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1 **The effect of Zr(IV) addition on the phosphate removal properties of MgAl-LDH**

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21 **Abstract**

22 Recovery of phosphate from wastewater represents a sustainable alternative to phosphate
23 rock, a limited resource. Magnesium aluminum layered double hydroxides (MgAl-LDH), are
24 promising sorbents due to their high phosphate removal capacity by ion-exchange (26-124 mgP/g).
25 Furthermore, an increased sorption capacity has been reported by the addition of zirconium (Zr(IV))
26 into the LDH lattice. However, ambiguity exists especially in relation to the incorporation of Zr and the
27 stability of the MgAl-LDH. To understand how Zr(IV)-addition affects the phosphate sorption
28 properties (both capacity and mechanism) on the atomic level, solid state multi-nuclear NMR
29 spectroscopy was combined with complimentary characterization techniques to study a series of
30 MgAl-LDH with Zr to Al ratios of 1:9 and 1:1, which had the Mg to (Al+Zr) ratio fixed at 2:1. The
31 LDH were synthesized by coprecipitation and subsequently aged or hydrothermally treated to improve
32 the crystallinity (particle size). No evidence of Zr(IV) incorporation in the LDH was observed, instead
33 Zr was present as Zr(IV)-hydroxide (X-ray amorphous) and crystalline Zr(IV) oxide after aging and
34 hydrothermal treatment, respectively. The segregation of Zr(IV) and resulting lower Al content in the
35 MgAl-LDH decreased the phosphate sorption capacity from 45-54 to 16-20 mgP/g. Zr (hydr)oxide
36 impurities contributed with less than 5 mgP/g. Moreover, ³¹P MAS NMR spectroscopy quantified
37 showed that the MgAl-LDH contribute to less than 60% of the total P removal capacity.

38

39 **Keywords:** Layered double hydroxides; phosphate; sorption; environmental remediation; solid state
40 NMR spectroscopy

41 **1. Introduction**

42 The global phosphorous (P) challenge receives increasing attention since phosphorous in
43 the form of orthophosphate ($H_xPO_4^{(3-x)-}$), is a fertilizer vital for global food security ([Cordell et al.,](#)
44 [2009](#); [Cordell and White, 2014](#); [Jupp et al., 2021](#); [Reitzel et al., 2019](#)). Traditionally, phosphate has
45 been extracted from phosphate rock ([Cordell et al., 2009](#); [Jupp et al., 2021](#)), a non-renewable resource,
46 and depletion is in the worst-case predicted within the next century ([Jupp et al., 2021](#); [Walan et al.,](#)
47 [2014](#)). A promising alternative is the recovery of phosphate accumulated in municipal and industrial
48 wastewater at wastewater treatment plants ([Bunce et al., 2018](#); [Egle et al., 2016](#)). Current recovery
49 approaches include the use of sludge and struvite ($NH_4MgPO_4 \cdot 6H_2O$) as a fertilizer, whereas vivianite
50 ($Fe_3(PO_4)_2 \cdot 8H_2O$) is an emerging technology ([Hall et al., 2020](#); [Lamastra et al., 2018](#); [Rahman et al.,](#)
51 [2014](#); [Talboys et al., 2016](#); [Wilfert et al., 2015](#)). The use of selective and ideally reusable phosphate
52 (ad)sorbents is a promising, but less developed technology ([Wu et al., 2020](#)). Layered double
53 hydroxides (LDH) have great potential due to a high affinity for orthophosphate and ion-exchange
54 capacity (26 - 124 mgP/g), depending on, e.g., the phosphate speciation ($H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}) and
55 LDH composition (Table S1) ([Ashekuzzaman and Jiang, 2014](#); [Luengo et al., 2017](#); [Lundehøj et al.,](#)
56 [2019a](#); [Lundehøj et al., 2019b](#); [Novillo et al., 2014](#)). Phosphate can subsequently be recovered and the
57 LDH reused or the phosphate loaded LDH can directly be applied as a fertilizer ([Bernardo et al., 2018](#);
58 [Borges et al., 2019](#); [Everaert et al., 2016](#)).

59 LDH have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A_{x/n}^{n-}) \cdot yH_2O$ (x typically 0.2 -
60 0.33), whereas M(II) and M(III) are divalent and trivalent cations and A^{n-} is a charge compensating
61 anion located in the interlayer together with water ([Duan and Evans, 2005](#); [Forano et al., 2006](#);
62 [Pushparaj et al., 2015](#)). Subsequently, the LDH will be abbreviated as M(II)M(III)-LDH. Especially,
63 the charge density (x), intercalated anion (A^{n-}), particle size, pH, and competing anions are important
64 parameters related to the removal capacity and stability of the LDH.

65 For environmental applications, mainly the non-toxic MgFe -, CaAl -, CaFe -, and MgAl-
66 LDH are relevant ([Al Jaber et al., 2019](#); [Ashekuzzaman and Jiang, 2014](#); [Bekele et al., 2019](#); [Kim et al., 2020](#); [Luengo et al., 2017](#); [Lundehøj et al., 2019b](#); [Novillo et al., 2014](#)). MgAl-LDH is the most
67 promising for phosphate removal, since the other LDH are highly unstable upon phosphate exposure
68 ([Al Jaber et al., 2019](#); [Bekele et al., 2019](#); [Kim et al., 2020](#)).

70 To enhance the function of LDH such as the phosphate sorption capacity, modification of
71 LDH with high-valent cations, especially Zr(IV) has been proposed. The rationale is that the Zr(IV)
72 will increase the cation layer charge and thereby the anion exchange capacity as Zr(IV) is speculated
73 to replace Al(III) ([Arias et al., 2018](#); [Chitrakar et al., 2010](#); [He et al., 2021](#); [Koilaraj and Kannan, 2010](#);
74 [Liu et al., 2014](#); [Miyachi et al., 2009](#); [Nowicki et al., 2016](#); [Poonosamy et al., 2018](#); [Velu et al., 1998](#);
75 [Wang et al., 2018](#); [Wang et al., 2017](#)). For example, incorporation of a Zr(IV) instead of a Al(III)
76 in the brucite layer would require one HPO_4^{2-} instead of half a HPO_4^{2-} for charge balance. This leads to
77 a higher anion-exchange capacity.

78 An increased P removal capacity has also been reported for Zr(IV) modified LDH as compared to the
79 corresponding M(II)M(III)-LDH in phosphate solution, seawater, and wastewater (Table 1). However,
80 most studies compare the P removal capacity of the Zr-modified LDH with the parent LDH, which has
81 carbonate as interlayer anion, c.f., Table 1. This suppresses the phosphate removal by the anion-
82 exchange pathway, due to the high affinity of the LDH for carbonate ([Forano et al., 2006](#); [Lundehøj et al., 2019b](#);
83 [Nuryadin et al., 2021](#)). Therefore, the increased phosphate removal capacity obtained by
84 addition of Zr can instead be explained by the co-presence of impurities such as Zr(IV) (hydr)oxides,
85 which also have a significant phosphate removal capacity (Table 1).

86 **Table 1.** Phosphate removal capacities (mgP/g) determined for Zr-doped LDH and the corresponding parent M(II)M(III)-LDH reported in literature and
 87 the current work. The chemical composition (M(II), M(III), anion) of the LDH, which was prepared by co-precipitation, the post synthesis treatment
 88 employed (aged or hydrothermal treated, HT), and the water medium tested (seawater, wastewater, phosphate solution) and the phosphate concentration(s)
 89 used (mgP/L). The P removal capacity for Zr(OH)₄ and ZrO₂ are given for a comparison. Finally, whether the conclusion was successful Zr doping into the
 90 LDH or not (yes/ no). RT = room temperature. HT = hydrothermal treatment. * = two phase system (M(II)M(III)-LDH and Zr-phase) purposely prepared.

