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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

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

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Keywords: Layered double hydroxides; phosphate; sorption; environmental remediation; solid state
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 ( <u>Cordell et al.</u> ,
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 <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O) as a fertilizer, whereas vivianite
50	(Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O) is an emerging technology ( <u>Hall et al., 2020</u> ; <u>Lamastra et al., 2018</u> ; <u>Rahman et al.</u> ,
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).

LDH have the general formula [M(II)<sub>1-x</sub>M(III)<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sub>x/n</sub><sup>n-</sup>)·yH<sub>2</sub>O (x typically 0.2 0.33), whereas M(II) and M(III) are divalent and trivalent cations and A<sup>n-</sup> is a charge compensating
anion located in the interlayer together with water (Duan and Evans, 2005; Forano et al., 2006;
Pushparaj et al., 2015). Subsequently, the LDH will be abbreviated as M(II)M(III)-LDH. Especially,
the charge density (x), intercalated anion (A<sup>n-</sup>), particle size, pH, and competing anions are important
parameters related to the removal capacity and stability of the LDH.

For environmental applications, mainly the non-toxic MgFe -, CaAl -, CaFe -, and MgAlLDH are relevant (<u>Al Jaberi et al., 2019</u>; <u>Ashekuzzaman and Jiang, 2014</u>; <u>Bekele et al., 2019</u>; <u>Kim et al., 2020</u>; <u>Luengo et al., 2017</u>; <u>Lundehøj et al., 2019b</u>; <u>Novillo et al., 2014</u>). MgAl-LDH is the most
promising for phosphate removal, since the other LDH are highly unstable upon phosphate exposure
(Al Jaberi 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 LDH with high-valent cations, especially Zr(IV) has been proposed. The rationale is that the Zr(IV) 71 72 will increased the cation layer charge and thereby the anion exchange capacity as Zr(IV) is speculated to replace Al(III)(Arias et al., 2018; Chitrakar et al., 2010; He et al., 2021; Koilraj and Kannan, 2010; 73 Liu et al., 2014; Miyauchi et al., 2009; Nowicki et al., 2016; Poonoosamy et al., 2018; Velu et al., 74 75 1998; Wang et al., 2018; Wang et al., 2017). For example, incorporation of a Zr(IV) instead of a Al(III) in the brucite layer would require one  $HPO_4^{2-}$  instead of half a  $HPO_4^{2-}$  for charge balance. This leads to 76 a higher anion-exchange capacity. 77

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

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
 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)

1000 used (mgP/L). The P removal capacity for  $Zr(OH)_4$  and  $ZrO_2$  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)	CO32-	-	Not available	NA	1	NA	-
	Aged (RT)	CO32-	Phosphate	3	1	39	Yes	-
	Aged (RT)	Cl	(1 - 10)	3	1	22	Yes	-
	Aged (RT)	CO32-	Phosphate (100)	3	1	50	Yes	-
	Aged (RT)	Cl		3	1	30	Yes	-
Zn, Al	Aged (65°C)	CO3 <sup>2-</sup>	Phosphate (10 - 250)	2 - 4	2.5	25 - 91	Yes	(Koilraj and Kannan, 2010)
	Aged (65°C)	CO32-		2 - 4	NA	9 - 60	NA	-
Mg, Al	Aged (RT)	$CO_{3}^{2}$	P enriched seawater	4	1	18	No	(Miyauchi et al., 2009)
	Aged (RT)	CO32-	- (0.33)	4	NA	1.3	NA	-
	HT (120°C)	CO3 <sup>2-</sup>	-	4	1	10	No	-
	HT (120°C)	CO3 <sup>2-</sup>	-	4	NA	0.6	NA	-
Mg, Fe	Aged (RT)	CO32-	P enriched seawater	2 - 4	1	15 - 27	No	(Chitrakar et al., 2010)
	Aged (RT)	Cl	(1 - 30)	Not available	NA	$\approx 3$	NA	-
	Aged (RT)	CO32-	Phosphate (100)	2 - 4	1	20 - 35	No	-
	Aged (RT)	Cl	-	Not available	NA	$\approx 50$	NA	-
Mg, Fe	Aged (80°C)	CO <sub>3</sub> <sup>2-</sup>	Phosphate (1 - 50)	Not available	2 - 0.5	35	No *	(Nuryadin et al., 2021)
	Aged (80°C)	CO32-	-	Not available	NA	18	NA	-
Mg, Al	Aging (RT)	CO32-	Phosphate (5 - 200)	Not available	NA	70	NA	(Motandi et al., 2022)
	Aging (RT)	CO32-	-	Not available	Not available	99	No *	-
ZrO <sub>2</sub>	Not available	None	Seawater (0.33)	Not available	Not available	1 - 12	Not available	(Miyauchi et al., 2009)
Zr(OH) <sub>4</sub>	Not available	None	Synthetic wastewater (10)	Not available	Not available	19 - 30	Not available	(Johir et al., 2016)
Zr(OH) <sub>4</sub>	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	This work
	Aged $(80^{\circ}C)$	Cl		2	1	20(2)	No	

