isolation stand, developed at the Laboratory of Physical Chemistry and Microbiology for the Environment (LCPME laboratory, Joint Research Unit-UMR 7564, CNRS/Université de Lorraine). The 50 m Ci ⁵⁷Co in Rh matrix radioactive source was mounted in a constant acceleration velocity transducer. Measurements were taken over a wide range of velocities (± 11 mm s⁻¹) for the Fe₃O₄@SiO₂-Mg₃Fe LDH. The hyperfine interaction parameters were determined by fitting the experimental spectra by a least-squares method using the Recoil software (Ottawa University) [5]. The Lorentzian multiple analysis model is used in the Recoil software as a fitting procedure for all spectra. The center shifts are reported with respect to that of 25 μm thick α-Fe foil at room temperature. The field depending magnetization curves for the sample before and after adsorption were characterized by Quantum Design MPMS-XL superconducting quantum interference device (SQUID) equipped with a 5 T DC magnet. Data were collected under a magnetic field from 0 to ±10000 Oe at 10 K.

1.5.5 Fourier transform infrared spectroscopy

Surface functional groups were characterized through Fourier transform infrared spectroscopy (FT-IR) by using a Perkin Elmer Frontier MIR/FIR + SP10 STD instrument with universal ATR sampling accessory in the wavenumber range of 400-4000 cm⁻¹.

1.5.6 Solid state ³¹P MAS NMR spectroscopy

Single pulse ³¹P MAS NMR spectra were collected by solid state nuclear magnetic resonance (SSNMR; JEOL ECZ500CR MHz NMR spectrometer; JEOL, Tokyo, Japan) equipped with a 11.7 T Oxford magnet and a 3.2 mm double resonance MAS NMR probe and spinning speeds of 15 and 17 kHz. The test samples were prepared by using only Mg₃Fe LDH as the magnetic nanoparticles is not compatible with NMR The samples were prepared by dispersing Mg₃Fe LDH (0.66 g/L) in an
aqueous solution of 10 mM KNO₃ electrolyte, 300 mg P/L added as KH₂PO₄ and kept stirring (300 rpm) under Ar atmosphere (to avoid CO₂ contamination) for 24h. The pH of the solution was controlled at 7, 9 and 11 by addition of 1 M HCl or NaOH solution during the reaction (SI 1.3). After Pi sorption, the solids were isolated via centrifugation (11630g, 10min) and dried at 60 ℃ for 24 h for NMR analysis. The spectra were recorded with a rotor-synchronized Hahn Echo (90° - τ - 180° - τ - acquisition), where τ was set to one rotor period (58.82 μs), with a 90° pulse of 3.2 μs and referenced relative to concentrated phosphoric acid (0 ppm) using struvite ((NH₄)Mg(PO₄)∙6H₂O) as a secondary reference (δiso(31P) = 6.2 ppm).

1.6 Visual MINTEQ calculations

Visual MINTEQ calculations were carried out by using the multi-problem function in Visual MINTEQ ver. 3.1 [6]. The calculations were performed by varying the initial Mg concentration from 0 to 130 mg Mg/L at different initial Pi concentration running from 0 to 300 mg P/L, and different pH at 5, 6, 7, 8, 9, 10 and 11. The Mg₃(PO₄)₂, MgHPO₄∙3H₂O and Mg(OH)₂ were set as possible solid phases. The program was run for predicting the precipitated Mg in percentage of initial total Mg (%).

The reason for choosing the above parameters is to mimic the conditions in Exp. 2. The maximum initial Mg concentration was set to 130 mg Mg/L due to the use of 1g/L of the Fe₃O₄@SiO₂-Mg₃Fe LDH composite which will contain 0.66 g/L Mg₃Fe LDH (information from SI 1.2) with the chemical formula  Mg₂.85Fe(OH)₇.7NO₃∙2H₂O (formula weight 355.18 g/mol).

1.7 Pi sorption efficiency of pristine Fe₃O₄ and Fe₃O₄@SiO₂

This experiment was carried out to compare the Pi sorption of separate Fe₃O₄ and Fe₃O₄@SiO₂ with the Fe₃O₄@SiO₂-Mg₃Fe LDH composite. The process is similar to that described in Exp. 3. Typically, 10 mg of the above particles were dispersed in 10 mL aqueous solution with initial Pi concentration running from 0 to 300 mg P/L, and different pH at 5, 6, 7, 8, 9, 10 or 11 (± 0.1 pH unit) by addition of HCl or NaOH solution (SI 1.3). The final solutions were filtered through 0.2 μm regenerated cellulose filter (Mikrolab Aarhus A/S) and stored at 4 ℃ until measurement of Pi.

1.8 Equations

\[
\text{Desorption efficiency (\%)} = \frac{C_d \times 0.05L}{q_e \times 0.05g} \times 100\%
\]

Equation S1

where \(q_e\) (mg P/g) is the Pi sorbed on the sorbents, and \(C_d\) (mg P/L) refer to the Pi concentration in the desorption solution.
The solid concentration of Mg3Fe LDH in the solution, when 1 g/L of Fe3O4@SiO2-Mg3Fe LDH was used, can be calculated by:

\[ C_{\text{Mg,Fe-LDH}} = \frac{C_{\text{Mg}} \times M_{\text{Mg,Fe-LDH}}}{2.85 \times M_{\text{Mg}} \times 1000} \quad \text{Equation S2} \]

where \( M_{\text{Mg,Fe-LDH}} \) and \( M_{\text{Mg}} \) are the molar weights (g/mol) of Mg3Fe LDH and Mg, respectively. \( C_{\text{Mg}} \) refers to Mg concentration in solution while 2.85 represents there are 2.85 mol of Mg in 1 mol of Mg3Fe LDH.