Cations	Treatment	Anion	Solution (mgP/ L)	M(II)/(M(III)+Zr)	M(III):Zr	P removal (mgP/ g)	Zr in LDH layer?	References
Mg, Al	Aged (RT)	CO ₃ ²⁻	P enriched seawater	3	1	25	Yes	(Chitrakar et al., 2007)
	Aged (RT)	Cl ⁻	(0 - 0.33)	3	1	9	Yes	
	Aged (RT)	CO ₃ ²⁻		Not available	NA	1	NA	
	Aged (RT)	CO ₃ ²⁻	Phosphate	3	1	39	Yes	
	Aged (RT)	Cl ⁻	(1 - 10)	3	1	22	Yes	
	Aged (RT)	CO ₃ ²⁻	Phosphate (100)	3	1	50	Yes	
	Aged (RT)	Cl ⁻		3	1	30	Yes	
Zn, Al	Aged (65°C)	CO ₃ ²⁻	Phosphate (10 - 250)	2 - 4	2.5	25 - 91	Yes	(Koilaraj and Kannan, 2010)
	Aged (65°C)	CO ₃ ²⁻		2 - 4	NA	9 - 60	NA	
Mg, Al	Aged (RT)	CO ₃ ²⁻	P enriched seawater	4	1	18	No	(Miyachi et al., 2009)
	Aged (RT)	CO ₃ ²⁻	(0.33)	4	NA	1.3	NA	
	HT (120°C)	CO ₃ ²⁻		4	1	10	No	
	HT (120°C)	CO ₃ ²⁻		4	NA	0.6	NA	
Mg, Fe	Aged (RT)	CO ₃ ²⁻	P enriched seawater	2 - 4	1	15 - 27	No	(Chitrakar et al., 2010)
	Aged (RT)	Cl ⁻	(1 - 30)	Not available	NA	≈ 3	NA	
	Aged (RT)	CO ₃ ²⁻	Phosphate (100)	2 - 4	1	20 - 35	No	
	Aged (RT)	Cl ⁻		Not available	NA	≈ 50	NA	
Mg, Fe	Aged (80°C)	CO ₃ ²⁻	Phosphate (1 - 50)	Not available	2 - 0.5	35	No *	(Nuryadin et al., 2021)
	Aged (80°C)	CO ₃ ²⁻		Not available	NA	18	NA	
Mg, Al	Aging (RT)	CO ₃ ²⁻	Phosphate (5 - 200)	Not available	NA	70	NA	(Motandi et al., 2022)
	Aging (RT)	CO ₃ ²⁻		Not available	Not available	99	No *	
ZrO ₂	Not available	None	Seawater (0.33)	Not available	Not available	1 - 12	Not available	(Miyachi et al., 2009)
Zr(OH) ₄	Not available	None	Synthetic wastewater (10)	Not available	Not available	19 - 30	Not available	(Johir et al., 2016)
Zr(OH) ₄	Not available	None	Phosphate (7 - 114)	Not available	Not available	38	Not available	(Luo et al., 2017)
Mg, Al	HT (120°C)	Cl ⁻	Phosphate (18 - 224)	2	No Zr	45(2)	No Zr	This work
	Aging (80°C)	Cl ⁻		2	No Zr	54(2)	No Zr	
	HT (120°C)	Cl ⁻	Phosphate (18 - 224)	2	9	43(2)	No	This work
	Aged (80°C)	Cl ⁻		2	9	47(2)	No	
	HT (120°C)	Cl ⁻	Phosphate (18 - 224)	2	1	16(2)	No	
Aged (80°C)	Cl ⁻		2	1	20(2)	No		

91 NA, not applicable as Zr was not used during the synthesis.

93 Studies have also investigated the physical mixtures of MgAl-LDH and Zr-(hydr)oxide
94 with the goal to either prepare nano-sized particle (ad)sorbents as Zr-(hydr)oxide on the surface of
95 LDH can suppress crystal growth ([Nuryadin et al., 2021](#)) or to modify the layer charge by the
96 introduction of Zr(IV)-O²⁻ acid base pairs ([Motandi et al., 2022](#)). Here an increased P removal capacity
97 for a mixed system was also reported (Table 1).

98 Several studies have concluded a successful incorporation of Zr(IV) into the LDH.
99 However, the successful incorporation of Zr(IV) into the LDH structure was mainly based on the
100 analysis of low-quality powder X-ray diffractograms and/ or the qualitative variation of the M-M
101 distance derived from the (110) reflection ([Velu et al., 1998](#); [Wang et al., 2018](#)). Thus, the insertion of
102 Zr(IV) was, in part, concluded based on an expansion of the unit cell parameter *a* with increasing
103 Zr(IV) content in ternary M(II)AlZr-LDH ([Chitrakar et al., 2007](#); [Koilaraj and Kannan, 2010](#); [Shen et](#)
104 [al., 2011](#); [Velu et al., 1998](#); [Wang et al., 2018](#)). A slight reduction in interlayer spacing (7.9 to 7.8 Å)
105 based on visual inspection of PXRD data was ascribed to an increased charge of the cation layer for
106 NiAl-LDH with nitrate as interlayer ion, i.e. successful incorporation of Zr(IV) into the LDH ([Wang et](#)
107 [al., 2017](#)). However, for LDH with nitrate as interlayer ion, a lower Al³⁺ results in a decreased
108 interlayer spacing, as nitrate ion can be parallel to the cation layer ([Karthikeyan et al., 2021](#)). However,
109 a reduced Al content in a M(II)_{1-x}Al_x-LDH will give a similar structural trend. Thus, it is not possible to
110 distinguish between *i*) the incorporation of Zr(IV) into the LDH and *ii*) the formation of both MgAl-
111 LDH and a Zr (hydr)oxide phase only by PXRD and bulk chemical analyses.

112 In more rigorous studies, the use of advanced structural characterization techniques and in
113 depth data analyses have clearly shown, that Zr(IV) was not incorporated into the LDH, but instead a
114 mixture of LDH and Zr(OH)₄ (or ZrO₂) was obtained ([Intissar et al., 2003](#); [Miyachi et al., 2009](#)). For
115 example ([Intissar et al., 2003](#)) investigated the local environment of metal cations for a series of

116 $M(II)_{0.75}Al_{0.25-y}M(IV)_y(OH)_2(CO_3)_{(y+0.25)/2},nH_2O$ ($M(II) = Mg, Co$; $M(IV) = Sn, Zr$) LDH using X-ray
117 absorption spectroscopy (XAS) and Mössbauer spectroscopy combined with detailed data analysis.
118 This clearly confirmed that the first metal ion coordination sphere for both Zr(IV) and Sn(IV) was
119 dominated by M(IV)-M(IV) correlations, i.e., the formation of separate Sn(IV) and Zr(IV) phases.
120 Similarly, ([Miyachi et al., 2009](#)) showed that ZrMgAl-LDH synthesized by coprecipitation had the
121 same k^3 -weighted Zr-K edge as ZrO_2 in the extended X-ray absorption fine structure (EXAFS) spectra.
122 Additionally, zirconium oxide impurities are generally only observed after hydrothermal treatment
123 above approximately $120^\circ C$ ([Chitrakar et al., 2007](#)), an approach usually employed to increase the
124 LDH particle size and thereby stability ([Pushparaj et al., 2015](#)). Such impurities were not observed,
125 when the LDH was aged below $100^\circ C$, a more common post synthesis treatment (Table 1). However,
126 amorphous Zr phases such as $Zr(OH)_4$ or ZrO_2 may still be present and not observed by Powder X-ray
127 Diffraction (PXRD), the routine characterization method.

128 A suite of bulk and atomic level characterization methods is necessary to link the
129 phosphate removal capacity and pathways to the LDH properties (chemical composition, particle size,
130 etc.). For example, inductively coupled plasma (ICP) spectroscopy and PXRD provides information
131 about the bulk content and crystalline phases, respectively, whereas solid state NMR spectroscopy
132 (SSNMR) gives detailed insight into the atomic level structure of the LDH and (amorphous) impurities
133 and/ or other phases ([Nielsen, 2021](#)). SSNMR combined with PXRD, electron microscopy, and
134 elemental analysis is crucial to obtain detailed insight into the LDH composition and anion-exchange
135 properties ([Kim et al., 2020](#); [Lundehøj et al., 2019a](#); [Pushparaj et al., 2015](#)).

136 In contrast to previous studies, we have performed a detailed investigation on how Zr(IV)
137 addition affects the phosphate removal capacity and pathways for MgAl-LDH with chloride (Cl^-) as the

138 interlayer anion prepared by two common post-synthesis treatments (aging and hydrothermal
139 treatment). This provided detailed insight into the different phosphate removal pathways and their
140 relative contributions. Thus, our goal was to assess if Zr(IV) addition will improve the performance of
141 MgAl-LDH based sorbents with a view to reusability. This was obtained by combining conventional
142 phosphate sorption isotherm and kinetics experiments with characterization of the LDH before and
143 after phosphate exposure using PXRD, FT-IR, inductively coupled plasma - optical emission
144 spectrometry (ICP-OES), zeta (ζ) potential measurements, electron microscopy (SEM, TEM), and
145 multinuclear MAS NMR spectroscopy.

146

147 **2. Experimental section**

148 **2.1. Materials**

149 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$ purity), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$ purity), $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($\geq 99\%$
150 purity), NaOH ($\geq 97\%$ purity), NaCl ($\geq 99\%$ purity) and K_2HPO_4 ($\geq 98\%$ purity), purchased from
151 Sigma-Aldrich, and HCl ($\geq 37\%$) purchased from Fisher Scientific, were used for the synthesis and
152 sorption experiments without further purification.

153

154 **2.2. Methods**

155 **2.2.1. Sample preparation**

156 The metal- and alkaline salts were dissolved in decarbonated water prepared by boiling
157 milli-Q water with nitrogen (N_2) flow for ca. one hour and then cooled to 25-35 °C under a nitrogen
158 (N_2) flow before use. MgAl- and Zr doped MgAl-LDH were synthesized by coprecipitation at constant
159 pH using earlier reported procedures ([Chitrakar et al., 2007](#)) with the following modifications: 500 mL
160 of a metal ion solution containing Mg^{2+} , Al^{3+} , and Zr^{4+} with a total metal ion concentration of 0.6 M

161 and 500 mL of an alkaline solution containing 1.2 M NaOH and 0.6 M NaCl were prepared. For each
 162 sample, the individual metal ion concentrations and mole percent are given in Table 2. 400 mL of the
 163 metal solution was added at a rate of 1.33 mL/min using a titrator (905 Titrand®; Metrohm AG,
 164 Herisau, Switzerland) into a 1 L three-necked-round-bottom flask which already contained 100 mL of
 165 decarbonated water under magnetic stirring (600 - 800 rpm). Simultaneously, the alkaline solution was
 166 added to maintain the pH at 10.0(2) at a rate like that for the metal solution. All synthesis were
 167 performed under a N₂ flow to minimize carbonate impurities.