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

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 LDH can suppress crystal growth (Nuryadin et al., 2021) or to modify the layer charge by the 95 introduction of Zr(IV)-O<sup>2-</sup> acid base pairs (Motandi et al., 2022). Here an increased P removal capacity 96 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; Koilraj and Kannan, 2010; Shen et al., 2011; Velu et al., 1998; Wang et al., 2018). A slight reduction in interlayer spacing (7.9 to 7.8 Å) 104 105 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 al., 2017). However, for LDH with nitrate as interlayer ion, a lower Al<sup>3+</sup> results in a decreased 107 interlayer spacing, as nitrate ion can be parallel to the cation layer (Karthikeyan et al., 2021). However, 108 a reduced Al content in a M(II)<sub>1-x</sub>Al<sub>x</sub>-LDH will give a similar structural trend. Thus, it is not possible to 109 distinguish between i) the incorporation of Zr(IV) into the LDH and ii) the formation of both MgAl-110 111 LDH and a Zr (hydr)oxide phase only by PXRD and bulk chemical analyses.

In more rigorous studies, the use of advanced structural characterization techniques and in 112 depth data analyses have clearly shown, that Zr(IV) was not incorporated into the LDH, but instead a 113 114 mixture of LDH and Zr(OH)<sub>4</sub> (or ZrO<sub>2</sub>) was obtained (Intissar et al., 2003; Miyauchi et al., 2009). For example (Intissar et al., 2003) investigated the local environment of metal cations for a series of 115

 $M(II)_{0.75}Al_{0.25-v}M(IV)_{v}(OH)_{2}(CO_{3})_{(v+0.25)/2}, nH_{2}O(M(II) = Mg, Co; M(IV) = Sn, Zr) LDH using X-ray$ 116 117 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, (Miyauchi et al., 2009) showed that ZrMgAl-LDH synthesized by coprecipitation had the same k<sup>3</sup>-weighted Zr-K edge as ZrO<sub>2</sub> in the extended X-ray absorption fine structure (EXAFS) spectra. 121 122 Additionally, zirconium oxide impurities are generally only observed after hydrothermal treatment 123 above approximately 120°C (Chitrakar et al., 2007), an approach usually employed to increases the LDH particle size and thereby stability (Pushparaj et al., 2015). Such impurities were not observed, 124 125 when the LDH was aged below 100°C, a more common post synthesis treatment (Table 1). However, amorphous Zr phases such as Zr(OH)<sub>4</sub> or ZrO<sub>2</sub> may still be present and not observed by Powder X-ray 126 127 Diffraction (PXRD), the routine characterization method.

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

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

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interlayer anion prepared by two common post-synthesis treatments (aging and hydrothermal 138 139 treatment). This provided detailed insight into the different phosphate removal pathways and their relative contributions. Thus, our goal was to assess if Zr(IV) addition will improve the performance of 140 141 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 ( $\zeta$ ) potential measurements, electron microscopy (SEM, TEM), and 145 multinuclear MAS NMR spectroscopy.

- 146
- 147 **2. Experimental section**
- 148 **2.1.** *Materials*

149 MgCl<sub>2</sub>·6H<sub>2</sub>O ( $\geq$ 98% purity), AlCl<sub>3</sub>·6H<sub>2</sub>O ( $\geq$ 99% purity), ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O ( $\geq$ 99% 150 purity), NaOH ( $\geq$ 97% purity), NaCl ( $\geq$ 99% purity) and K<sub>2</sub>HPO<sub>4</sub> ( $\geq$  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

The metal- and alkaline salts were dissolved in decarbonated water prepared by boiling milli-Q water with nitrogen (N<sub>2</sub>) flow for ca. one hour and then cooled to 25-35 °C under a nitrogen (N<sub>2</sub>) flow before use. MgAl- and Zr doped MgAl-LDH were synthesized by coprecipitation at constant pH using earlier reported procedures (Chitrakar et al., 2007) with the following modifications: 500 mL of a metal ion solution containing Mg<sup>2+</sup>, Al<sup>3+</sup>, and Zr<sup>4+</sup> 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 Titrando®; 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 N <sub>2</sub> flow to minimize carbonate impurities.