Estimation of crystal size along the ab-plane and c-axis of LDH and the crystal size of Fe3O4 was calculated using the Scherrer equation:

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \quad \text{Equation S3} \]

Where \( \tau \) is the mean size of the ordered (crystalline) domains (Å), \( K \) is a dimensionless shape factor (\( K=0.9 \) in this study), \( \lambda \) is the X-ray wavelength (Co K\( \alpha = 1.789 \) Å), \( \beta \) is the line broadening at half the maximum intensity (FWHM), and \( \theta \) is the Bragg angle.

The Pi sorption kinetics data were fitted with a pseudo-second-order model[8]:

\[ q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad \text{Equation S4} \]

Where \( q_e \) and \( q_t \) refer to Pi sorbed (mg P/g) at equilibrium and at time \( t \) (min) respectively, and \( k_2 \) is the pseudo-second-order rate constant (g/mg P∙min\(^{-1}\)) for the Pi adsorption process.

The Pi sorption isotherm data was fitted with the Freundlich model:

\[ q_e = K_F C_e^{\frac{1}{n}} \quad \text{Equation S5} \]

Where \( q_e \) (mg P/g) and \( C_e \) (mg P/L) refer to the amount of Pi sorbed, and the solution Pi concentration at equilibrium, \( K_F \) is the Freundlich constant (mg\(^{1-n}\) L\(^n\)/g) and \( n \) is a fitting constant (non-linearity index).

Data for the Mg dissolution kinetics were fitted with a pseudo-second-order model:
\[ C_t = \frac{k_2 t}{1 + k_2 C_t t} \]  
\textit{Equation S6}

Where \( C_t \) and \( C_f \) is the Mg concentration in solution (mg/L) at equilibrium and time \( t \) (min) respectively, and \( k_2 \) is the pseudo-second-order rate constant (L/mg·min\(^{-1}\)) for the process.

The phosphate adsorption efficiency (%) was calculated by:

\[ \text{Adsorption efficiency} = \frac{C_0 - C_e}{C_0} \times 100\% \]  
\textit{Equation S7}

Where \( C_0 \) (mg P/L) is the initial P\(_i\) concentration and \( C_e \) (mg P/L) is the P\(_i\) concentration in solution after reaching equilibrium.

The relative Mg release (R\(_{Mg}\), %) was calculated by:

\[ R_{Mg} = \frac{C_{iMg}}{C_{Mg\,total}} \times 100\% \]  
\textit{Equation S8}

Where the \( C_{Mg\,total} \) (mg/L) is the total Mg concentration in suspension and \( C_{iMg} \) (mg/L) is the Mg concentration in solution after reaching equilibrium.

The amount of Fe\(_3\)O\(_4@\)SiO\(_2\) in the Fe\(_3\)O\(_4@\)SiO\(_2\)-Mg\(_3\)Fe LDH composite can be calculated by:

\[ R_{Fe3O4@SiO2} = \frac{M_{\text{composite}} - M_{LDH}}{M_{Fe3O4@SiO2} - M_{LDH}} \times 100\% \]  
\textit{Equation S9}

where \( M_{\text{composite}} \), \( M_{LDH} \) and \( M_{Fe3O4@SiO2} \) refers to the magnetization for the Fe\(_3\)O\(_4@\)SiO\(_2\)-Mg\(_3\)Fe LDH composite, Fe\(_3\)O\(_4@\)SiO\(_2\) and Mg\(_3\)Fe LDH at ± 10,000 Oe (10K), respectively.

The theoretical Mg concentration after P\(_i\) sorption at different pH and initial P\(_i\) concentration can be calculated by:

\[ C_{Mg\,theoretical} = C_{Mg\,total} \times \left( \frac{R_{LDH}}{1 - R_{LDH}} \right) \left( \frac{66\,\text{wt}\%}{34\,\text{wt}\%} \right) \]  
\textit{Equation S10}
The C_{\text{Mg theoretical}} (mg/L) is the calculated Mg concentration due to dissolution of Mg_{3}Fe LDH after Pi sorption (Exp. 2). The C_{\text{Mg total}} is total Mg concentration (SI 1.2). The R_{\text{LDH}} is the calculated amount (wt\%) of Mg_{3}Fe LDH in the final solids after Pi sorption, which is estimated from Rietveld profile-fitting of PXRD data (SI 1.5, Table S6).

The percentage of P_{i} sorbed in form of magnesium phosphate precipitates (M_{\text{Mg-P precipitates}}, wt\%) can be calculated by:

\[
M_{\text{Mg-P precipitates}} = \frac{P_{i} \text{ sorbed as magnesium phosphate precipitates}}{\text{calculated P}_{i} \text{ sorption}} \times 100 \text{ wt\%} \quad \text{Equation S11}
\]

The nominator is calculated P_{i} sorption (mg P/g) (Z axis value in Fig. 5) and the denominator is the P_{i} precipitated as magnesium phosphate (mg P/g) (Z axis value in Fig. S19).