168
 169 **Table 2.** The absolute concentrations of the metal cation solutions (mol/L) used in the syntheses with
 170 the relative percentage of Mg, Al and Zr (mol%) in the parenthesis. Moreover, the metal ion
 171 composition (mol%) for Mg, Al, and Zr for the synthesized LDH and these LDH after phosphate

Sample	Synthesis conditions (mol/L) / (mol%)			Synthesized composition (mol%)			Composition after P exposure (mol%)		
	Mg	Al	Zr	Mg	Al	Zr	Mg	Al	Zr
MgAl-A	0.4 (66.7)	0.2 (33.3)	0 (0)	66.3(2)	33.7(1)	n. a.	65.5(1)	34.5(1)	n. a.
MgAl-HT	0.4 (66.7)	0.2 (33.3)	0 (0)	66.0(1)	34.0(1)	n. a.	65.7(3)	35.2(1)	n. a.
Zr0.1-A	0.4 (66.7)	0.18 (30.0)	0.02 (0.03)	66.7(1)	30.9(1)	2.3(1)	67.0(2)	31.9(1)	1.1(1)
Zr0.1-HT	0.4 (66.7)	0.18 (30.0)	0.02 (0.03)	68.6(1)	28.8(1)	2.5(1)	66.9(1)	31.8(1)	1.3(1)
Zr0.5-A	0.4 (66.7)	0.1 (16.7)	0.1 (16.7)	70.1(1)	18.6(1)	11.3(1)	68.3(1)	19.4(1)	12.3(2)
Zr0.5-HT	0.4 (66.7)	0.1 (16.7)	0.1 (16.7)	74.8(1)	19.7(1)	5.5(1)	72.6(1)	20.6(1)	6.8(1)
Zr(OH) ₄	0 (0)	0 (0)	0.2 (100)	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.
ZrO ₂	0 (0)	0 (0)	0.2 (100)	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.

172 exposure. n. a. = not applicable.

173
 174 After addition of the metal- and alkaline solutions, the obtained solids were isolated by
 175 centrifugation (10.000 rpm, 10 min) using a Sigma Laboratory Centrifuge (2-16P) and then roughly
 176 divided into two batches: the first batch was redispersed into 350 mL of decarbonated water and aged
 177 at 80°C in a 500 mL three-necked-round-bottom flask under reflux and magnetic stirring for 16 h. The

178 second batch was redispersed into decarbonated water (350 mL) and subsequently hydrothermally
179 treated in multiple 70 mL Teflon® lined steel autoclaves (ca. 2/3 filled) for 16 h at 150°C in a Binder
180 GmbH oven. Subsequently, both batches, were washed with 40 mL deionized water in 50 mL conical
181 centrifuge tubes (Sarstedt, 114×28 mm) and shaken thoroughly followed by removal of the supernatant
182 after centrifugation (10.000 rpm, 10 min). The washing was repeated thrice. Finally, zirconium
183 hydroxide ($\text{Zr}(\text{OH})_4$) and zirconium oxide (ZrO_2) were synthesized using 500 mL of a 0.2 M
184 $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and 500 mL of 1.2 M NaOH solution using the same titrator, volume, metal-solution
185 rate, and pH as above. After synthesis, the batch was also divided into two and the post-synthesis was
186 either aging or hydrothermal treatment. Aging resulted in the formation of amorphous $\text{Zr}(\text{OH})_4$,
187 whereas crystalline ZrO_2 was obtained after hydrothermal treatment. All solid products were dried at
188 50°C overnight (\approx 16-18 h) and ground to a fine powder using an agate mortar and pestle before
189 analyses.

190 Table 2 summarized the nomenclature for all materials and their synthetic compositions.
191 Briefly, MgAl-A and MgAl-HT corresponds to conventional MgAl-LDH with either aging (A) at 80°C
192 or hydrothermally treatment (150°C, HT), respectively. The Zr modified LDH are named after their
193 ideal composition based on the reactant ratios: Zr0.1-A and Zr0.1-HT corresponds to the LDH
194 synthesized with Zr^{4+} and Al^{3+} concentration of 0.02 mol/L and 0.18 mol/L, respectively. This
195 corresponds to an Al to Zr ratio of 9 to 1; $\text{Al}/\text{Zr} = 9/1$), and ideally a $\text{Mg}_2\text{Al}_{0.9}\text{Zr}_{0.1}$ -LDH, whereas
196 Zr0.5-A and Zr0.5-HT are MgAl-LDH synthesized with 0.1 mol/L Zr^{4+} and 0.1 Al^{3+} ($\text{Al}/\text{Zr} = 1/1$,
197 ideally $\text{Mg}_2\text{Al}_{0.5}\text{Zr}_{0.5}$ -LDH). $\text{Al}/\text{Zr} = 1$ was chosen to match earlier studies (Table 1) whereas the ratio
198 $\text{Al}/\text{Zr} = 9$ were selected to investigate if a small Zr(IV) doping was masked by the Zr(IV) impurities in
199 the $\text{Al}/\text{Zr} = 1$ samples. For samples obtained after P exposure a "-P" is added as a suffix, for example
200 MgAl-HT-P is MgAl-HT after phosphate exposure.

201

202 **2.2.2. Phosphate isotherm batch experiments**

203 The phosphate sorption isotherm experiments were performed in 15 mL polypropylene
204 conical centrifuge tubes (Sarstedt, 120×17 mm) containing 10.00 mL phosphate solution and 10.0(1)
205 mg LDH, which were shaken at 400 rpm using an orbital shaker for 24 h at room temperature ($\approx 20^\circ\text{C}$).
206 All phosphate isotherm experiments were performed as duplicates. The concentration of the phosphate
207 solutions ranged from 30 to 400% (≈ 18 to 224 mgP/L) theoretical anion exchange capacity (TAC) for
208 HPO_4^{2-} calculated for a $\text{Mg}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ LDH under the assumption of the complete ion exchange
209 of Cl^- for HPO_4^{2-} (Table S1). The pH of the solutions was adjusted to 7.5 (67% HPO_4^{2-} , 33% H_2PO_4^-)
210 using 0.1 M HCl. To mimic industrial applications of LDH sorbents, the pH was not actively
211 controlled. [Moreover, pH control is known to drive the dissolution of the LDH with the lowest](#)
212 [dissolution observed at pH 8 \(Imran et al., 2016\)](#). After 24 h, the supernatant was collected using a 2
213 mL disposable pipette and filtrated through a 0.45 μm PTFE syringe filter. All phosphate solutions
214 were prepared in milli-Q water.

215 The ortho-phosphate concentration was quantified by the molybdate blue method ([Nagul](#)
216 [et al., 2015](#)) using a UV-Vis-spectrometer (UV-600PC; VWR, U.S.A) at 880 nm. The equilibrium
217 phosphate sorption (q_e (mgP/g)) capacity were then calculated using *Eq. 1* and plotted as a function of
218 the equilibrium concentration (C_e (mgP/L)), i.e., the concentration in the solution remaining at the end
219 of the experiment. Lastly, the sorption isotherms were modelled by the Langmuir (*Eq. 2*) and
220 Freundlich (*Eq. 3*) models using Origin (Version 2017, OriginLab Corporation).

$$221 \quad q_e = (C_o - C_e) \cdot (V / m) \quad (\text{Eq. 1})$$

$$222 \quad q_e = (Q_m K_L C_e) / (1 + K_L C_e) (\text{Eq. 2})$$

223
$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 3})$$

224 Where C_0 is the initial concentration (mgP/L), V (L) is the total volume and m (g) is the mass of LDH.
225 Q_m is the maximum monolayer coverage (mgP/g), K_L is the Langmuir isotherm constant (ml^3/mg)
226 related to the affinity of binding sites, K_F (mgP/g) is the Freundlich constant (related to the sorption
227 capacity) and n is related to the sorption intensity ([Foo and Hameed, 2010](#)).

228

229 **2.2.3. Powder X-ray diffraction**

230 PXRD were recorded on a Rigaku Miniflex 600 X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda =$
231 1.5406 \AA) with $K\beta$ -filter and a D/Tex Ultra-high-speed silicon strip detector using a voltage of 40 kV
232 and a current of 15 mA from $2\theta = 5$ to 70° , with a step size of 0.02° at 10 degrees per minute. Le Bail
233 fitting was performed to determine the cell-parameters using the FullProf software ([Rodríguez-](#)
234 [Carvajal, 1993](#)). The structural model used a $\text{Zn}_2\text{Al-Cl}$ LDH (ICSD code 155051) as starting structures
235 (where Zn were exchanged for Mg) (ICSD code 155051) ([Lombardo et al., 2005](#)). For Zr0.5-HT the
236 CIF for ZrO_2 (ICSD code 105553 ([Katz, 2006](#))) was also used in the refinement. Both CIF were found
237 through search-and-match in the PXRD software PDXL2. Generally, the parameters refined were W ,
238 X , U , cell parameters (a and c), shape1 , B_{ov} , zero shift, and the background. The background was
239 chosen manually by linear interpolation and described by the Pseudo-Voigt function. A Le Bail
240 refinement was chosen instead of Rietveld refinement due the complexity of the reflection in mid
241 angles ($2\theta \approx 30 - 50^\circ$), resulting from stacking faults and/ or mix of multiple polytypes. Next, the
242 average crystallite size was estimated using the Scherrer equation (Eq. 4) for the (003) reflection and
243 experimental broadening was corrected for using the (111) reflection at $2\theta = 28.5^\circ$ (FWHM = 0.10°)
244 for a Si standard. The full-width-half-max (FWHM) used for calculation of crystallite size were
245 likewise calculated in WinPLOTR in FullProf suite.

$$B(2\theta_{003}) = (K \cdot \lambda) / (\tau \cdot \cos(\theta)) \quad (\text{Eq. 4})$$

Were $B(2\theta)$ is the FWHM of the (003) peak, K is the crystallite shape constant (here approximated to 0.9 assuming a spherical morphology ([Forano et al., 2006](#)), λ is the wavelength, θ is the diffraction angle, and τ is the crystallite diameter in Ångström (Å).

