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Stability of magnetic LDH composites used for phosphate recovery

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18 **Abstract**

19 Layered double hydroxides (LDH) and their magnetic composites have been intensively
20 investigated as recyclable high-capacity phosphorus (P) sorbents but with little attention to
21 their stability as function of pH and phosphate concentration. The stability of a
22 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Mg}_3\text{Fe}$ LDH P sorbent as function of pH (5-11) and orthophosphate (P_i)
23 concentration (1-300 mg P/L) was investigated. The composite has high adsorption
24 capacity (approx. 80 mg P/g) at pH 5 but with fast dissolution of the LDH component
25 resulting in formation of ferrihydrite evidenced by Mössbauer spectroscopy. At pH 7 more
26 than 60 % of the LDH dissolves within 60 min, while at alkaline pH, the LDH is more
27 stable but with less than 40 % adsorption capacity as compared to pH 5. The high P_i
28 sorption at acid to neutral pH is attributed to P_i bonding to the residual ferrihydrite. Under
29 alkaline conditions P_i is sorbed to LDH at low P_i concentration while magnesium
30 phosphates form at higher P_i concentration evidenced by solid-state ^{31}P MAS NMR,
31 powder X-ray diffraction and chemical analyses. Sorption as function of pH and P_i
32 concentration has been fitted by a Rational 2D function allowing for estimation of P_i
33 sorption and precipitation. In conclusion, the instability of the LDH component limits its
34 application in wastewater treatment from acid to alkaline pH. Future use of magnetic LDH
35 composites requires substantial stabilisation of the LDH component.

36 **Key words:** phosphate removal, pH effect, phosphate concentration, LDH dissolution,
37 ferrihydrite, precipitation.

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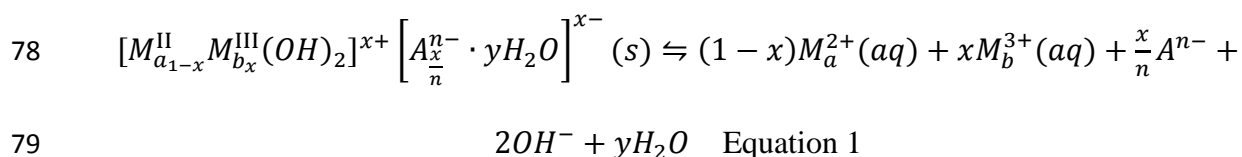
40 **1. Introduction**

41 Phosphorus in the form of orthophosphate is a limited resource which is mainly used as
42 fertilizer and critical for feeding the world population [1, 19, 20]. Phosphorus use is highly
43 unsustainable with substantial parts of phosphorus wasted and going out of circulation [2],
44 and at the same time phosphorus overuse and poor control via waste streams have caused
45 widespread eutrophication. The presence of trace amounts of phosphate in discharged
46 wastewater may trigger eutrophication, leading to poor water quality, toxic algal blooms,
47 and ecosystem destabilization [21]. Toxic algal blooms leads to accumulation of toxic
48 cyanopeptides produced by cyanobacteria [22]. Thus, phosphorus emission reduction and
49 management is one of the UN sustainability goals [3]. The EU Water Framework defines a
50 cut-off total P concentration for lake eutrophication at 0.1 mg P/L, while WHO set this
51 threshold concentration at 0.05 mg P/L (here the phosphate concentration is given in terms
52 of mass of P (in phosphate) per liter [23, 24]. Thus, development of a phosphorus capture
53 and recovery technology has high priority.

54 Phosphate removal from wastewater by adsorption is an alternative to chemical
55 precipitation and biological treatment methods. Adsorption processes are often easier to
56 control, faster, cheaper and scalable compared with often more complex precipitation and
57 biological methods [25-30]. Layered double hydroxide (LDH) with the general formula of
58 $[M_a^{II}{}_{1-x}M_b^{III}{}_x(OH)_2]^{x+}[A_{x/n}\cdot yH_2O]^{x-}$, where M_a^{II} , M_b^{III} and A^{n-} are di- and trivalent metal
59 cations and n^- valent anion respectively [4], have been intensively investigated as P_i
60 sorbents because of their anion exchange property, high sorption capacity and fast sorption
61 kinetics [5-7]. In general, P_i sorption to LDH mainly takes part via electrostatic interactions,
62 interlayer anion exchange, and surface complex formation [8-12]. P_i could also be removed

63 via precipitation, e.g. with use of CaFe and CaAl LDHs [9]. LDH and its composites have
 64 high P_i sorption capacity, ranging from 50 mg P/g to 100 mg P/g, at weak acid (pH 6) to
 65 intermediate pH (pH 7~8) [13]. On the contrary, they have low P_i sorption capacity at high
 66 pH (pH 9 ~ 10), typically lower than 5 mg P/g (Table S1). Moreover, the type of interlayer
 67 ion may affect the sorption capacity. For example carbonate and sulfate decrease the
 68 adsorption capacity compared with nitrate and chloride due to competitive ion-exchange
 69 [14]. The lamellar structure and the sub- to micrometer size of LDH particles make them
 70 difficult to be used in packed filter columns and even to collect by filtration or
 71 sedimentation [9]. However, by attaching the LDHs to magnetic nanoparticles such as
 72 magnetite, the magnetic composites can be separated in a magnetic field and thus be
 73 regenerated after P_i sorption [15]. Examples of such magnetic LDH P sorbents comprise
 74 magnetic nanoparticle decorated ZnFeZr LDH [15], MgAl LDH [16] and MgFeZr LDH [17]
 75 composites (Table S1).