2. Characterization of Fe_{3}O_{4}@SiO_{2} and Mg_{3}Fe LDH

The TEM image of separate magnetite nanoparticles (Fig. S3a) shows relative well-dispersed particles with an average diameter of 11 ± 3 nm. The crystal size of the Fe_{3}O_{4} particles was also calculated using the Scherrer equation to 11.3 nm (Eq. S3), which in good agreement with the TEM result. After coating Fe_{3}O_{4} with SiO_{2}, aggregates with diameters around 80 ± 10 nm were formed (Fig. S3b). The FT-IR spectrum of the Fe_{3}O_{4}@SiO_{2} sample (Fig. S4) shows an absorption band at 1071 cm\(^{-1}\) attributed to the Si-O bond, reflecting the presence of a SiO_{2} layer on the magnetite. Nitrate ion in the Mg_{3}Fe LDH interlayer of the composite is seen from the IR band at 1356 cm\(^{-1}\) (Fig. S4). The formula for the Mg_{3}Fe LDH formula is Mg_{2.85}Fe(OH)_{7.7}NO_{3} \cdot 2H_{2}O [2]. TEM shows the LDH particles to be of hexagonal platy shape with an average lateral 2D dimension around 68 ± 4 nm (Fig. S3c).

After combining suspensions of Fe_{3}O_{4}@SiO_{2} and Mg_{3}Fe LDH, the PXRD pattern of the composite (Fig. S2a) shows the presence of both the Mg_{3}Fe LDH (JCPDS No. 01-070-2150) and magnetite (JCPDS No. 19-0629). Based on the (003) position, the basal spacing was determined to 0.79–0.80 nm for Mg_{3}Fe LDH which is in agreement with earlier studies of MgFe LDH with NO_{3}^{-} as interlayer ion [2, 9]. The crystallite domain size of the Mg_{3}Fe LDH estimated from peak broadening and using the Scherrer equation (Eq. S3) is 7.3 nm based on the (110) reflection along the ab-plane and 14.8 nm based on the (003) reflection along the c-axis, respectively. The unit cell parameter of Mg_{3}Fe LDH was determined at 3.1 Å and 23.9 Å for a and c, respectively. The prepared suspension of composite (7.6 g/L) was completely separated after contact with an NdFeB magnet for 1 min (Fig. S5). Hence,
the synthesis of the Mg3Fe LDH-magnetite composite was successful as the LDH particles sticks to the Fe3O4@SiO2 support. The composite exhibits large aggregates with sizes of several hundred nanometer as seen by TEM and SEM (Fig. S2b and S7a).

3. Calculation of Pi sorption capacity of the residual ferrihydrite phase after sorption at pH 5.

During Pi sorption at pH 5, a poorly crystalized ferrihydrite phase forms due to dissolution of Mg3Fe LDH; this residual phase shows a high Pi sorption capacity (Fig. 2b and 3b). We may estimate the Pi sorption capacity of this newly formed ferrihydrite phase based on the mass of ferrihydrite present. First, we estimate the amount of ferrihydrite formed. The pristine Fe3O4@SiO2-Mg3Fe LDH contains 106.5 mg/g (SI 1.2). As the Mg3Fe LDH formula is Mg2.85Fe(OH)7.7NO3∙2H2O, then there should be 0.55 g/L of LDH in 1g/L of the pristine composite (Eq. S2). The magnetization data for the composite before sorption (Fig. S15) show there is 0.34 g Fe3O4@SiO2 per 1g of the pristine Fe3O4@SiO2-Mg3Fe LDH composite used (calculated from Eq. S9). Thus, there should be 0.11 g (mass of ferrihydrite = 1 g of composite - 0.34 g of Fe3O4@SiO2 - 0.55 g of Mg3Fe LDH) of ferrihydrite per gram of pristine Fe3O4@SiO2-Mg3Fe LDH composite used.

The comparison of Pi sorption to the magnetic core (Fe3O4 and Fe3O4@SiO2) and composites shows the magnetic core component has minor contribution to Pi sorption on the composite (Fig. S9). According to the data for Mg release after Pi sorption at pH 5 (Fig, S10), the Fe3O4@SiO2-Mg3Fe LDH composite released 91% of total Mg when the initial Pi concentration was 300 mg P/L. The ferrihydrite phase concentration after Pi sorption at pH 5 should be 0.23 g/L, when the initial Fe3O4@SiO2-Mg3Fe LDH composite concentration is 1 g/L. As the Fe3O4@SiO2 particle didn’t adsorb Pi at pH 5 (Fig. S9), most of the adsorbed Pi is attributed to the ferrihydrite phase. This results in a Pi sorption capacity of the ferrihydrite phase of 344 mg P/g at a solution Pi concentration of 221 mg P/L. This sorption capacity is much higher than commonly reported Pi sorption capacities of ferrihydrite (56 mg P/g for 1.5 nm ferrihydrite and 34 mg P/L for synthetic 2-lines ferrihydrite) [10, 11]. It can be explained by the ultra-small particle size of the ferrihydrite phase. It is worth to mention that the Fe:P ratio is close to 1:1 in the sorbent, indicating the possibility of forming strengite (FePO4) [12, 13].