2.2.4. Solid State ^1H , ^{27}Al , and ^{31}P MAS NMR spectroscopy

Single pulse ^{27}Al and ^{31}P magic angle spinning (MAS) NMR spectra and ^{27}Al triple quantum magic angle spinning (3QMAS) NMR spectra were recorded on a JEOL ECZ500CR 500 MHz NMR spectrometer (11.7 T) using a 3.2 mm double resonance MAS NMR probe with 15 kHz spinning speed for the single pulse and 14 - 15 kHz for the 3QMAS experiments. The relaxation delay was optimized for each sample but were generally 1 s for the single pulse ^{27}Al MAS NMR ($< 10^\circ$ pulse width for quantitative excitation) and 30 - 90 s for single pulse ^{31}P MAS NMR (45° excitation pulse). The ^{27}Al 3QMAS experiment were recorded using a three-pulse z-filter sequence ([Amoureux and Fernandez, 1998](#)).

Single pulse ^1H MAS NMR spectra were recorded on an Agilent Inova 600 MHz NMR spectrometer (14.1 T) using a 1.6 mm triple resonance MAS NMR probe and 30 - 32 kHz spinning speed. The ^1H , ^{27}Al , and ^{31}P and NMR spectra were referenced using H_2O ($\delta_{\text{iso}}(^1\text{H}) = 4.6$ ppm), 1.0 M solution of AlCl_3 ($\delta_{\text{iso}}(^{27}\text{Al}) = 0$ ppm) and concentrated phosphoric acid (85% H_3PO_4 ; $\delta_{\text{iso}}(^{31}\text{P}) = 0$ ppm), respectively. Deconvolution of the ^{27}Al single pulse MAS NMR spectra were performed in Quadfit ([Kemp and Smith, 2009](#)) using two sites: one with $C_Q = 1.6$ MHz and $\eta = 0$ (LDH) and a second site with $C_Q = 3.3$ MHz and $\eta = 0.2$ (amorphous aluminum hydroxide, will be discussed later) ([Jensen et al., 2016](#); [Pushparaj et al., 2015](#); [Staal et al., 2017](#)). The ^{27}Al 3QMAS NMR spectra were

268 processed in ssNake (v1.1), ([van Meerten et al., 2019](#)) whereas single-pulse ^1H and ^{31}P MAS NMR
269 spectra were analyzed by deconvolution in MestReNova (ver. 14.2.1.).

270

271 **2.2.5. Zeta potential - and hydrodynamic size measurements**

272 The zeta (ζ) potential of MgAl/Zr composite, $\text{Zr}(\text{OH})_4$, and ZrO_2 were determined by
273 electrophoretic light scattering utilizing a Zetasizer nano ZS analyzer from Malvern Panalytical fitted
274 with a 4 mW 632.8 nm “red” laser. For the measurement, powdered samples were dispersed (ca. 0.1
275 mg/mL) in deionized water and stirred 24 h and then sonicated for 15 min at room temperature. The
276 Zeta potential values were calculated by determining the electrophoretic mobility and then applying the
277 Henry equation.

278

279 **2.2.6. Transmissions electron microscopy**

280 Transmission electron microscopy (TEM) images were acquired with a JEOL 2100Plus
281 microscope (200 kV) fitted with LaB_6 electron gun. Elemental analysis of individual particles was
282 acquired by energy dispersive X-ray spectroscopy. 20 μL of an aqueous suspension of 1 mg sample per
283 mL water was deposited on a carbon grid covered with a forward carbon film and dried at 40°C under
284 air.

285

286 **2.2.7. Elemental analysis**

287 Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the
288 quantification of Mg, Al, Zr, and P.. Approximately 0.02 g LDH and 10.00 mL of concentrated nitric
289 acid (HNO_3 , 65%) were mixed followed by microwave digestion at 200°C for 15 min. The resulting

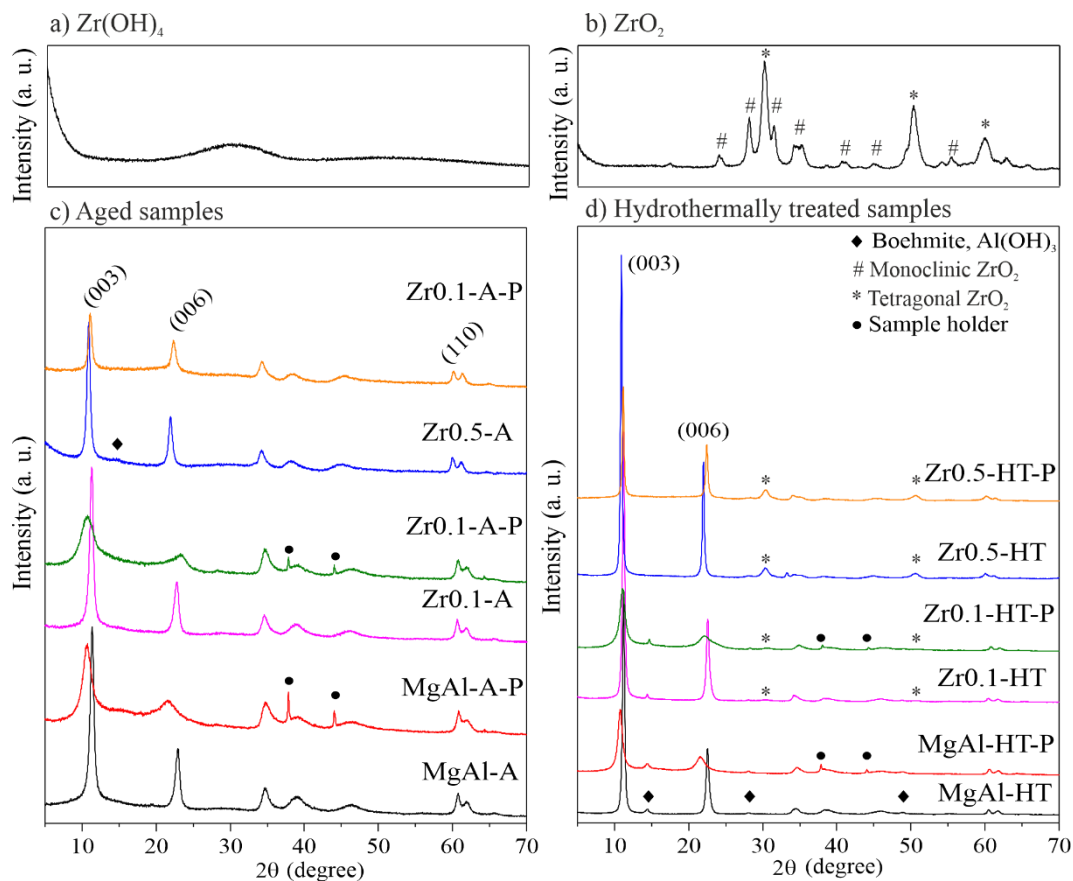
290 supernatant were diluted appropriately in milli-Q water before analysis on an Optima 2100 DV,
291 PerkinElmer, USA.

292

293 **3. Results and discussion**

294 *3.1. The effect of the Zr content on the phosphate removal capacity of MgAl-LDH*

295 The successful synthesis of hydrotalcite LDH was confirmed for all samples based on the
296 observation of the characteristic (003), (006), and (110) reflections by PXRD (Figure 1). However, the
297 phosphate sorption capacity of the LDH samples will be presented prior to detailed analysis of the
298 PXRD data. Sorption will in the following be used to describe the phosphate removal properties of the
299 LDH materials since multiple processes contribute including surface sorption, ion-exchange, and the
300 removal of P by impurity phases. The individual contribution cannot be distinguished unambiguously
301 from the sorption data alone.