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			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 <sub>2</sub>	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

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

second batch was redispersed into decarbonated water (350 mL) and subsequently hydrothermally 178 179 treated in multiple 70 mL Teflon<sup>®</sup> 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 (Zr(OH)<sub>4</sub>) and zirconium oxide (ZrO<sub>2</sub>) were synthesized using 500 mL of a 0.2 M ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O and 500 mL of 1.2 M NaOH solution using the same titrator, volume, metal-solution 184 185 rate, and pH as above. After synthesis, the batch was also divided into two and the post-synthesis was either aging or hydrothermal treatment. Aging resulted in the formation of amorphous Zr(OH)<sub>4</sub>, 186 whereas crystalline ZrO<sub>2</sub> was obtained after hydrothermal treatment. All solid products were dried at 187 188 50°C overnight ( $\approx$  16-18 h) and ground to a fine powder using an agate mortar and pestle before analyses. 189

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

202

# 2.2.2. Phosphate isotherm batch experiments

The phosphate sorption isotherm experiments were performed in 15 mL polypropylene 203 conical centrifuge tubes (Sarstedt,  $120 \times 17$  mm) containing 10.00 mL phosphate solution and 10.0(1) 204 mg LDH, which were shaken at 400 rpm using an orbital shaker for 24 h at room temperature ( $\approx 20^{\circ}$ C). 205 All phosphate isotherm experiments were performed as duplicates. The concentration of the phosphate 206 solutions ranged from 30 to 400% ( $\approx$  18 to 224 mgP/L) theoretical anion exchange capacity (TAC) for 207 HPO<sub>4</sub><sup>2-</sup> calculated for a Mg<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O LDH under the assumption of the complete ion exchange 208 of Cl<sup>-</sup> for HPO<sub>4</sub><sup>2-</sup> (Table S1). The pH of the solutions was adjusted to 7.5 (67% HPO<sub>4</sub><sup>2-</sup>, 33% H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) 209 using 0.1 M HCl. To mimic industrial applications of LDH sorbents, the pH was not actively 210 controlled. Moreover, pH control is known to drive the dissolution of the LDH with the lowest 211 212 dissolution observed at pH 8 (Imran et al., 2016). After 24 h, the supernatant was collected using a 2 mL disposable pipette and filtrated through a 0.45 µm PTFE syringe filter. All phosphate solutions 213 214 were prepared in milli-Q water.

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

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

222 
$$q_e = (Q_m K_L C_e)/(1 + K_L C_e)(Eq. 2)$$

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

Where  $C_0$  is the initial concentration (mgP/L), V (L) is the total volume and *m* (g) is the mass of LDH.  $Q_m$  is the maximum monolayer coverage (mgP/g),  $K_L$  is the Langmuir isotherm constant (ml<sup>3</sup>/mg) related to the affinity of binding sites,  $K_F$  (mgP/g) is the Freundlich constant (related to the sorption capacity) and *n* is related to the sorption intensity (Foo and Hameed, 2010).

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

$$B(2\theta_{003}) = (K \cdot \lambda) / (\tau \cdot \cos(\theta))$$
 (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),  $\lambda$  is the wavelength,  $\theta$  is the diffraction angle, and  $\tau$  is the crystallite diameter in Ångstrøm (Å).

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# 251

# 2.2.4. Solid State <sup>1</sup>H, <sup>27</sup>Al, and <sup>31</sup>P MAS NMR spectroscopy

Single pulse <sup>27</sup>Al and <sup>31</sup>P magic angle spinning (MAS) NMR spectra and <sup>27</sup>Al triple 252 253 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 254 spinning speed for the single pulse and 14 - 15 kHz for the 3QMAS experiments. The relaxation delay 255 was optimized for each sample but were generally 1 s for the single pulse  $^{27}$ Al MAS NMR (< 10° pulse 256 width for quantitative excitation) and 30 - 90 s for single pulse  $^{31}$ P MAS NMR (45° excitation pulse). 257 The <sup>27</sup>Al 30MAS experiment were recorded using a three-pulse z-filter sequence (Amoureux and 258 Fernandez, 1998). 259