4. Calculation of Mg/P ratio in Mg-P precipitates after P sorption at pH 11

The Rietveld profile-fitting of the PXRD for pristine Fe3O4@SiO2-Mg3Fe LDH demonstrate the composite contains 34 wt% of Fe3O4 and 66 wt% of Mg3Fe LDH (Table S6). For the composite after Pi sorption at initial Pi concentration 300 mg P/L (pH 11), Rietveld profile-fitting shows the composite contains 57 wt% of Mg3Fe LDH and 43 wt% of Fe3O4 (Table S6). Hence, the Mg release from Mg3Fe LDH in the composite is estimated to 36 mg Mg/g as a result of Pi sorption at pH 11 (Eq. S10). After treating this sample with 1 M NaOH, a Pi desorption efficiency of 26 % was achieved (Eq. S1, Fig. S16), inferring that 34 mg P/g of adsorbed Pi remains in the solids as a magnesium phosphate.
precipitate. This indicates, that this precipitate has a molar Mg/P ratio of 1.4 which is close to the chemical composition of trimagnesium phosphate (Mg$_3$(PO$_4$)$_2$·xH$_2$O mixed with MgHPO$_4$·xH$_2$O, at a mole ratio of these two compounds of 4:1. The result indicates the formation of Mg$_3$(PO$_4$)$_2$·xH$_2$O precipitates after P$_i$ sorption at pH 11 at high initial P$_i$ concentration.

5. Fitting of P$_i$ sorption versus pH and solution P$_i$ and semi-quantitative estimation of P$_i$ sorption as precipitate

According to the previous discussion, the P$_i$ can be sorbed to ferrihydrite, sorbed to the Mg$_3$Fe LDH and it can also be sorbed via precipitation of magnesium phosphate.

The P$_i$ sorbed in form of magnesium phosphate can be estimated by using Rietveld profile-fitting of the PXRD patterns of the solids and the measured Mg concentration in solution after P$_i$ sorption (Fig. S11). Rietveld profile-fitting is used to determine the content of Mg$_3$Fe LDH in the crystal phase in final solids after P$_i$ sorption (Exp. 2) (Table S6). As the pristine Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH composite after synthesis has 66 wt% of the Mg$_3$Fe LDH (Table S6), the theoretical Mg concentration in solution after P$_i$ sorption can be calculated through Eq. S10, with the assumption that the Mg release is proportional to the amount of Mg$_3$Fe LDH that has dissolved which is estimated by the Rietveld fitting method (Table S6).

Next, the difference between the calculated theoretical and measured Mg concentration after P$_i$ sorption shows that the calculated Mg release is higher than the measured values, especially in the samples at high pH and high solution P$_i$ concentrations (Fig. S18). This difference is attributed to the formation of magnesium phosphate precipitates. By using this principle, the amount of P$_i$ sorbed in form of magnesium phosphate under various pH and P$_i$ concentration is estimated (assuming the precipitates has the formula Mg$_3$(PO$_4$)$_2$·xH$_2$O). For example, the calculated Mg concentration based on the PXRD patterns and Rietveld fitting calculations show that 40% of total Mg has released after P$_i$ sorption at pH 11 at an initial P$_i$ concentration at 300 mg P/L, while the measured Mg concentration shows that only 2% of total Mg has dissolved (Fig. S18d). As the total Mg concentration is 106.5 mg Mg/L (SI 1.2), the amount of P$_i$ contained in precipitates can be calculated to 34.4 mg P/L:

$$\frac{106.5 \text{ mg/L} \times (40\% - 2\%)}{\frac{100}{3} \text{ mg/mol} \times \frac{3 \times 31000 \text{ mg P/mol}}{1 \text{ g/L}}} = 34.4 \text{ mg P/g}$$

After these calculations, a 3D surface (Fig. S20) was generated by fitting the mass of P$_i$ sorbed in precipitates at different pH and equilibrium P$_i$ concentration with the Rational Taylor Function in Origin 9.6 software (details in Table S7) [14]. The obtained 2D surface shows the mass of P$_i$ sorbed as magnesium phosphate as a function of pH and equilibrium P$_i$ concentration.
Subsequently, the 2D surface in Fig. 5 was generated by fitting the sorption isotherm data at different pH (Fig. 2b) with the Rational 2D Function in Origin 9.6 software (details in Table S8) [15].

Finally, the colour map in Fig. 5, representing the percentage (wt%) of \( \text{Pi} \) sorbed in form of magnesium phosphate precipitates, is calculated by comparing the calculated amount of \( \text{Pi} \) sorbed as precipitates with estimated \( \text{Pi} \) sorption at various pH and equilibrium \( \text{Pi} \) concentrations (Eq. S11).
Fig. S1 shows the experimental processes in this study comprising composite synthesis, P$_i$ sorption, Mg dissolution experiments and MINTEQ calculation. After that, multiple characterization techniques were used and followed by semi-quantitative analysis.
Figure S2. (a) PXRD patterns of Fe₃O₄, Mg₃Fe LDH and final Fe₃O₄@SiO₂-Mg₃Fe LDH composite, and (b) TEM image of the Fe₃O₄@SiO₂-Mg₃Fe LDH composite.
Figure S3. TEM images of synthesized (a) Fe₃O₄, (b) Fe₃O₄@SiO₂ and (c) Mg₃Fe LDH.

Figure S4. FTIR spectra of precursor phases, Fe₃O₄, Fe₃O₄@SiO₂, Mg₃Fe LDH and final Fe₃O₄@SiO₂-Mg₃Fe LDH composite.
Figure S5. Illustration of Fe₃O₄@SiO₂-Mg₃Fe LDH composite suspension (7.6 g/L) a) before, and b) after exposure to external magnet (NdFeB magnet, N48) for 1 minute.