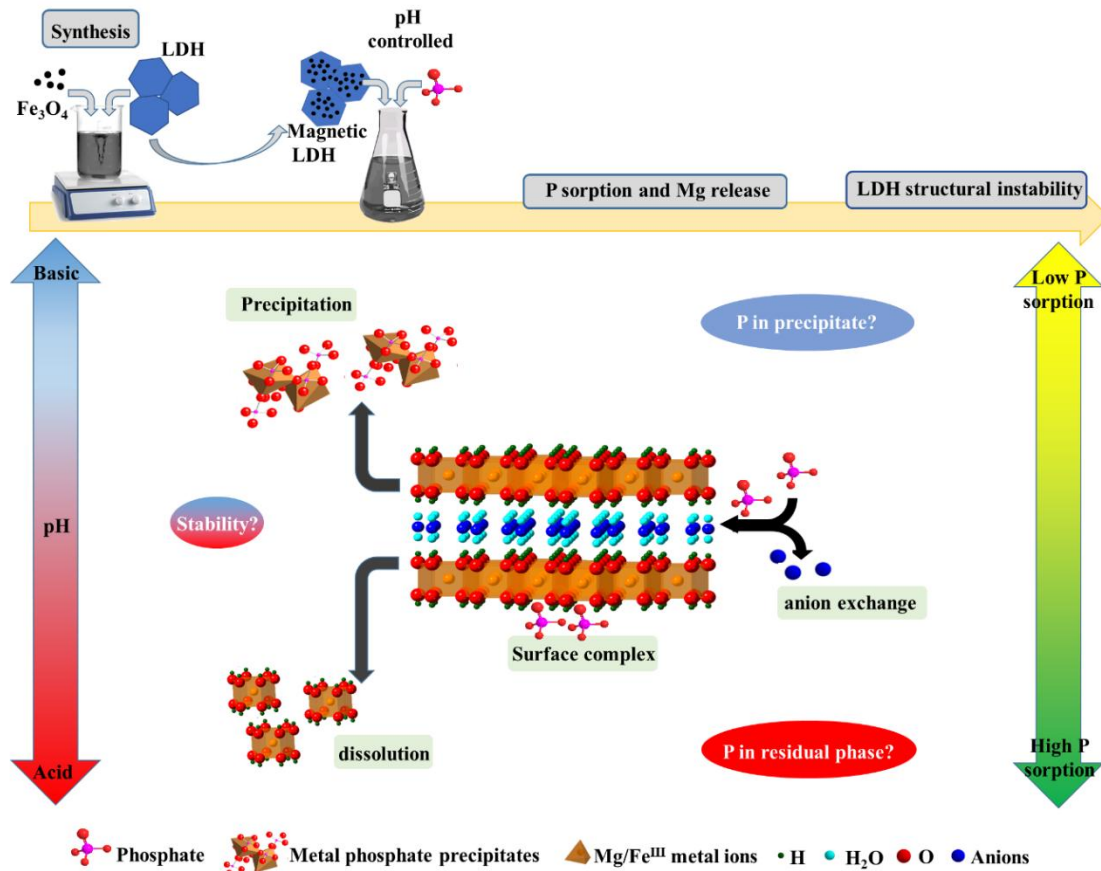
76 LDHs are known to buffer pH due to dissolution in water with release of hydroxide (and
 77 metal) ions [18]:



80 Note, that the trivalent metal ions which are produced would form (hydr)oxide precipitates
 81 due to the negligible solubility of M_b^{III} hydroxides/oxides. The extent and rate of
 82 dissolution of the LDH is controlled by the nature of the divalent metal cations and the
 83 interlayer anions [31-33]. For example, the LDHs are strongly thermodynamically favored

84 over the separate M_a hydroxides in the order $Mg^{2+} < Mn^{2+} < Co^{2+} \approx Ni^{2+} < Zn^{2+}$, when Cl^- is
85 the interlayer anion [32].

86 Environmentally benign materials are required for water cleaning. This limits the suitable
87 LDH candidates for wastewater treatment to MgAl, MgFe, CaAl, CaFe and Fe(II)Fe(III)
88 LDH [35]. Despite a vast number of publications on LDH P_i sorbents, the stability of LDHs
89 for practical applications has not been evaluated. Most waste waters have pH in the range
90 from 6.5 to 8.5 [34], which clearly would challenge the use of LDH as recyclable sorbents
91 in magnetic composites due to the solubility of the LDH phase. For example, the well
92 studied $Fe_3O_4/MgAl-NO_3$ LDH composite showed 33% dissolution of Mg over 6 h in a
93 sorption study with initial pH at 7. In a study of synthetic MgAl and ZnAl LDHs for P
94 recovery from urine, 12% of Mg and even more Zn dissolved during sorption at constant
95 pH 8 for 24 h. P_i sorption to hydrocalumite-type CaAl and CaFe LDH showed ready
96 dissolution of LDH and formation of $Ca_5(PO_4)_3OH$ and $Ca(HPO_4) \cdot 2H_2O$ precipitates in
97 non-buffered solutions [12, 36]. MgFe- CO_3 LDH dissolved completely with formation of
98 $MgHPO_4 \cdot 3H_2O$ in 24h when exposed to very high P_i concentrations (> 1 M) at pH 7,
99 demonstrating that not only the pH but also the high P_i concentration could also stimulate
100 the dissolution of LDH. For P_i sorption at pH where the LDH dissolves, residual M_b
101 (hydr)oxides may form strong sorbents of P_i . Thus, P_i retention by LDHs not only comprise
102 anion exchange and surface complexation by the LDH, but may also comprise P_i sorption
103 to dissolution residues and precipitation processes, see Fig. 1.



104

105 **Figure 1. Schematic illustration of the phase changes and P_i sorption processes**
 106 **addressed in the study.**

107 The instability of the LDH may hamper regeneration and re-use of the LDH during P_i
 108 sorption, but to which extent is still unclear. Although P_i sorption to MgFe-LDH has been
 109 extensively studied due to its high sorption capacity compared with MgAl LDH [17, 37], its
 110 stability and mode of P_i sorption at pH and P_i concentrations in wastewater needs to be
 111 critically examined. In this study, we aim to assess the stability of the potential recyclable
 112 magnetic MgFe LDH sorbent as a function of pH and P_i concentration (Fig. 1). The
 113 investigation focus on quantification of LDH dissolution as a function of pH (especially at
 114 pH neutral) and P_i sorption combined with solid-state analysis of alteration in the MgFe
 115 LDH structure and formation of new phases during sorption.