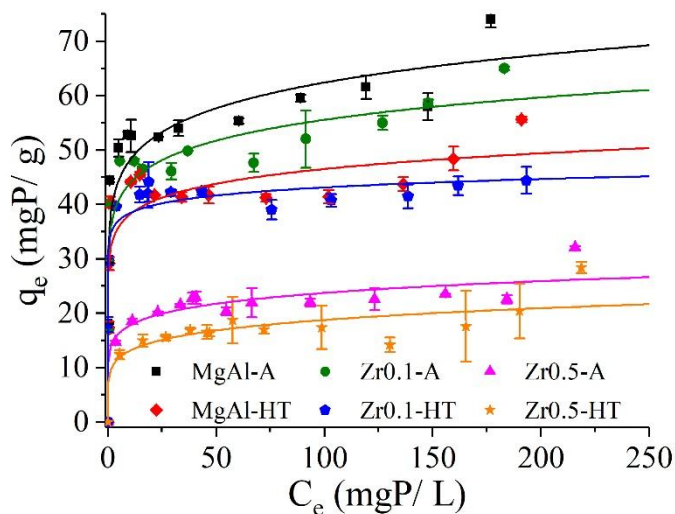
302

303 **Figure 1.** PXRD diffractograms of the synthesized LDH samples and these after phosphate exposure
 304 for c) aged samples and d) hydrothermally treated samples, as well as of $Zr(OH)_4$ (a) and ZrO_2 (b). The
 305 reflections from the sample holder (•) are observed in some diffractograms due to limited sample
 306 quantities.

307 The phosphate removal capacity as a function of both the time and the concentration were
 308 obtained from sorption kinetics and isotherms. The sorption isotherm does not reach a clear plateau,
 309 even at 400% TAC (Figure 2). Visual inspection of the isotherm shows that two sequential processes
 310 contribute (Figure 2). First, one process at low equilibrium concentrations, below a C_e of approximately
 311 75 mgP/L, and a second above. This is explained by the presence of multiple phosphate removal
 312 mechanisms: both ion-exchange, adsorption to the LDH surface (e.g., charge interactions, grafting),

313 and adsorption to impurities (details in the next section) may result in phosphate removal. Moreover,
314 dissolution of the LDH and/or Zr(IV) (hydr)oxides followed by precipitation of phosphate phases (e.g.,
315 Al-P, Mg-P) may also contribute. The contribution from two or more pathways explains the
316 inadequately fitting by both the Freundlich ($R^2 = 0.78$ to 0.90) and Langmuir ($R^2 = 0.56$ to 0.91)
317 (Figure S2, Table S2). Thus, the sorption capacity is estimated visually (Table 1) at the clear break-off
318 in the isotherm due to these non-ideal fits, which is at about C_e of. Noteworthy, the kinetic sorption
319 experiments showed a quick phosphate uptake and reached an equilibrium within the first hour (Figure
320 S1).

321 In contrast to previous studies (Table 1), an increased Zr(IV) content in the LDH samples
322 is accompanied by a drastic decrease in the phosphate adsorption capacity: For Zr0.5-A and Zr0.5-HT
323 the experimental sorption capacity is only 20(2) and 16(2) mgP/g, respectively. The MgAl-A and
324 MgAl-HT (conventional MgAl-LDH) exhibit the highest phosphate removal capacities of 54(2) and
325 45(2) mgP/g, respectively (see also Table 1). To understand this trend, detailed characterization of the
326 samples was performed.



327

328 **Figure 2.** Phosphate sorption isotherm, which is inadequately modelled by both the Freundlich (shown)
 329 and Langmuir isotherms (Figure S2) with the parameters given in Table S2. Multiple processes
 330 contribute to the sorption capacity which was estimated visually at the break-off point (Table 1, see
 331 text). The error-bars are based on a duplicate of sorption experiments with triplicate determination of
 332 the phosphate concentration.

333

334 3.2. Characterization of the synthesized LDH with and without Zr doping

335 The parent LDH with and without Zr were characterized using PXRD, ICP-OES, FT-IR, TEM, SEM,
 336 ^1H , ^{25}Mg and ^{27}Al MAS NMR, and zeta potential measurements. The unit cell parameters for the
 337 pristine LDH were obtained by Le Bail fitting (Tables 3 and S3, Figure S3). For the LDH after
 338 phosphate sorption experiments, these were estimated based on the (003) and (110) reflections due to
 339 the increased complexity of the PXRD diffractograms. Agreement factors generally show a good fit
 340 with χ^2 values of 2 - 8 and R- and R_f -factors of < 3% (Table S3). Aged samples are less crystallinity
 341 (i.e., lower intensity, increased FWHM; Table 3) as compared to the samples after hydrothermal
 342 treatment (Figure S1), an observation in agreement with earlier studies ([Pushparaj et al., 2015](#))

343 **Table 3.** Properties of the synthesized samples and these after phosphate exposure based on PXRD,
 344 SSNMR spectroscopy, ICP-OES, and zeta potential measurements. For a comparison, the zeta potential
 345 for Zr(OH)₄ and ZrO₂ were -18(5) and -8(4) mV respectively.

346 ^a The cell parameters obtained from Le Bail fitting (Figure S3), ^b Cell parameters based on the position
 347 of the (003) and (110) reflections. FWHM is for the (003) reflection. n. a. = Data not available. τ = is

	<i>a</i> (Å)	<i>c</i> (Å)	FWHM (°)	τ (Å)	AOH (%Al)	x (²⁷ Al+ICP)	x (¹ H)	Zeta (mV)
MgAl-A ^a	3.048(2)	23.303(3)	0.641(2)	124	29.0(3)	0.27(2)	0.23(2)	29(5)
MgAl-HT ^a	3.060(2)	23.617(3)	0.3249(6)	246	22.6(3)	0.28(2)	0.26(2)	27(6)
Zr0.1-A ^a	3.078(2)	23.417(3)	0.647(2)	123	29(2)	0.25(2)	0.20(2)	28(5)
Zr0.1-HT ^a	3.076(2)	23.576(3)	0.341(6)	234	19(1)	0.25(2)	0.27(2)	25(6)
Zr0.5-A ^a	3.080(2)	24.245(3)	0.526(2)	152	20(2)	0.18(2)	0.22(2)	12(4)
Zr0.5-HT ^a	3.092(2)	24.211(3)	0.2415(4)	330	< 5	0.20(2)	0.18(2)	30(5)
MgAl-A-P ^b	3.043(3)	24.859(4)	1.593(7)	50	32.0(2)	0.26(2)	n. a.	-17(4)
MgAl-HT-P ^b	3.054(3)	24.650(4)	0.775(2)	103	23.1(5)	0.29(2)	n. a.	-17(4)
Zr0.1-A-P ^b	3.047(3)	24.947(4)	2.30(12)	35	27(1)	0.26(2)	n. a.	-19(4)
Zr0.1-HT-P ^b	3.043(3)	23.935(4)	0.943(3)	85	26.0(1)	0.26(2)	n. a.	-18(4)
Zr0.5-A-P ^b	3.075(3)	23.861(4)	0.526(2)	152	21.8(3)	0.18(2)	0.21(2)	-11(4)
Zr0.5-HT-P ^b	3.073(3)	23.750(4)	0.2484(9)	331	9.5(3)	0.20(2)	n. a.	-9(4)

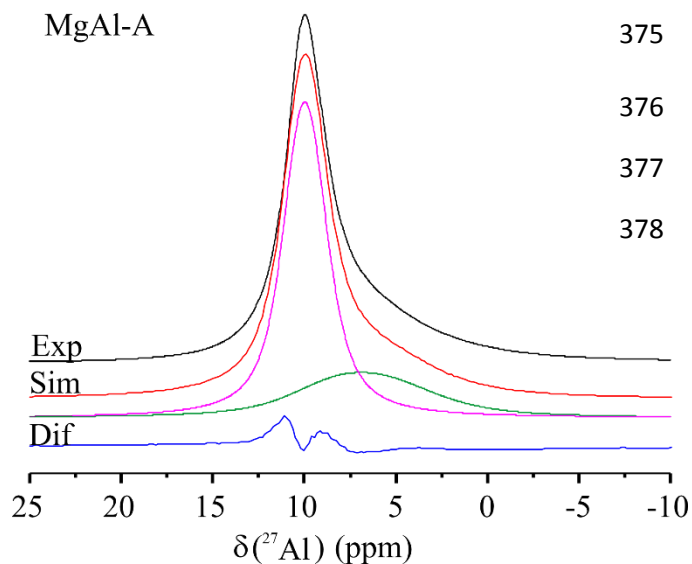
348 the crystallite size approximated from the Scherrer equation using the (003) reflection.

349 The *a*-cell parameter (the M-M distance) increased ca. 0.03 Å at highest Zr(IV) doping
 350 (Table 3, Figures S4). Diffractograms of MgAl-A and the Zr modified samples after aging (Zr0.1-A,
 351 Zr0.5-A) only contain LDH reflections (beside Al(OH)₃ impurities). In contrast, hydrothermal

352 treatment leads to the formation of additional crystalline phases (Figures 1 and S3). For MgAl-HT only
353 boehmite ($\text{AlO}(\text{OH})$) is detected, which is formed by dehydroxylation of Al hydroxides during the
354 hydrothermal treatment ([Pushparaj et al., 2016](#)). In contrast, two new reflections are observed at $2\theta \approx$
355 32° and 51° for the Zr modified LDH (Zr0.1-HT, Zr0.5-HT), which are assigned to ZrO_2 formed by
356 dehydroxylation of $\text{Zr}(\text{OH})_4$. This is supported by the conversion of amorphous $\text{Zr}(\text{OH})_4$ to crystalline
357 ZrO_2 , when hydrothermally treated similar to the LDH samples. To identify the presence of $\text{Zr}(\text{OH})_4$ in
358 the aged samples FT-IR, TGA, TEM, SEM, and SSNMR were performed.