Figure S6. Change of pH versus time when Fe₃O₄@SiO₂-Mg₃Fe LDH (1 g/L) was dispersed in water without HEPES buffer (Exp. 1).

Figure S7. FE-SEM images of the Fe₃O₄@SiO₂-Mg₃Fe LDH (a) before and (b) after 24 h Pᵢ sorption at initial Pᵢ concentration of 50 mg P/L at pH 7 (Exp. 2), 25 °C.
Figure S8. PXRD patterns of Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH before and after sorption with and without the pH controlled by HEPES buffer, the pristine Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH is also shown here for comparison.

Figure S9. Phosphate sorption efficiency of pristine Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ compared with Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH composite at different pH values, after 1 h P$_i$ adsorption at initial P$_i$ concentration of 10 mg P/L (Exp. 3 and SI 1.7).

Separate Fe$_3$O$_4$@SiO$_2$ particles, which remains when the LDH component dissolves, had less than 10 % P$_i$ sorption capacity compared with the composite (Fig. S9), illustrating that the magnetic core component has minor contribution to P$_i$ sorption on the composite.
Figure S10. 2D plot of Mg concentration in solution after P, sorption (sorbent concentration 1 g/L, contact time 24 h, Exp. 2) vs P, sorbed to Fe₃O₄@SiO₂-Mg₃Fe LDH at different pH.
Figure S11. PXRD patterns of Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption at (a) pH 5, (b) pH 7, (c) pH 9, and (d) pH 11 at different initial Pᵢ concentrations (Exp. 2).
Figure S12. PXRD patterns (focus on the 60°<2θ<80° range) of Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption at pH 5, pH 7, pH 9 and pH 11 at different initial Pᵢ concentrations (Exp. 2). The dash lines denote the (110) and (113) peak of Mg₃Fe LDH phase.
Figure S13. Field-dependent magnetization curves (10K) for (a) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2$-$\text{Mg}_3\text{Fe}$ LDH composite before and after sorption at pH 5 (initial $P_i$ concentration 10 mg P/L, 25 °C and 24 h), (b) $\text{Mg}_3\text{Fe}$ LDH before and after sorption at pH 5 (initial $P_i$ concentration 10 mg P/L, 25 °C and 24 h).

The magnetization data shows the solid after $P_i$ sorption at pH 5 (Fig. S13a and b) has a composition of 55 wt% of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and 45 wt% of non-magnetic materials, comprising residual LDH and poorly crystalized ferrihydrite. Consequently, 77.7 mg/L of Mg has been dissolved, in full agreement with the measured solution Mg concentration of 77 mg/L (Fig. S10).
Figure S14. PXRD of Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption at pH 11 for 24 h (initial Pᵢ concentration 300 mg P/L, room temperature). Inset: expanded view of the pattern from 10° to 32.5° 2θ degree. The solids were isolated with an external magnet and directly dried at 60 °C overnight. The obtained solids were grinded before PXRD.
Figure S15. $^{31}$P MAS NMR spectra of Mg$_3$Fe LDH exposure to phosphate solution with constant pH at (A) 7, (B) 9 and (C) 11 (initial P$_i$ concentration 300 mg P/L, room temperature, contact time 24 h). The insets show the region for the isotropic resonances.

The narrow resonance at $\delta^{(31P)} = 2.5(2)$ ppm is assigned to the formation of an ill-defined (amorphous) magnesium phosphate phase whereas the broad resonance ($\delta^{(31P)} = 1.8(2)$ ppm is tentatively assigned to outer sphere complexation of P$_i$ to the surface of Mg$_3$Fe LDH [2]. The pH 9 and 11 samples both show the presence of a narrow resonance superimposed on broader resonance (Fig. S15 B and C). The absence of a paramagnetic shift implies that P$_i$ is adsorbed via formation of amorphous magnesium phosphate precipitate and outer sphere complexation with the LDH structure, based on our recent study [2].
Figure S16. Comparison of $P_i$ sorbed on the solids after sorption at pH 11 at initial $P_i$ concentration 300 mg P/L (solution volume 50 mL, solid concentration 1 g/L, room temperature, 24 h) and desorption by 50 mL of 1 M NaOH solution (24 h).
Figure S17. Visual MINTEQ calculations of precipitated Mg (in percentage of initial total Mg concentration, %) corresponding to different initial P_i concentrations (mg P/L) and initial total Mg concentrations (mg Mg/L) at different pH values (The colour bar denotes the percentage (%) precipitated Mg in percentage of initial Mg).
Figure S18. Comparison of theoretical Mg release (calculated from the Rietveld profile-fitting of the PXRD data in Fig. S11, SI 5) with measured Mg release from Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption (Exp. 2) at (a) pH 5, (b) pH 7, (c) pH 9, and (d) pH 11 at different initial Pᵢ concentrations (25 °C, 24h). Rietveld profile-fitting of the PXRD data was used to estimate how much Mg₃Fe LDH had dissolved (SI 1.5, Table S6) resulting in an estimate of the maximum amount of Mg had been released from the LDH phase.
Figure S19. 3D surface curve (calculation details in SI 5) of the amount of sorbed P_i as magnesium phosphate precipitate as a function of pH and equilibrium P_i solution concentration (1 g/L of Fe_3O_4@SiO_2-Mg_3Fe LDH, 25 °C, contact time 24h). The X axis represent pH, the Y axis represent the equilibrium P_i concentration (mg P/L), and sorbed P_i as magnesium phosphate precipitates (mg P/g) is along the Z axis. (The colour bar denotes the amount of P_i sorbed as magnesium phosphate precipitate, mg P/g).
Figure S20. Comparison of calculated Mg₃Fe LDH dissolution (according to the Rietveld profile-fitting results, Table S6) with measured Mg release from Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption (Exp. 2).