116 **2. Materials and methods**

117 **2.1 Materials**

118 All chemicals were purchased from Sigma and directly used without further purification.

119 All sample solutions were prepared with ultrapure water (18.2 M Ω ·cm) (SI 1.1).

120 **2.2 Synthesis of Fe₃O₄@SiO₂-Mg₃Fe LDH**

121 The Fe₃O₄@SiO₂-Mg₃Fe LDH composite (referred to as composite in this paper) was
122 synthesized by previous reported methods [35, 37, 38]. For experimental details, see SI
123 (1.2).

124 **2.3 Phosphate sorption and Fe₃O₄@SiO₂-Mg₃Fe LDH dissolution**

125 **Experiment 1 (Exp. 1)** The kinetics of P_i sorption and LDH dissolution from the
126 composite was followed by monitoring the P_i and Mg concentrations in pH buffered
127 suspensions. The composite (1 g/L) was dispersed in an aqueous solution of 10 mM KNO₃
128 electrolyte, 11.92 g/L HEPES buffer and 50 mg P/L added as KH₂PO₄. The pH of the
129 solution was buffered by HEPES at pH 7.2 throughout the experiment. At various times (1,
130 2, 5, 10, 30 min, 1, 2, 3, 6, 12 and 24 h), 2 mL of the suspension was sampled and filtered
131 through a 0.2 μ m regenerated cellulose filter (Mikrolab Aarhus A/S) and the filtrate stored
132 at 4 °C until determination of P_i and Mg. In a separate experiment, the pH buffering effect
133 of the composite was illustrated by preparing the same suspension as above but without
134 adding HEPES buffer. The pH of the suspension was measured at 1, 2, 5, 10, 30 min, 1, 2,
135 3, 6, 12 and 24 h.

136 **Experiment 2 (Exp. 2)** In this experimental series dissolution and P_i sorption of the
137 composite as function of solution P_i concentration and pH was studied. The experiments
138 were carried out as described for Exp. 1, but with initial P_i concentrations at 1, 2, 5, 10, 20,
139 50, 100, 200 and 300 mg P/L. No HEPES buffer was used, but suspension pH was
140 controlled at 5, 7, 9 and 11 by addition of HCl or NaOH solution (SI 1.3). All suspensions
141 were placed on a shaking table at 250 rpm for 24 h once the pH had stabilized.

142 **Experiment 3 (Exp. 3)** This experiment was similar to Exp. 2 but only P_i concentrations of
143 10 mg P/L was tested to avoid side reactions due to high P_i concentrations and to operate
144 with P_i concentrations typical for wastewater influents [3]. In addition equilibration time
145 was reduced to 1 h to have short contact time for real waste water treatment [39]. The pH of
146 the suspensions was controlled at pH 5, 6, 7, 8, 9, 10 or 11 (± 0.1) by addition of HCl or
147 NaOH solution (SI 1.3).

148 The solid phases were collected by an NdFeB magnet after P_i sorption and dried at 60°C
149 overnight, while the solutions were filtered through 0.2 μm regenerated cellulose filter
150 (Mikrolab Aarhus A/S) and stored at 4 °C. P_i and Mg concentrations were determined in all
151 the filtrates. P_i concentrations in solution were measured by the Molybdenum-Blue method
152 using a ultraviolet–visible spectroscopy (UV-Vis) and Mg was determined by Atomic
153 Absorption Spectroscopy (AAS). The content of Mg in the solids after sorption was
154 determined with ICP. For further information about solid state characterization techniques,
155 see SI 1.5.

156 **2.4 Solubility calculations**

157 Visual MINTEQ equilibrium speciation software ver 3.1 was used to estimate
158 supersaturation of solutions with respect to magnesium phosphates, such as $\text{Mg}_3(\text{PO}_4)_2$,
159 MgHPO_4 , $\text{Mg}(\text{H}_2\text{PO}_4)_2$. The thermodynamic database supplied with the software was used
160 (SI 1.6).

161 **2.5 P_i sorption and phase distribution versus pH and P_i concentration.**

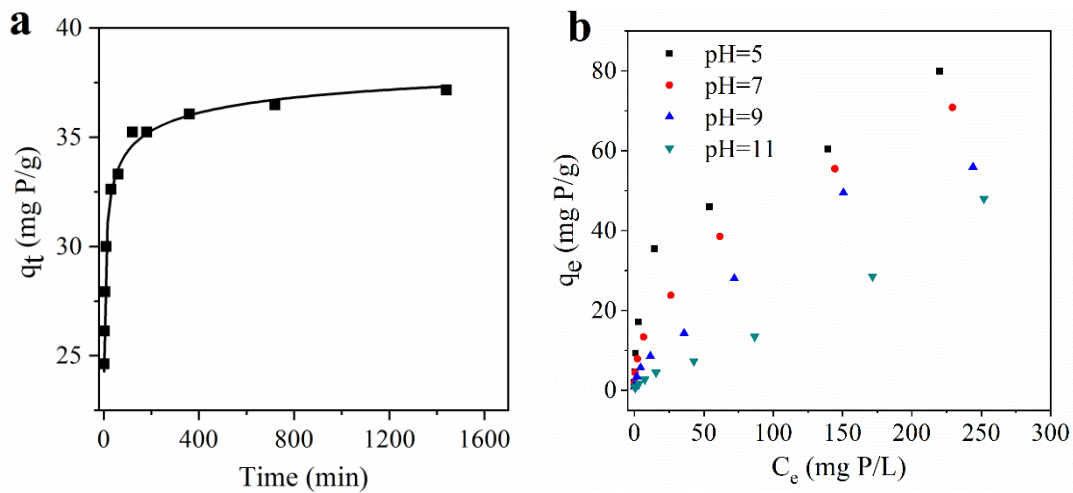
162 All sorption data from Exp. 2 were fitted to produce a "sorption surface" with sorbed P_i
163 versus pH and equilibrium P_i concentration using the nonlinear surface fit function in
164 Origin 9.6 software using a Rational 2D Function [40]. Fitting parameters are listed in
165 Table S8.