359 FT-IR spectra (Figure S5) of the pristine LDH, both with and without Zr(IV), exhibit the
360 typical LDH bands including hydroxides ($3500 - 3600 \text{ cm}^{-1}$), interlayer water ($1600 - 1650 \text{ cm}^{-1}$), and
361 the metal oxides bands, MO_6 , ($696 - 717 \text{ cm}^{-1}$) and OMO bands ($500 - 400 \text{ cm}^{-1}$); M = metal cation
362 ([Goh et al., 2008](#); [Staal et al., 2017](#)). Minor carbonate contamination is also observed at $1350\text{-}1380 \text{ cm}^{-1}$
363 ¹ due the high affinity of LDH for carbonate ([Forano et al., 2006](#); [Goh et al., 2008](#)). When the Zr(IV)
364 content is increased from 0.1 to 0.5 the intensity of the AlO_6 stretching mode ($850\text{-}950 \text{ cm}^{-1}$) decreased
365 strongly for both the aged and hydrothermally treated LDH samples. This indicates depletion of Al in
366 the LDH cation layer corresponding to the reduced reactant concentration (Table 2).

367 From the single pulse ^{27}Al MAS- (Figure 3, Figures S6-7) and 3QMAS NMR two
368 resonances are identified: Al in the LDH ($\delta_{\text{iso}}(^{27}\text{Al}) \approx 10 - 12 \text{ ppm}$) and Al in amorphous Al hydroxide
369 (AOH) ($\delta_{\text{iso}}(^{27}\text{Al}) \approx 5 - 10 \text{ ppm}$) ([Lundehøj et al., 2019b](#); [Staal et al., 2017](#)). The concentration of AOH
370 is higher in the aged samples (30%) compared to hydrothermally treated (20%) samples, in accordance
371 with earlier studies ([Pushparaj et al., 2015](#); [Staal et al., 2017](#)). The adjusted Mg:Al ratio in the LDH
372 phase was calculated using ICP-OES and ^{27}Al NMR (or ^1H MAS NMR; Table S4). They all results in
373 Mg:Al ratios within the known stable range for LDH (0.2 - 0.33) ([Forano et al., 2006](#)), as summarized
374 in Table 3.



379

380 **Figure 3.** A representative deconvolution of a single pulse ^{27}Al MAS NMR spectrum using two phases:

381 $\delta_{\text{iso}}(^{27}\text{Al}) \approx 10$ ppm (LDH, pink) and $\delta_{\text{iso}}(^{27}\text{Al})$ centered at ≈ 7 ppm (AOH, green). The ^{27}Al MAS NMR

382 spectra of the other samples, which are similar, are shown in Figures S6 and S7.

383

384 TGA (Figure S8) and ^1H MAS NMR (Figure 4, Figures S9-11) probed the thermal

385 degradation and water content: Zr0.5-A exhibited a mass loss of 22(2)% and Zr0.5-HT of only 11(2)%

386 below 200°C implying a higher water or hydroxide content in the aged sample compared to the

387 hydrothermally treated. Moreover, ^1H MAS NMR showed an increased intensity around 5 ppm, which

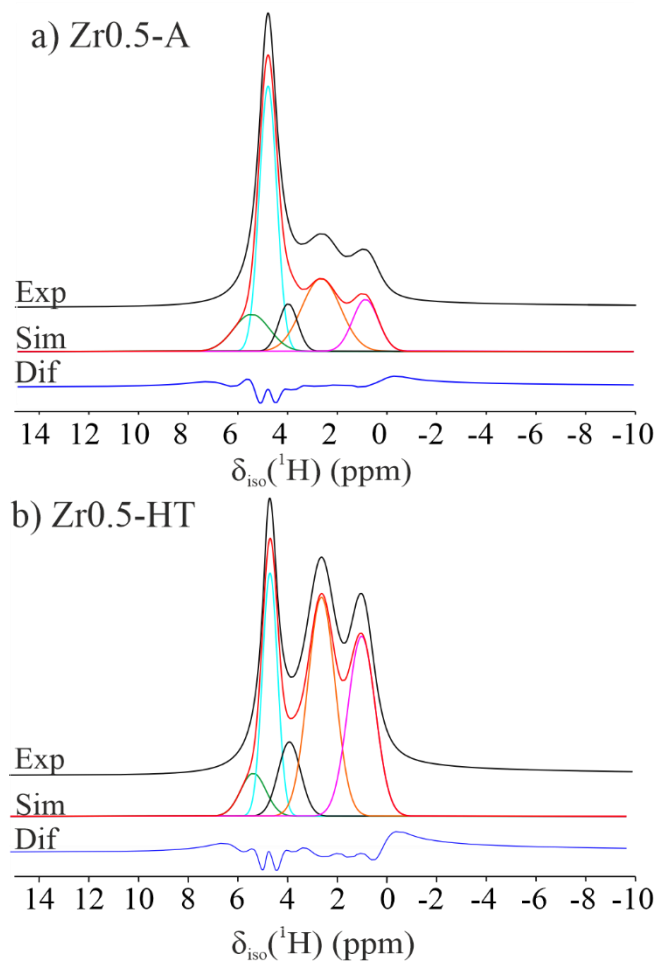
388 is ascribed to the overlap of the ^1H NMR resonances from $\text{Zr}(\text{OH})_4$ ($\delta_{\text{iso}}(^1\text{H}) = 4.8$ ppm; Figure S9) and

389 water in the LDH ($\delta_{\text{iso}}(^1\text{H}) = 4.5 - 5.0$ ppm; Table S4 and Figures S10-11). Deconvolution of the ^1H

390 MAS NMR spectra showed resonances at $\delta_{\text{iso}}(^1\text{H}) \approx 4.8(2)$ ppm for Zr0.5-HT (26(5)%) and for Zr0.5-A

391 (37(5)%) (Figure 4).

392 This intensity difference is ascribed to the presence of ^1H NMR resonance of $\text{Zr}(\text{OH})_4$,
393 which overlap with H_2O (see also Figure S9). Thus, $\text{Zr}(\text{OH})_4$ must be present in Zr0.5-A. To further
394 probe this, SEM provided insight into particle size, morphology, and homogeneity (Figure S12).



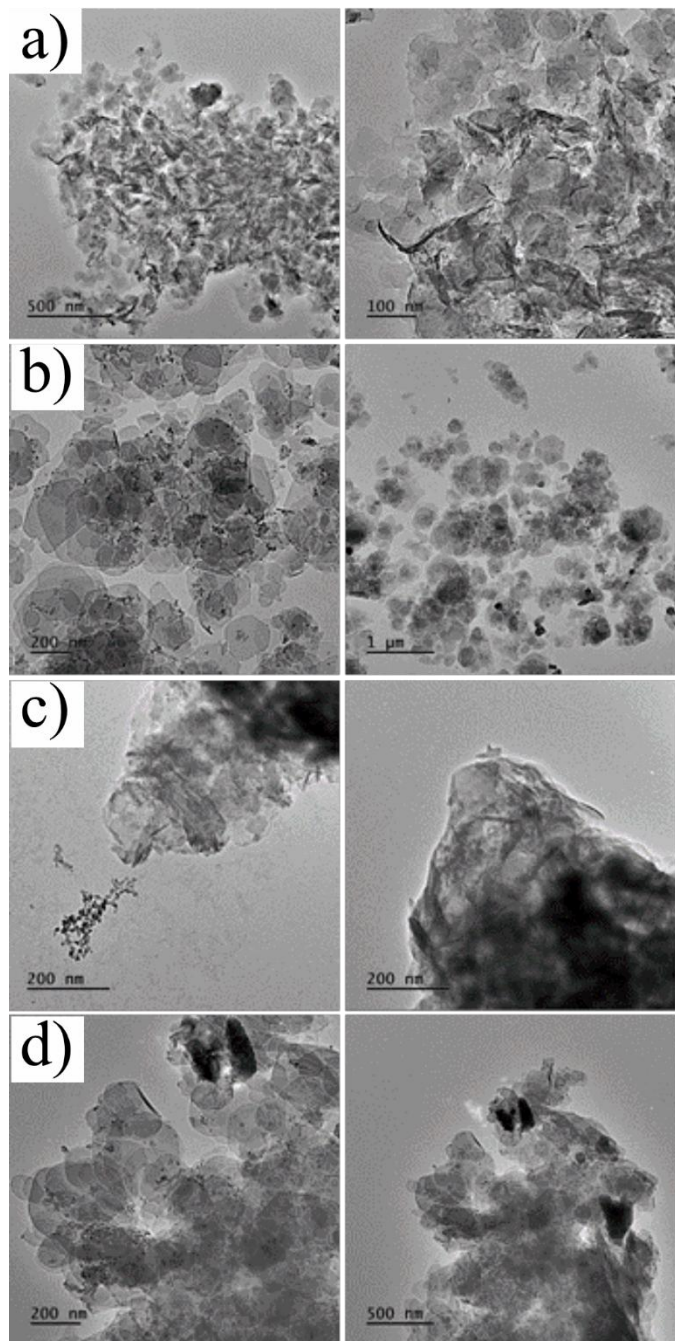
395
396 **Figure 4.** Deconvolution of the ^1H MAS NMR spectra of a) Zr0.5-A and b) Zr0.5-HT with the
397 experimental (black), simulated (red), and difference between the experimental and simulated spectrum
398 (dark blue), as well as the individual sites AOH (green), H_2O (turquoise), $\text{Zr}(\text{OH})_4$, orange for Mg_2Al -
399 OH, pink for $\text{Mg}_3\text{-OH}$ and black is an unknown site needed for the satisfactory simulation of the
400 experimental spectra.