The selected data points in this figure are from Table S6. These samples have Mg₃Fe LDH diffractions (Fig. S12) and with few/no magnesium precipitates formed after Pᵢ sorption. Fig. S20 demonstrates the calculated Mg₃Fe LDH dissolution has good linear relationship between the measured Mg concentration after Pᵢ sorption (R²=0.996). In addition, the slope of the fitted result can be used to present the total Mg concentration, which is about 102.9 mg/L. This is very close to the measured total Mg concentration, which is 106.5 mg Mg/L (Fig. 3a, SI 1.2). These results indicate the Rietveld profile-fit results (Table S6) can be used to quantify the Mg₃Fe LDH dissolution and the Mg release from the Fe₃O₄@SiO₂-Mg₃Fe LDH after Pᵢ sorption.
Table S1. Phosphate adsorption properties of various LDHs

<table>
<thead>
<tr>
<th>Type of LDH</th>
<th>Adsorption capacity (mg P/g) / equilibrium P&lt;sub&gt;i&lt;/sub&gt; concentration (mg P/L)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>P&lt;sub&gt;i&lt;/sub&gt; sorption affinity (L/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Initial pH (without further pH control)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncalcined chloride-Mg–Al LDHs</td>
<td>18.3 / 140</td>
<td>0.5</td>
<td>pH 7.5</td>
<td>[16]</td>
</tr>
<tr>
<td>Uncalcined Ca–Fe LDHs</td>
<td>28.8 / 100</td>
<td>0.6</td>
<td>pH 7–7.5</td>
<td>[17]</td>
</tr>
<tr>
<td>Calcined Mg–Al LDHs (500 °C)</td>
<td>49 / 50</td>
<td>4.9</td>
<td>pH 8</td>
<td>[18]</td>
</tr>
<tr>
<td>Calcined Mg–Mn LDHs (300 °C)</td>
<td>34.1 / —</td>
<td>—</td>
<td>—</td>
<td>[19]</td>
</tr>
<tr>
<td>Calcined Mg–Mn LDHs (300 °C)</td>
<td>7.3 / 1.2</td>
<td>6.5</td>
<td>pH 7</td>
<td>[20]</td>
</tr>
<tr>
<td>Calcined Mg–Al LDHs</td>
<td>49.6 / —</td>
<td>—</td>
<td>pH 6</td>
<td>[21]</td>
</tr>
<tr>
<td>Calcined Mg–Al LDHs</td>
<td>44 / 120</td>
<td>1.6</td>
<td>pH 8.6</td>
<td>[22]</td>
</tr>
<tr>
<td>Uncalcined Mg–Al LDHs (commercial)</td>
<td>47.3 / 150</td>
<td>4</td>
<td>—</td>
<td>[23]</td>
</tr>
<tr>
<td>MgFe–LDH(CO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>48 / 31</td>
<td>6.3</td>
<td>pH 7</td>
<td>[24]</td>
</tr>
<tr>
<td>Magnetite anchored ZnFeZr LDH</td>
<td>93.5 / —</td>
<td>26</td>
<td>pH 7.3</td>
<td>[25]</td>
</tr>
<tr>
<td>MgAl LDH combined with iron oxide</td>
<td>37.5 / 150</td>
<td>—</td>
<td>pH 7</td>
<td>[26]</td>
</tr>
<tr>
<td>ZnMgNiAl LDH combined with Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>36.9 / 50</td>
<td>3.5</td>
<td>pH 7</td>
<td>[27]</td>
</tr>
<tr>
<td>MgFcZr LDH combined with Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>35 / 12</td>
<td>27.5</td>
<td>pH 4.5</td>
<td>[28]</td>
</tr>
<tr>
<td>MgAl LDH combined with Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>23.73 / 90</td>
<td>9</td>
<td>pH 5.95 to 7.32</td>
<td>[29]</td>
</tr>
</tbody>
</table>

<sup>a</sup> The adsorption capacity is the maximum P<sub>i</sub> sorption capacity reported in the reference and the equilibrium P<sub>i</sub> concentration is the P<sub>i</sub> concentration in the solution when the sorbents reached its maximum sorption capacity.

<sup>b</sup> The P<sub>i</sub> sorption affinity is defined by the slope of the adsorption isotherms at low P<sub>i</sub> concentration range (from 0 to 5 mg P/L) in solution.
Table S2. Freundlich isotherm model parameters of P<sub>i</sub> sorption to Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Mg<sub>3</sub>Fe LDH at different pH (Exp. 2).