166 The extent of P_i sorption in form of magnesium phosphate precipitates was estimated based
167 on estimations of mass of LDH derived from PXRD traces of samples taken after P_i
168 sorption. First, Rietveld profile-fitting in X'pert Highscore Plus software [41] with the
169 Pseudo Voigt profile function was used to analyse the PXRD data (SI 1.5.3) to determine
170 the amount of LDH and Fe_3O_4 in crystalline phases after P_i sorption (Exp. 2). Next, the
171 theoretical concentration of Mg released was calculated (SI 5, Eq. S10), assuming that the
172 Mg release is proportional to the amount of dissolved LDH. Last, the theoretical Mg release
173 was compared with the observed Mg concentration after P_i sorption, and the difference
174 between these two values was then allocated to Mg in magnesium phosphate precipitates
175 (Details in SI5). Estimates of the fraction of P_i in magnesium precipitates (Eq. S11) was
176 added to the "sorption surface" using OriginPro 2019 software.

177 **3. Results and discussion**

178 In this study, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Mg}_3\text{Fe}$ LDH composite was first synthesized and
 179 characterized in detail (SI 2), followed by P_i sorption and dissolution experiments at
 180 controlled pH, ranging from 5 to 11, with exposure to various solution P_i concentrations
 181 (1~300 mg P/L). Different solid state characterization techniques, such as PXRD, TEM,
 182 ^{57}Fe Mössbauer spectroscopy and ^{31}P MAS NMR were used to characterize the composite
 183 before and after P_i sorption. LDH dissolution in terms of Mg release and P_i sorption was
 184 correlated with solid phase analysis to conclude on dissolution, P_i phase distribution and
 185 modes of P_i sorption versus pH and P_i concentration.

186 3.1 Phosphate sorption to $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Mg}_3\text{Fe}$ LDH

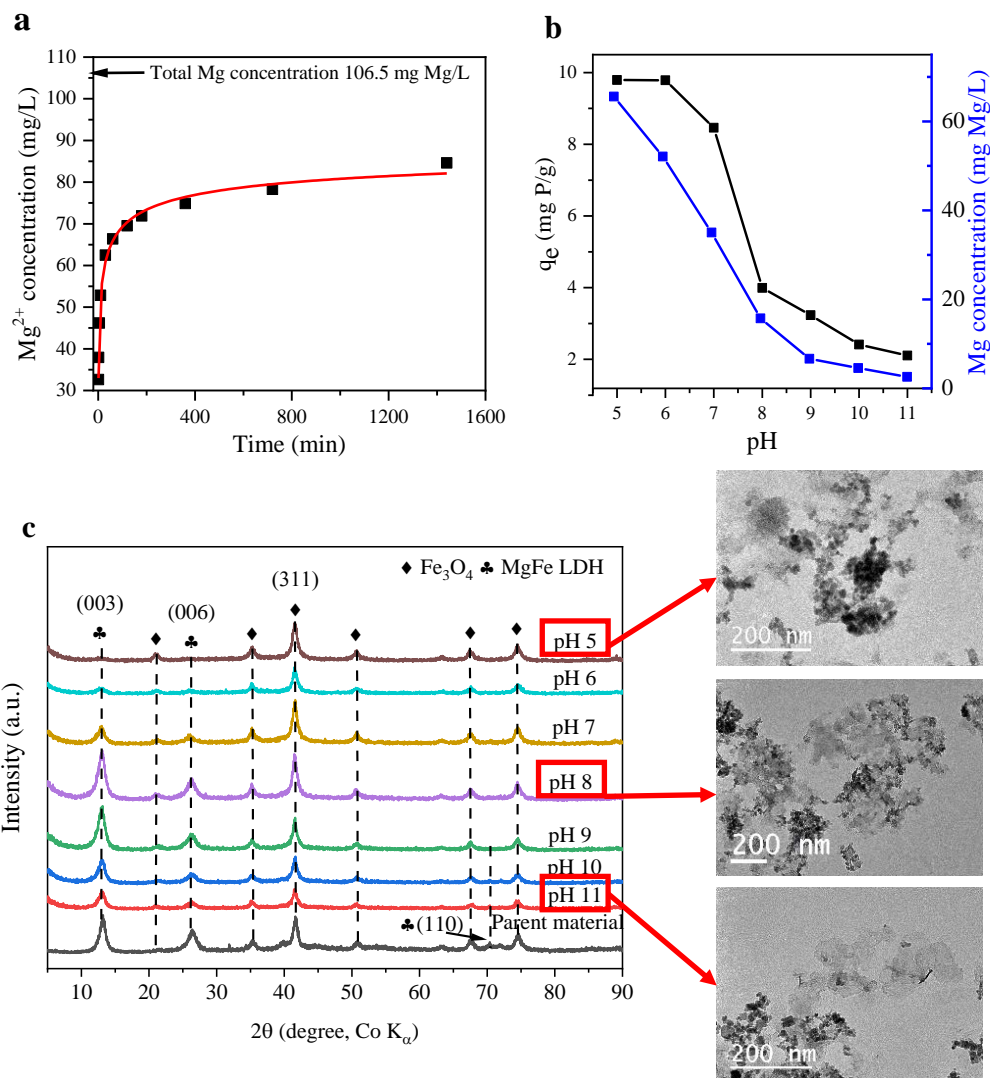


187

188 **Figure 2. (a) Kinetics of P_i sorption (q_t) to $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Mg}_3\text{Fe}$ LDH and the**
 189 **corresponding fit by pseudo second-order kinetics (Eq. S4) (sorbent concentration 1**
 190 **g/L; 50 mg P/L; pH 7.2, 25 °C). (b) Isotherms for P_i sorption (q_e) versus solution P_i**
 191 **concentration (C_e) at different pH values (sorbent concentration 1 g/L, contact time 24**
 192 **h, Exp. 2).**

193 After mixing with the pH buffered P_i solution (Exp. 1), the composite showed fast P_i
194 sorption, which was well fitted by pseudo second-order kinetics (Eq. S4, R^2 0.999) with a
195 rate constant of 5.4×10^{-3} g/mg P min⁻¹. Equilibrium was reached within 120 min (Fig. 2a),
196 demonstrating relatively fast P_i removal. Sorption isotherms (Exp. 2) showed that P_i
197 bonding to the composite was of the Freundlich type (Eq. S5, R^2 0.979~0.999 Table S2)
198 with no clear sorption maxima (Fig. 2b). The P_i sorption capacity decreased remarkably
199 with increasing pH from 5 to 11, with 3 to 8 times less sorption at pH 11 than pH 5
200 depending on the solution P_i concentration (Fig. 2b and 3b) which is similar with other
201 observations in previous studies on LDHs P_i sorbents [42-44].