401 Scanning electron microscopy (Figure S12) showed that MgAl-A and MgAl-HT consist
402 of hexagonal, plate-like particles with a width ranging from 200 to 600 nm, as typically observed for
403 LDH ([Pushparaj et al., 2015](#)). In addition, LDH with Zr added (Zr0.1-A, Zr0.5-A, Zr0.1-HT, Zr0.5-HT)
404 contain smaller ill-defined (< 100 nm) particles (see white arrows on Figure S12b, c, e, and f), which
405 are assigned to Zr phases (ZrO_2 and $\text{Zr}(\text{OH})_4$ for Zr0.5-HT and Zr0.5-A respectively). Their presence is
406 also supported by TGA and ^1H MAS NMR.

407 Further characterization by transmission electron microscopy (TEM) of selected samples
408 (Figure 5), show that the hydrothermal treatment increases the particle size and improves the shape
409 homogeneity of the LDH-HT particles as compared to the particles aged at 80°C (Figure 5a and b).
410 Hydrothermal treatment prevents aggregation and favors a face-to-face orientation of individual
411 hexagonal platelets while for Zr0.1-A the particles are in dense, disordered agglomerates. EDX analysis
412 (Figure S13) reveal an increase in the Mg:Al ratio in the LDH from 2.0 to 2.5, for Zr0.1-A and Zr0.1-
413 HT respectively.. ZrO_2 nanoparticles (≈ 10 nm) are clearly observed on the surface of Zr0.1-HT
414 platelets as well as dispersed black spots (Figure 5B). The absence of these dark spots on the TEM
415 images of Zr0.1-A confirms the formation of amorphous $\text{Zr}(\text{OH})_4$ nanoclusters most likely covering
416 the LDH surface as also observed by ^1H MAS NMR, TGA, and SEM analysis.

417 It is clear that the hydrothermal treatment converts these highly dispersed $\text{Zr}(\text{OH})_4$
418 nanoclusters into ZrO_2 nanoparticles, which are very evident in the TEM images, as illustrated for
419 Zr0.5-A (Figure S14c and d). The sorption of phosphate on both the Zr0.1-A and Zr0.1-HT samples
420 forces the collapse of individual particles into densely packed aggregates most likely due to the change
421 in surface charge properties and inversion of the zeta potential. These Zr-based nanoparticles are still
422 observed after P sorption (Figures S14c and d). The presence of Al hydroxides or boehmite rods in

423 addition to Zr0.1-A and Zr0.1-HT-P particles (Figures 14) supported the results from ^{27}Al MAS NMR
424 spectra, which show a significant AOH content (Table 3).



425
426 **Figure 5.** Two representative TEM images for each of a) Zr0.1-A, b) Zr0.1-HT), c) Zr0.1-A-P, and d)
427 Zr0.1-HT-P.

428 Moreover, ^{25}Mg MAS NMR spectra supported a higher Mg:Al ratio in the LDH than the
429 targeted 2:1 (Figure S15), in agreement with ^{27}Al -, ^1H MAS NMR, and ICP-OES, as the second order
430 quadrupolar line shape is more undefined as the Mg:Al ratio increases ([Sideris et al., 2012](#)).

431 To summarize, Zr is segregated as amorphous $\text{Zr}(\text{OH})_4$ for Zr0.1- and Zr0.5-A and as
432 crystalline ZrO_2 for Zr0.1-HT and Zr0.5-HT, i.e., Zr is not incorporated into the LDH structure. The
433 presence of ZrO_2 and $\text{Zr}(\text{OH})_4$ is expected to influence the phosphate sorption capacity. Therefore, the
434 theoretical sorption capacity can be estimated using the Mg:Al ratio from ^{27}Al MAS NMR and ICP-
435 OES (Table S1) combined with the AOH and Zr(IV) content from ICP-OES. From the detailed
436 characterization, it can be unambiguously concluded that the samples contain three phases: 1) MgAl-
437 LDH 2) AOH, and 3) $\text{Zr}(\text{OH})_4$ (aged samples) or ZrO_2 (hydrothermally treated). Based on ^{27}Al MAS
438 NMR and ICP-OES the contribution from each phase can be calculated. The adjusted Mg:Al ratio in
439 the MgAl-LDH and their removal capacities are summarized in Table S1. The LDH phase represents
440 90-98 mass% of the sample. The AOH and Zr (hydr)oxide content corresponds to 1-10 mass%, with
441 $\text{Zr}(\text{OH})_4/\text{ZrO}_2$ contribution 2-6 mol% based on ICP-OES. Thus, based on the Zr (hydr)oxide content,
442 this phase accounts for less than 5 mgP/g (Table 1). Therefore, mainly the LDH and the AOH
443 contribute to the sample's phosphate removal capacity. Finally, the decreased sorption capacity is a
444 direct consequence of the decrease in Al content.

445

446 *3.3.Characterization of the LDH after phosphate sorption*

447 The phosphate loaded LDH (MgAl-A-P, MgAl-HT-P, Zr0.1-A-P, Zr0.1-HT-P, Zr0.5-A-
448 P, and Zr0.5-HT-P) were characterized in detail to understand the stability of the LDH during P
449 exposure and the pathway of removal.

450 As expected, phosphate sorption on the surface of aged and hydrothermally treated
451 samples reversed the charge of the platelets. Thus, the zeta potential value changes from 29 - 27 mV
452 (MgAl-A and MgAl-HT) to -17 mV (MgAl-A-P and MgAl-HT-P) (Table 3). No significant different is
453 observed between the MgAl-LDH and the lowest Zr-doping level. Increasing the Zr(IV) content to 0.5
454 in the aged LDH leads to a clear change of surface charge from +29 mV to -12 mV. Hydrothermal
455 treatment leads to phase segregation and formation of ZrO₂, which has limited effect on the mean
456 (bulk) zeta potential (Table 3).

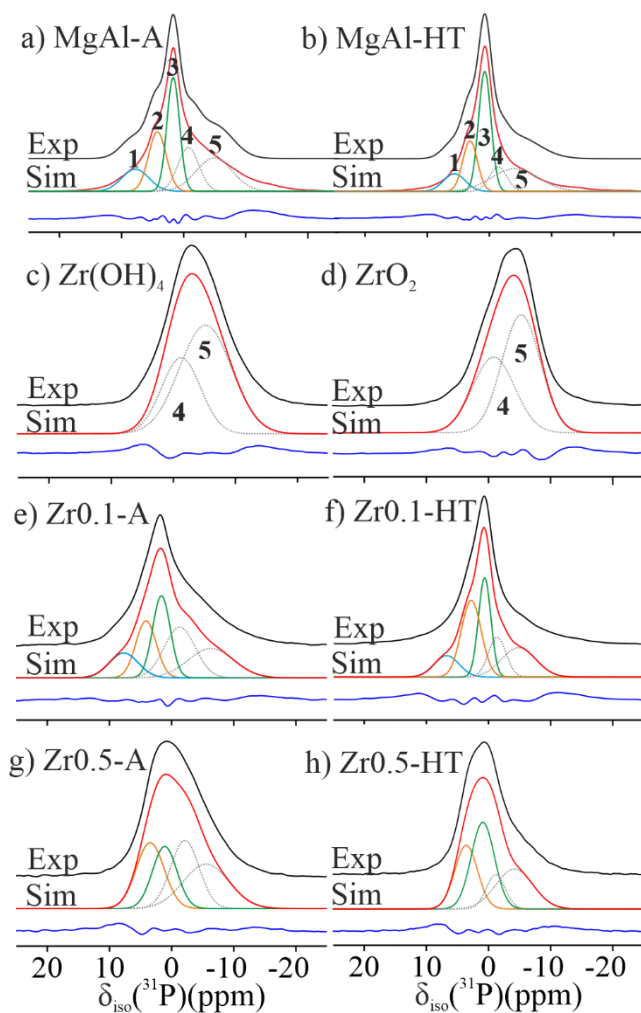
457 PXRD showed an increased stacking disorder and decrease in crystallinity of the
458 phosphate loaded LDH (Table 3), also observed in the ¹H- and ²⁵Mg MAS NMR (Figures S10-11,
459 S15), and in agreement with earlier studies of MgAl-LDH ([Lundehøj et al., 2019a](#)). The lower
460 resolution of the ¹H MAS NMR spectra prevented unambiguous deconvolution and thereby
461 determination of the Mg:Al ratio. However, ²⁷Al MAS NMR (Figure S16), FT-IR (Figure S5) and
462 PXRD (Figure 1) supported preservation of the LDH structure, but with an increased stacking disorder.
463 For example, the M-M distance in the LDH (unit cell parameter *a*) does not change after phosphate
464 exposure (Table 3 and Figure S4). Similarly, ICP-OES (Table 1) and ²⁷Al MAS NMR shown no
465 significant change in the bulk composition of Mg, Al, and Zr or relative concentration of the LDH,
466 respectively.