<table>
<thead>
<tr>
<th>pH value</th>
<th>R&lt;sup&gt;2&lt;/sup&gt; of Freundlich isotherm model</th>
<th>K&lt;sub&gt;F&lt;/sub&gt; (mg&lt;sup&gt;1-n&lt;/sup&gt; L&lt;sup&gt;n&lt;/sup&gt;/g)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.984</td>
<td>79.9</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>0.999</td>
<td>70.8</td>
<td>0.26</td>
</tr>
<tr>
<td>9</td>
<td>0.982</td>
<td>55.9</td>
<td>0.18</td>
</tr>
<tr>
<td>11</td>
<td>0.979</td>
<td>32.8</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table S3. Crystallite size of the Mg<sub>3</sub>Fe LDH component in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Mg<sub>3</sub>Fe LDH along c-axis after P<sub>i</sub> sorption at different pH (Exp. 3, initial P<sub>i</sub> concentration 10 mg P/L; 25 °C; reaction time 1h).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallite size of the Mg&lt;sub&gt;3&lt;/sub&gt;Fe LDH content (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 5</td>
<td>0</td>
</tr>
<tr>
<td>pH 6</td>
<td>4.6</td>
</tr>
<tr>
<td>pH 7</td>
<td>5.3</td>
</tr>
<tr>
<td>pH 8</td>
<td>6.9</td>
</tr>
<tr>
<td>pH 9</td>
<td>6.9</td>
</tr>
<tr>
<td>pH 10</td>
<td>6.9</td>
</tr>
<tr>
<td>pH 11</td>
<td>6.9</td>
</tr>
<tr>
<td>Raw MgFe LDH</td>
<td>7.1</td>
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</table>
Table S4. Mössbauer parameters of Fe₃O₄@SiO₂-Mg₃Fe LDH

<table>
<thead>
<tr>
<th>Fe₃O₄@SiO₂-Mg₃Fe LDH before sorption measured at 140 K</th>
<th>( \delta^a ) (mm/s)</th>
<th>( \Delta^b ) (mm/s)</th>
<th>( \text{Heff}^c ) (kOe)</th>
<th>RA(^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₃Fe LDH</td>
<td>0.42</td>
<td>0.61</td>
<td>522</td>
<td>36</td>
</tr>
<tr>
<td>Maghemite</td>
<td>0.47</td>
<td>-0.006</td>
<td>503</td>
<td>35</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.41</td>
<td>-0.009</td>
<td>477</td>
<td>20</td>
</tr>
</tbody>
</table>

| Mg₃Fe LDH                                              | 0.45                  | 0.54                  | 522                      | 36        |
| Poorly crystallized ferric oxide                       | 0.45                  | 1.03                  | 503                      | 35        |
| Maghemite                                               | 0.43                  | -0.008                | 490                      | 20        |
| Magnetite                                               | 0.41                  | -0.028                | 452                      | 11        |

| Mg₃Fe LDH                                              | 0.51                  | 1.02                  | 522                      | 36        |
| Poorly crystallized ferric oxide                       | 0.68                  | 2                     | 522                      | 36        |
| Maghemite                                               | 0.66                  | -0.006                | 522                      | 36        |
| Magnetite                                               | 0.37                  | -0.008                | 485                      | 6         |

\(^a\) Center shift.

\(^b\) Quadrupole splitting or shift.

\(^c\) Hyperfine field.

\(^d\) Relative abundance.

Additional information: The data in Fig. 5a were fitted with 3 hyperfine magnetic fields (\( \text{Heff} \)) of 477, 503 and 522 kOe. The \( \text{Heff} \) of 477 kOe with small quadrupole shift (\( \varepsilon \)) can be assigned to mixed valence Fe\(^{2.5+}\) located in octahedral sites and the \( \text{Heff} \) of 503 kOe can be assigned to high
spin Fe$^{3+}$ in tetrahedral sites. Both sites are refered to magnetite (55%). Another curve fit with a larger H$_{\text{eff}}$ of 522 kOe may be assigned to Fe$^{3+}$ octahedral site corresponding to maghemite (9%) due to the oxidation of magnetite to maghemite [30]. The 25 K spectrum (Fig. 4c) exhibits a magnetic broad sextet and a single line with $\delta$ of 0.68 mm/s. The broadening and the lower hyperfine magnetic field for the sextet observed is correspond to the disordered iron atoms. The single line is due to the presence of superparamagnetic Fe$^{3+}$ containing particles, resulting from incomplete transition of superparamagnetic state to magnetic state of the poorly crystalized ferrihydrite at 25 K which has been reported in the nanosized two lines ferrihydrite [31].

Table S5 Crystal structure data for Mg$_3$Fe LDH [32] and magnetite [33] for Rietveld profile-fitting study.

<table>
<thead>
<tr>
<th>Mg/Fe–CO$_3$ LDH Crystal system: Hexagonal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group R3-m</td>
<td></td>
</tr>
<tr>
<td>Atom type</td>
<td>Wyckoff position</td>
</tr>
<tr>
<td>Mg</td>
<td>3a</td>
</tr>
<tr>
<td>Fe</td>
<td>3a</td>
</tr>
<tr>
<td>O hydroxy group</td>
<td>6c</td>
</tr>
<tr>
<td>O CO$_3$$^{2-}$ group</td>
<td>18h</td>
</tr>
<tr>
<td>C</td>
<td>6c</td>
</tr>
<tr>
<td>H1</td>
<td>6c</td>
</tr>
<tr>
<td>H2</td>
<td>6c</td>
</tr>
</tbody>
</table>

Magnetite Crystal system: Cubic

<table>
<thead>
<tr>
<th>Space group Fd-3m</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom type</td>
<td>Wyckoff position</td>
</tr>
<tr>
<td>Fe tetrahedral</td>
<td>8a</td>
</tr>
<tr>
<td>Fe octahedral</td>
<td>16d</td>
</tr>
<tr>
<td>O</td>
<td>32e</td>
</tr>
</tbody>
</table>

$^a$ Site occupation factors
Table S6 Composition of crystal phase in final solids (wt%) after P$_i$ sorption at different pH and initial P$_i$ concentration, obtained from Rietveld profile-fitting of the PXRD patterns of the final solids (Fig. S11). The Rietveld profile-fitting of the PXRD of pristine Fe$_3$O$_4$@SiO$_2$-Mg$_3$Fe LDH indicates the sample has 66 wt% of Mg$_3$Fe LDH and 34 wt% of Fe$_3$O$_4$.