202 **3.2 Dissolution of $Fe_3O_4@SiO_2$ -MgFe LDH during P_i sorption**



203

204 **Figure 3. (a) Kinetics of Fe₃O₄@SiO₂-Mg₃Fe LDH dissolution measured as the**
 205 **concentration of Mg in the solution during P_i sorption (Exp. 1). (b) P_i adsorbed and**
 206 **Mg released from the Fe₃O₄@SiO₂-Mg₃Fe LDH at different pH values (Exp. 3). (c)**
 207 **PXRD patterns of the solids after sorption at different pH and the corresponding**
 208 **TEM images of the solids after Exp. 3 at pH 5, 8 and 11.**

209 In Exp. 1, when the composite was dispersed in water, pH increased from 7.0 to 9.3 within
 210 3 h (Fig. S6). This is attributed to release of hydroxide ions during dissolution of the LDH

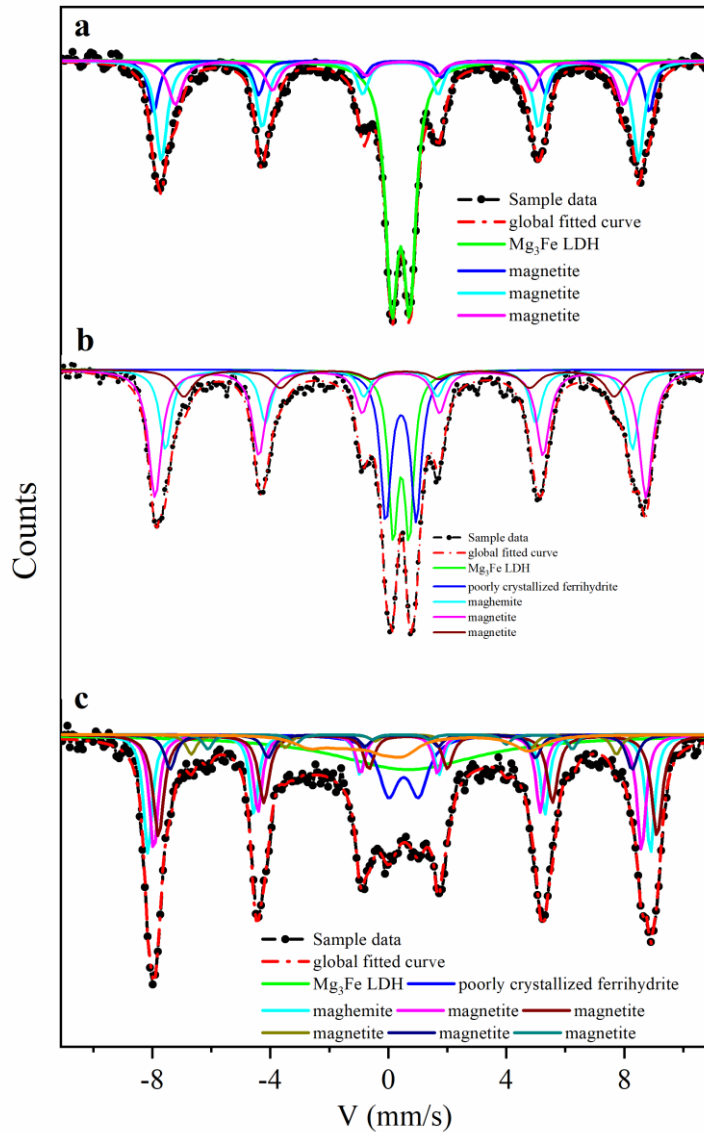
211 (Eq. 1) [31, 45-47]. However, when pH is kept constant at pH 7.2 in HEPES buffered
212 solution, substantial parts of the Mg₃Fe LDH in the composite dissolves as more than 60 %
213 of the total Mg dissolves within 60 min (Fig. 3a). The kinetics of Mg release was well fitted
214 by pseudo second-order kinetic resulting in a kinetic constant of 2.6×10^{-3} L/mg min⁻¹ (Eq.
215 S6; R² 0.999), demonstrating fast dissolution at pH 7.2. This is in line with our previous
216 study of Zn doped MgFe LDH, which showed a similar fast dissolution kinetics (k =
217 2.53×10^{-3} L/mg min⁻¹) at pH 7 [46]. The PXRD data show a dramatic decrease in intensity
218 of the Mg₃Fe LDH reflections, compared with the LDH kept at pH 9.3 (Fig. S8). In
219 conclusion, both the solubility and the structural degradation of the LDH confirms that the
220 composite is unstable at pH 7.2 and dissolves rapidly.