467 The *c* unit cell parameters, i.e., the interlayer spacing, increases ca 0.5 Å after P sorption,
468 which combined with the increase in the FWHM of the (00l) reflections (Table 3) reflects the
469 intercalation of phosphate into the LDH as previously observed ([Costantino et al., 1997](#); [Hou et al.,](#)
470 [2003](#); [Lundehøj et al., 2019a](#)). Moreover, the $\nu_3(\text{PO}_4^{3-})$ vibration ([Badreddine et al., 1999](#)) observed by
471 FT-IR (Figure S5) also proves phosphate related to the material and the negative surface charge (-9 to -
472 19 mV; Table 3) indicates surface complexation. To summarize, characterization show no changes in

473 the sample composition (i.e., limited dissolution and degradation) of the LDH layer after phosphate
474 exposure but strong surface modifications.

475

476 3.4. Quantification of the different phosphate removal pathways by ^{31}P MAS NMR spectroscopy



477

478 **Figure 6.** Experimental ^{31}P MAS NMR spectra of the LDH samples after phosphate sorption (a, b, e, f),
479 $\text{Zr}(\text{OH})_4$ (c), and ZrO_2 (d) and the respective deconvolutions with experimental (black), simulation
480 (red), error (blue) and the individual sites: 1: turquoise, 2: orange, 3: green and site 4 and 5: grey.

481

482 To investigate the phosphate removal pathways and the different phosphate sites present,
483 ^{31}P MAS NMR spectra were recorded (Figure 6). Deconvolution of the ^{31}P MAS NMR spectra of LDH
484 can be challenging due to broad resonances and/ or overlapping sites as observed previously ([Borges et](#)
485 [al., 2019](#); [Hou et al., 2003](#); [Lundehøj et al., 2019a](#); [Lundehøj et al., 2019b](#)). Generally, each LDH here
486 contains four or five different P sites, i.e., five different phosphorous local environments. These sites
487 are **site 1**: $\delta_{\text{iso}}(^{31}\text{P}) = 6.8$ to 7.8 ppm, **site 2**: $\delta_{\text{iso}}(^{31}\text{P}) = 2.9$ to 4.2 ppm, **site 3**: $\delta_{\text{iso}}(^{31}\text{P}) = 0.6$ - 1.7 ppm, **site**
488 **4** $\delta_{\text{iso}}(^{31}\text{P}) = -0.8$ to -2.2 ppm and finally **site 5** $\delta_{\text{iso}}(^{31}\text{P}) = -4.1$ to -6.4 ppm (details in Table S5)

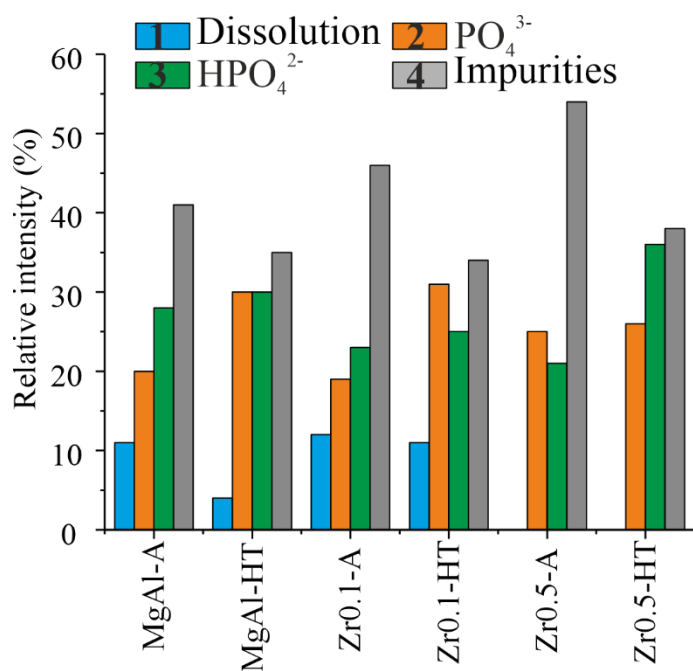
489 Sites 2 (20 - 31%) and 3 (21 - 36%) account for most of the intensity and are therefore
490 assigned to intercalation of ortho-phosphate in the LDH, given that it is the main removal pathway.
491 This is agreement with phosphate related to a ZnAl-LDH were found at $\delta_{\text{iso}}(^{31}\text{P}) = 4.5(5)$ and $0.6(3)$
492 ppm doing phosphate sorption at pH 5 ([Lundehøj et al., 2019b](#)). Furthermore, two sites at $\delta_{\text{iso}}(^{31}\text{P}) = 3.2$
493 ppm for HPO_4^{2-} and a site at 6.2 ppm for PO_4^{3-} were identified for MgAl-LDH based on visual
494 inspection ([Hou et al., 2003](#)). These reported $\delta_{\text{iso}}(^{31}\text{P})$ does not fully match the values for site 2 and site
495 3 (Table S5), but determination of the isotropic resonances in spectra with overlapping sites with
496 overlapping resonances is less precise. Therefore, Sites 2 and 3 are assigned to intercalation of $\text{H}_x\text{PO}_4^{(3-x)-}$
497 species.

498 Sites 4 (10 - 26%) and site 5 (20 - 28%) are assigned to phosphate removed by AOH, and
499 the Zr phase(s), $\text{Zr}(\text{OH})_4$ for aged samples and ZrO_2 for hydrothermally treated samples, respectively.
500 This was based on a comparison with ^{31}P MAS NMR spectra recorded for $\text{Zr}(\text{OH})_4\text{-P}$ and $\text{ZrO}_2\text{-P}$
501 (Figure 6c and d) combined with previous studies ([Lundehøj et al., 2019a](#); [Lundehøj et al., 2019b](#)).
502 Differentiation between the AOH, $\text{Zr}(\text{OH})_4$, and ZrO_2 cannot be done because of broad and overlapping
503 resonances and is beyond the scope of this work.

504 Finally, Site 1 (4 - 12%; $\delta_{\text{iso}}(^{31}\text{P}) = 6.8$ to 7.8 ppm) has the lowest intensity and is not
 505 detected for Zr0.5-A or Zr0.5-HT. Furthermore, this site is most prominent for aged samples,
 506 Therefore, this site is tentatively assigned to dissolution of the LDH, as the smaller particles are less
 507 stable. The lack of site 1 for Zr0.5-A and Zr0.5-HT is explained by the high Mg:Al ratio in the LDH.

508 Phosphate sorbed to impurities (AOH, $\text{Zr}(\text{OH})_4$, and ZrO_2) is the major pathway (41 -
 509 54%) for aged samples in accordance with ^{27}Al - and ^1H MAS NMR. For a comparison, the impurities
 510 contribute 34 - 38% for hydrothermally treated samples. Thus, the impurity content in the LDH must
 511 be controlled, otherwise the phosphate will be strongly bound to the impurities instead of readily
 512 released from the LDH. This will decrease the recyclability of the LDH sorbents.

513



514

515 **Figure 7.** The relative intensity between the different ^{31}P sites and their assignment based on
 516 deconvolution of the ^{31}P MAS NMR spectra (Table S5). Dissolution and re-precipitation process

517 (blue), $H_xPO_4^{(3-x)-}$ removed by the LDH (orange and green) and the contribution from impurities, i.e.,
518 AOH, ZrO_2 , $Zr(OH)_4$ (grey).

519

520 **4. Conclusions**

521 Detailed insight into the phosphate removal capacity and stability of a series of MgAl-
522 LDH with different Zr(IV) modifications was achieved using global and local characterization
523 techniques. Our results clearly demonstrate, that Zr(IV) cannot be incorporated into the LDH lattice
524 and thereby improve the phosphate removal capacity. Instead separate phase of $Zr(OH)_4$ or ZrO_2 were
525 present for the aged and hydrothermal treated samples, respectively. Especially detection of the X-ray
526 amorphous $Zr(OH)_4$ in the aged samples required advanced characterization techniques (1H - and ^{27}Al
527 MAS NMR, SEM, TEM and TGA). The unsuccessful incorporation of Zr(IV) together with the
528 decreased Al doping resulted in a drastic decrease in the phosphate removal capacity (45 - 54 to 16 - 20
529 mgP/g). Single pulse ^{31}P MAS NMR showed that 42 - 62% of the ortho-phosphate was intercalated in
530 the LDH by ion-exchange. However, ^{31}P MAS NMR also showed that up to 54% of phosphate was
531 removed by impurity phases or dissolution of the LDH. Thus, phosphate has a high affinity towards the
532 common impurities and the synthesis methods for LDH with limited impurities (coprecipitation
533 followed by hydrothermal treatment) is important for the reusability of the LDH based sorbents. Our
534 study clearly show that large particle size (crystallinity) is favored and that impurity phases should be
535 minimized. Moreover, it is emphasized that phosphate removal pathways cannot be reliably assessed
536 based on sorption studies only. Detailed characterization of the LDH sorbent before and after
537 phosphate exposure is paramount for reliable assessment of the LDH sorbent performance and stability.

538

539 **Declaration of Competing Interest**

540 The authors declare no competing interest.

541

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550

551 **Appendix A. Supplementary data**

552 Supporting information provide additional information about PXR, Le Bail refinement,
553 FT-IR, SEM, ^1H , ^{25}Mg , ^{31}P , ^{27}Al 1D MAS NMR together with 2D MAS NMR (^{27}Al 3QMAS) and
554 kinetics experiments together with isotherm refinement parameters.

555

556 **Data availability**

557 Data will be available upon request.

558

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