<table>
<thead>
<tr>
<th>Initial P$_i$ concentration (mg P/L)</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 9</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg$_3$Fe LDH</td>
<td>Fe$_3$O$_4$</td>
<td>Rwp $^a$</td>
<td>GOF $^b$</td>
</tr>
<tr>
<td>1</td>
<td>29.5</td>
<td>70.5</td>
<td>23</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>29.1</td>
<td>70.9</td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>27.2</td>
<td>72.8</td>
<td>20</td>
<td>1.46</td>
</tr>
<tr>
<td>10</td>
<td>33.6</td>
<td>66.4</td>
<td>20</td>
<td>1.29</td>
</tr>
<tr>
<td>20</td>
<td>28.1</td>
<td>71.9</td>
<td>21</td>
<td>1.53</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Weighted R profile, %  
$^b$ Goodness of fit

The data points marked in bold red are used for plotting Fig. S20 and the corresponding linear fit. The reasons we didn’t choose the rest data points are:

a) The PXRD reflections of sample at pH 5 and 7 with relative high P$_i$ concentration (>50 mg P/L for pH 5 and >200 mg P/L for pH 7) are not obvious to see, thus the Rietveld profile-fitting can not be carried out on those samples and we just assume 100 % of crystal phase in those sample is magnetite.

b) For the sample at pH 9 and 11, the magnesium phosphate precipitates could form when the P$_i$ concentration higher than 50 mg P/L (according to the Visual MINTEQ calculation Fig. S17). This secondary precipitate phase would have impact on the correspond linear fit of the LDH dissolution and Mg concentration in solution, as the Mg concentration is not proportional to the LDH dissolution any more.
Table S7 Fitting parameters of the Rational Taylor Function for P₃ sorption (mg P/g) and magnesium phosphate precipitates as function of pH and solution P₃ concentration (mg P/L)

<table>
<thead>
<tr>
<th>Function</th>
<th>Rational Taylor [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$z = \frac{z_0 + A_{01}pH + B_{01}C_e + B_{02}C_e^2 + C_{02}pH<em>C_e}{1 + A_1pH + B_1C_e + A_2pH^2 + B_2C_e^2 + C_2pH</em>C_e}$</td>
</tr>
<tr>
<td>Notes</td>
<td>$z$ is P₃ sorbed as magnesium phosphate precipitates (mg P/g), $C_e$ is equilibrium P₃ concentration (mg P/L)</td>
</tr>
<tr>
<td>$z_0$</td>
<td>$0 \pm 0$</td>
</tr>
<tr>
<td>$A_{01}$</td>
<td>$0 \pm 0$</td>
</tr>
<tr>
<td>$B_{01}$</td>
<td>$-0.016 \pm 0.02$</td>
</tr>
<tr>
<td>$B_{02}$</td>
<td>$-3.916E-5 \pm 3.546E-5$</td>
</tr>
<tr>
<td>$C_{02}$</td>
<td>$0.005 \pm 0.002$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$-0.25 \pm 0.02$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$0.016 \pm 0.002$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$0.001 \pm 6.11E-4$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$-2.32E-7 \pm 1.10E-6$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$-1.07E-4 \pm 7.45E-5$</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
<td>$8.70$</td>
</tr>
<tr>
<td>R-Square (COD)</td>
<td>$0.94$</td>
</tr>
</tbody>
</table>

Table S8 Fitting parameters of the Rational 2D Function for P₃ sorption (mg P/g) as function of pH and solution P₃ concentration (mg P/L).

<table>
<thead>
<tr>
<th>Function</th>
<th>Rational 2D [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$q_e = \frac{z_0 + A_{01}pH + B_{01}C_e + B_{02}C_e^2 + B_{03}C_e^3}{1 + A_1pH + A_2pH^2 + A_3pH^3 + B_1C_e + B_2C_e^2}$</td>
</tr>
<tr>
<td>Notes</td>
<td>$q_e$ is P₃ sorption, $C_e$ is equilibrium P₃ concentration (mg P/L)</td>
</tr>
<tr>
<td>$z_0$</td>
<td>$-89.50 \pm 88.73$</td>
</tr>
<tr>
<td>$A_{01}$</td>
<td>$18.41 \pm 18.72$</td>
</tr>
<tr>
<td>$B_{01}$</td>
<td>$30.81 \pm 30.29$</td>
</tr>
<tr>
<td>$B_{02}$</td>
<td>$0.11 \pm 0.15$</td>
</tr>
<tr>
<td>$B_{03}$</td>
<td>$-2.83E-4 \pm 4.18E-4$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$7.03 \pm 6.87$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$-2.87 \pm 2.93$</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$0.30 \pm 0.31$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$0.81 \pm 0.90$</td>
</tr>
<tr>
<td>B2</td>
<td>-0.001 ± 0.00</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
<td>4.90</td>
</tr>
<tr>
<td>R-Square (COD)</td>
<td>0.99</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.99</td>
</tr>
</tbody>
</table>

References