221 In Exp. 3, the Mg₃Fe LDH stability was investigated in non-buffered solutions as function
222 of constant pH ranging between 5 and 11 at a constant initial P_i concentration of 10 mg P/L.
223 Fig 3b shows a dramatic decrease of P_i sorption with increasing pH. At pH 5, almost 100 %
224 of the P_i added is removed, while at pH 11 sorption is down to 20 %. In addition, the P_i
225 sorption is followed by a concurrent release of Mg depending on pH. More than 50 % of
226 total Mg was released at pH 5 but less than 3 % Mg released at pH 11 within 1 h. PXRD of
227 the composite after P_i sorption at pH > 8 (Fig. 3c) showed that the LDH basal (003)
228 reflection has a relative intensity of 96 % compared with the pristine composite (Fig. S2a),
229 demonstrating that the composite is stable at pH > 8 at low P_i concentration (10 mg P/L), in
230 agreement with our recent study [35]. However, at lower pH of 7, 6 and 5 the relative
231 intensity of the basal reflections dropped to 37%, 20% and 0 % of the initial values,
232 respectively (Fig. 3c). TEM images of the sorbents after P_i sorption (Fig. 3c) reveal a full
233 destruction of the LDH and formation of amorphous material at pH 5, while at pH 8 more

234 LDH remained, but still with some amorphous material present compared with the pristine
235 LDH (Fig. S2). At pH 11, the intact Mg_3Fe LDH is present. In addition, the LDH platelet
236 thickness estimated from the width of the (003) reflections was in the range 6.9-7.1 nm for
237 $pH > 8$, and decreased to 5.3 nm, 4.6 nm and 0 nm when P_i had sorbed at pH 7, 6 and 5,
238 respectively (Table S3), due to dissolution. Thus, Mg_3Fe LDH dissolves at acidic to
239 intermediate pH, while it is stable at high pH.

240 The combined effect of pH and P_i sorption on LDH dissolution is depicted in Fig. S10,
241 showing that about 90, 80 and 40 % of total Mg has dissolved at the highest P_i sorption at
242 pH 5, 7 and 9, respectively. PXRD of the residual solids after P_i sorption (Fig. S11 and Fig.
243 S12) showed a dramatic decrease in intensity of the LDH reflections in the samples from
244 pH 5 and 7 (Fig. S11a, b; Fig. S2a), confirming the instability of the LDH structure at acid
245 and neutral pH [35, 46]. Furthermore, the (003) and (110) reflections of the Mg_3Fe LDH
246 phases weakened or disappeared when initial P_i concentrations exceeded 50 mg/L at higher
247 pH, such as pH 9 and 11, revealing that exposure to relative high P_i concentrations also
248 stimulated LDH dissolution (Fig. S11c, d and Fig. S12) [35, 48]. Finally, magnetization
249 data shows that the fraction of magnetic materials decreases from 66 to 45 wt% in the
250 composite after P_i sorption at pH 5 (Fig. S13a and b, Eq. S9).

251 **3.3 Residual phase formed at pH 5**



252

253 **Figure 4. Mössbauer spectra of $\text{Fe}_3\text{O}_4@SiO_2\text{-Mg}_3\text{Fe}$ LDH before P_i sorption measured**
 254 **at 140K (a), after P_i sorption (Exp. 3) (at pH 5 with initial P_i concentration at 10 mg**
 255 **P/L for 1h) measured at 125K (b) and 25K (c) (Full lines correspond to fitting,**
 256 **parameters listed in Table S4).**

257 The ^{57}Fe Mössbauer spectrum of the pristine composite at 140 K (Fig. 4a) shows one sharp
 258 quadrupole doublet with center shift (δ) 0.42 mm/s and quadrupole splitting (Δ) of 0.61
 259 mm/s which is attributed to octahedrally coordinated Fe^{3+} in the Mg_3Fe LDH [49]. The 125

260 K spectrum of the composite after P_i sorption (Fig. 4b) displays two quadrupole doublets
261 with the same δ of 0.45 mm/s and different Δ of 0.54 mm/s and 1.03 mm/s, respectively.
262 The Δ of 0.54 mm/s corresponds to the presence of Mg_3Fe LDH, while the Δ of 1.03 mm/s
263 corresponds to presence of Fe^{3+} in poorly crystalized ferrihydrite [50]. The 25 K spectrum
264 (Fig. 4c) confirms this identification with a contribution of a single-line with δ of 0.68
265 mm/s and a magnetic broad sextet with Δ of 2 mm/s and very low magnetic field of 132
266 kOe attributed to poorly crystalized ferrihydrite [50].

267 The high sorption capacity at low pH (79.5 mg P/g in Fig. 1b) is in agreement with the high
268 sorption capacity for ferrihydrite at low pH [51-54]. Thus, we estimate the obtained poorly
269 crystalized ferrihydrite has a P_i sorption capacity around 344 mg P/g (details in SI 3), which
270 is much higher than common values (34~56 mg P/L) reported for ferrihydrite [54, 55]. We
271 attribute this high sorption capacity to the possible formation of amorphous strengite
272 ($FePO_4$) [56, 57] as the Fe:P ratio is close to 1:1. Apparently, extensive Mg dissolution
273 causes formation of ultra-small ferrihydrite particles, leading to a strengite type product
274 [58].

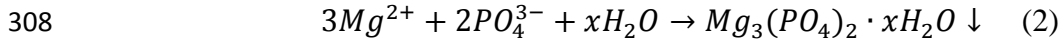
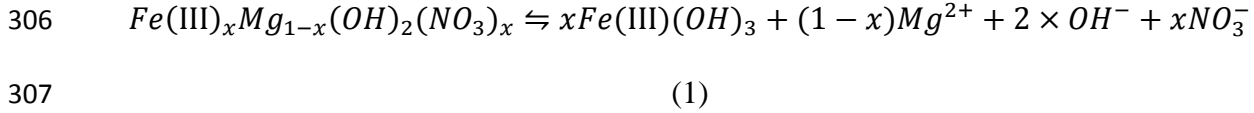
275 **3.4 Precipitation of magnesium phosphates at high pH**

276 In Exp. 2, although the composite did not release more than about 40% of total Mg into
277 solution at pH 9 at an initial P_i concentration of 300 mg P/L (Fig S10), the LDH structure
278 was almost destroyed as seen from the PXRD pattern (Fig. S11c). At pH 11, there was
279 barely any Mg release to solution (Fig. S9), while the relative intensity of the Mg_3Fe LDH
280 (003) and (110) peaks decreased to 26 % and 59 % of the intensity of the pristine composite,
281 respectively (Fig. S11d, Fig. S12), reflecting substantial dissolution of the LDH phase.

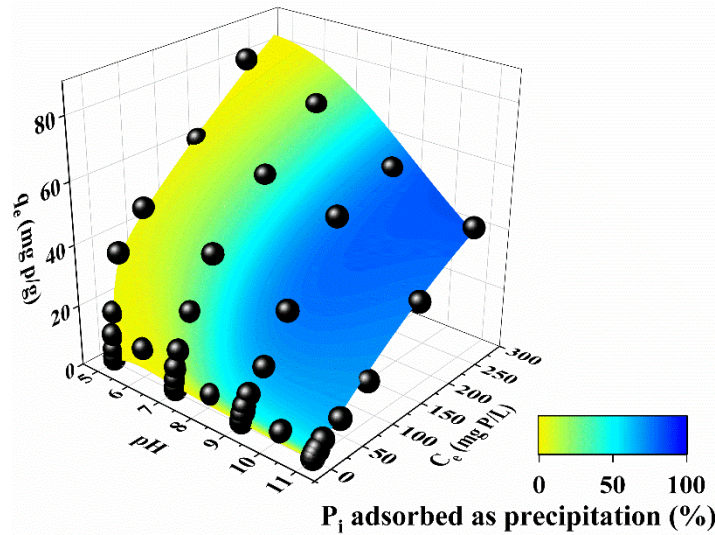
282 According to the previous studies of MgFe-CO₃ LDH [48], precipitation of magnesium
283 phosphates is therefore likely to take place. In order to test this, the solids after P_i sorption
284 at pH 11 and initial P_i concentration of 300 mg P/L were examined by PXRD without prior
285 washing (Fig. S14). This test confirmed the partial dissolution of the Mg₃Fe LDH phase
286 seen from the decrease in intensity of basal reflections. Also, the size of crystallite domains
287 of the Mg₃Fe LDH phase along the ab-plane and c-axis was 33 % and 66 % smaller after P_i
288 sorption than before as determined from peak broadening (Eq. S3; SI 2). Solid-state ³¹P
289 MAS NMR spectroscopy (Fig. S15) of the LDH after P_i sorption at pH 9 and 11 showed
290 the presence of narrow resonance with $\delta(^{31}\text{P}) = 2.5(2)$ ppm and $3.9(2)$ ppm at pH 9 and pH
291 11, respectively, demonstrating formation of an amorphous magnesium phosphate phase
292 [35]. The Mg-P precipitate had a molar Mg/P ratio in the Mg-P precipitates of 1.4 (SI 5),
293 which is in good agreement with formation of Mg₃(PO₄)₂. Thus, at high pH and elevated P_i
294 concentrations LDH dissolves and magnesium phosphates precipitate.

295 Visual MINTEQ was used to compute supersaturation with respect to magnesium
296 phosphates using the measured solution Mg and P_i concentrations at different pH (Fig. S17).
297 No magnesium phosphates form at pH < 6, but when pH is increased to 7, MgHPO₄·3H₂O
298 precipitate at high Mg and P_i concentrations, while Mg₃(PO₄)₂ precipitate at pH > 8 at high
299 P_i concentration. When pH is further increased to 9, Mg₃(PO₄)₂ precipitate at P_i
300 concentrations above 62.5 mg P/L, which is in line with the observations in Fig. S10 and
301 S11c. When pH increased to 11, Mg₃(PO₄)₂ precipitate even at low P_i concentrations (1 mg
302 P/L). Thus, VMINTEQ calculations confirm that magnesium phosphates precipitate at high
303 pH and high P_i concentrations with Mg₃(PO₄)₂·8H₂O as a likely phase. Hence, at

304 intermediate to high pH, P_i may also be retained due to the dissolution-precipitation
 305 reaction [32].



309 **3.5 P_i sorbed to $Fe_3O_4@SiO_2$ - Mg_3Fe LDH versus pH and equilibrium P_i concentration**

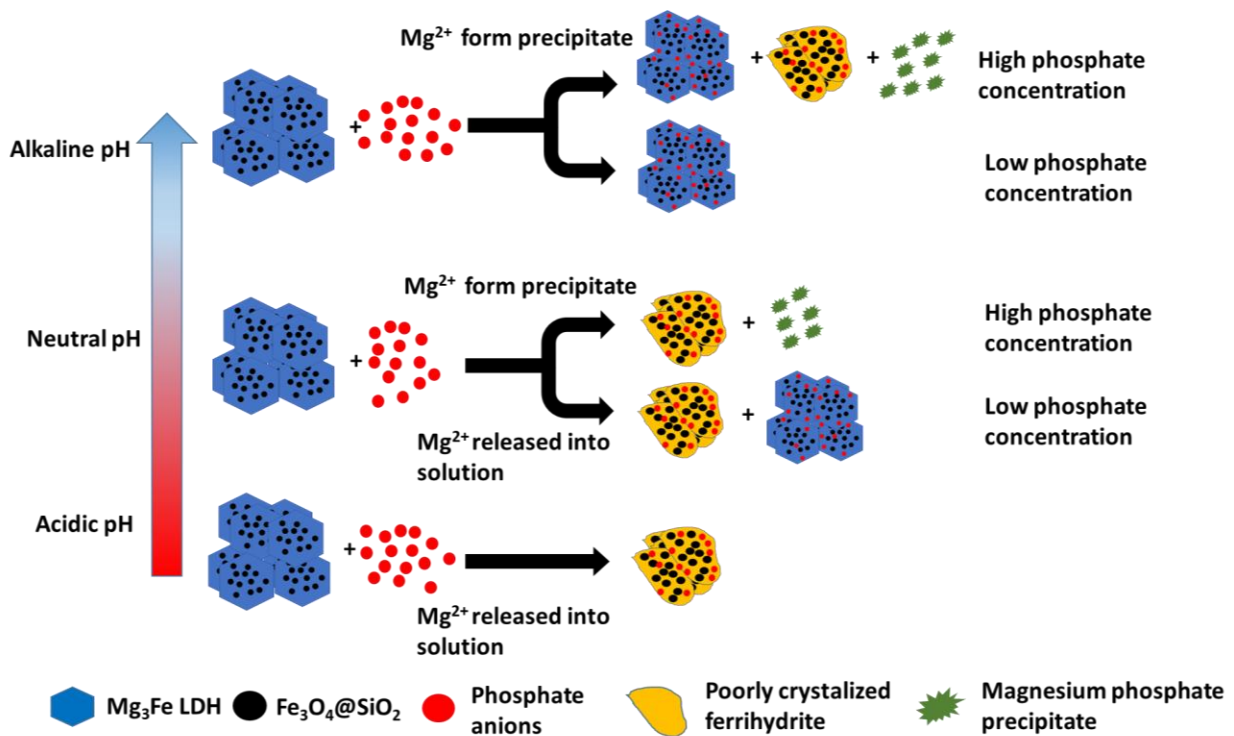


310
 311 **Figure 5. Sorbed P_i (black dots) to $Fe_3O_4@SiO_2$ - Mg_3Fe LDH as a function of pH and**
 312 **P_i solution concentration (Exp. 2 and 3; SI 5) with Rational 2D fit. The colour bar**
 313 **denotes the estimated percentage (%) of P_i sorbed due to precipitation.**

314 Our investigation shows that P_i sorption by $Fe_3O_4@SiO_2$ - Mg_3Fe LDH comprises at least
 315 three reactions: P_i bonding to iron hydroxides (ferrihydrite), bonding to LDH and
 316 precipitation of magnesium phosphates. By fitting the P_i sorption data with the Rational 2D
 317 function ($R^2 = 0.99$), a sorption surface (Fig. 5) can be produced to help estimate P_i sorption

318 versus pH and equilibrium P_i concentration. The colour map shows that barely no P_i was
319 removed by precipitation at acid and neutral pH (Fig. 5). When pH increased to 9, at least
320 40 % of sorbed P_i was present in magnesium phosphates at P_i concentrations > 50 mg P/L,
321 further increasing at higher pH and P_i concentrations.

322 We propose a set of sorption pathways for P_i bonding to the composite (Fig. 6). At acidic
323 pH, the LDH is readily and fully dissolved. Despite high Mg concentrations in solution, the
324 solubility of magnesium phosphates does not exceed saturation and hence P_i is adsorbed
325 to the amorphous poorly crystallized ferrihydrite. At neutral pH, the LDH only partially
326 dissolves. Hence, P_i is sorbed on the remaining LDH as well as to the poorly crystallized
327 ferrihydrite; at higher P_i concentrations, P_i is also retained due to precipitation of
328 magnesium phosphates. Finally, at alkaline pH where the LDH phase has its highest
329 stability, Mg_3Fe LDH is the primary sorbent of P_i at low P_i concentration. However, at
330 higher P_i concentration, the Mg_3Fe LDH phase is not stable and magnesium phosphates
331 precipitate is the main sorption pathway.



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Figure 6. Pathways for P_i sorption to $Fe_3O_4@SiO_2$ - Mg_3Fe LDH at various pH and P_i concentrations.

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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 Recent study of P_i sorption to $MgFe-NO_3$ LDH showed precipitation of amorphous magnesium phosphate precipitate at a solution P_i of about 100 mg P/L at pH 7.4 [35]. The solubility of LDHs decrease with the divalent cation in the order $Mg^{2+} > Mn^{2+} > Co^{2+} \approx Ni^{2+} > Zn^{2+}$, while for the trivalent cation the order is $Fe^{3+} > Al^{3+}$ [32]. Hence, many Fe^{3+} containing LDHs have higher or equal solubility as the MgFe-LDH. Most stable LDHs would be of the type with Co^{2+} or Ni^{2+} as divalent cation [59]. However, these compounds are not environmentally friendly. Solubility and dissolution kinetics may be decreased using larger particles and using carbonate interlayered forms rather than forms with

346 monovalent anions [60-62]. On the other hand, the presence of complexing agents in
347 solution such as humic matter will increase solubility [63].

348 Although LDHs are seen as promising material for treatment of municipal wastewater [64],
349 the significant dissolution of LDHs filter material during the sorption process at neutral pH
350 limits its practical application as wastewater has pH 6.5~8.5 [34]. Vast amounts of Mg^{2+}
351 ions could be released to the environment in a scaled-up application, which would increase
352 water hardness and block the filters and pipes due to formation of precipitates. In addition,
353 the loss of relative expensive MgFe LDH materials would also increase the cost of
354 wastewater treatment. Furthermore, high P_i concentrations in wastewater would also
355 stimulate the dissolution of LDHs at higher pH resulting in formation of precipitates. Thus,
356 the widely reported LDH regeneration and P recovery strategy, where adsorbed P is
357 extracted with alkali solution and the LDH re-used for P sorption, would be challenged [15,
358 65].

359 **4. Conclusions**

360 In this study, we demonstrate the MgFe LDH has poor stability and dissolves in the pH
361 range of wastewater (pH 6~8). In addition to the pH controlled LDH solubility, high P_i
362 concentrations causes LDH dissolution even at high pH, by formation of magnesium
363 precipitates. ^{57}Fe Mössbauer spectroscopy confirms the formation of poorly crystalized
364 ferrihydrite at acid pH while ^{31}P MAS NMR spectroscopy demonstrate the precipitation of
365 magnesium phosphate at high pH and high P_i concentration. A combined analysis of
366 solubility and PXRD data indicate that precipitates is the main sorption pathway at high pH
367 and high P_i concentration. The main sorption pathways are summarized as sorption by

368 ferrihydrite at acid pH, sorption by ferrihydrite and LDH at neutral pH and high pH with
369 low P_i concentration, and precipitation of magnesium phosphates at high pH and high P_i
370 concentration. This study demonstrates that LDHs are intrinsically unstable from pH 5 ~ 11
371 when used for P_i sorption which hence prevents their use as recyclable sorbents. Future
372 application of magnetic LDHs as recyclable sorbents is only possible if the stability of the
373 LDH component can be substantially increased.

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380 **Appendix supplementary data**

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

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