Single pulse <sup>1</sup>H MAS NMR spectra were recorded on an Agilent Inova 600 MHz NMR 260 spectrometer (14.1 T) using a 1.6 mm triple resonance MAS NMR probe and 30 - 32 kHz spinning 261 speed. The <sup>1</sup>H, <sup>27</sup>Al, and <sup>31</sup>P and NMR spectra were referenced using H<sub>2</sub>O ( $\delta_{iso}(^{1}H) = 4.6$  ppm), 1.0 M 262 solution of AlCl<sub>3</sub> ( $\delta_{iso}(^{27}Al) = 0$  ppm) and concentrated phosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>;  $\delta_{iso}(^{31}P) = 0$ 263 ppm), respectively. Deconvolution of the <sup>27</sup>Al single pulse MAS NMR spectra were performed in 264 Quadfit (Kemp and Smith, 2009) using two sites: one with  $C_0 = 1.6$  MHz and  $\eta = 0$  (LDH) and a 265 second site with  $C_Q = 3.3$  MHz and  $\eta = 0.2$  (amorphous aluminum hydroxide, will be discussed later) 266 (Jensen et al., 2016; Pushparaj et al., 2015; Staal et al., 2017). The <sup>27</sup>Al 3QMAS NMR spectra were 267

processed in ssNake (v1.1), (van Meerten et al., 2019) whereas single-pulse <sup>1</sup>H and <sup>31</sup>P MAS NMR
spectra were analyzed by deconvolution in MestReNova (ver. 14.2.1.).

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

The zeta ( $\zeta$ ) potential of MgAl/Zr composite, Zr(OH)<sub>4</sub>, and ZrO<sub>2</sub> were determined by electrophoretic light scattering utilizing a Zetasizer nano ZS analyzer from Malvern Panalytical fitted with a 4 mW 632.8 nm "red" laser. For the measurement, powdered samples were dispersed (ca. 0.1 mg/mL) in deionized water and stirred 24 h and then sonicated for 15 min at room temperature. The Zeta potential values were calculated by determining the electrophoretic mobility and then applying the Henry equation.

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#### 2.2.6. Transmissions electron microscopy

Transmission electron microscopy (TEM) images were acquired with a JEOL 2100Plus microscope (200 kV) fitted with LaB<sub>6</sub> electron gun. Elemental analysis of individual particles was acquired by energy dispersive X-ray spectroscopy. 20  $\mu$ L of an aqueous suspension of 1 mg sample per mL water was deposited on a carbon grid covered with a forward carbon film and dried at 40°C under air.

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#### 286 2.2.7. Elemental analysis

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the quantification of Mg, Al, Zr, and P.. Approximately 0.02 g LDH and 10.00 mL of concentrated nitric acid (HNO<sub>3</sub>, 65%) were mixed followed by microwave digestion at 200°C for 15 min. The resulting

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supernatant were diluted appropriately in milli-Q water beforeanalysis on an Optima 2100 DV,PerkinElmer, USA.

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<b>3. Results and discussi</b>
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#### *3.1. The effect of the Zr content on the phosphate removal capacity of MgAl-LDH*

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



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

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

and adsorption to impurities (details in the next section) may result in phosphate removal. Moreover, 313 314 dissolution of the LDH and/or Zr(IV) (hydr)oxides followed by precipitation of phosphate phases (e.g., Al-P, Mg-P) may also contribute. The contribution from two or more pathways explains the 315 inadequately fitting by both the Freundlich ( $R^2 = 0.78$  to 0.90) and Langmuir ( $R^2 = 0.56$  to 0.91) 316 317 (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 Ce of. Noteworthy, the kinetic sorption experiments showed a quick phosphate uptake and reached an equilibrium within the first hour (Figure 319 320 S1).

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



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

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

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

**Table 3.** Properties of the synthesized samples and these after phosphate exposure based on PXRD,

- for  $Zr(OH)_4$  and  $ZrO_2$  were -18(5) and -8(4) mV respectively.
- <sup>a</sup> The cell parameters obtained from Le Bail fitting (Figure S3), <sup>b</sup> Cell parameters based on the position
- of the (003) and (110) reflections. FWHM is for the (003) reflection. n. a. = Data not available.  $\tau$  = is

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

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

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

<sup>344</sup> SSNMR spectroscopy, ICP-OES, and zeta potential measurements. For a comparison, the zeta potential

treatment leads to the formation of additional crystalline phases (Figures 1 and S3). For MgAl-HT only boehmite (AlO(OH)) is detected, which is formed by dehydroxylation of Al hydroxides during the hydrothermal treatment (Pushparaj et al., 2016). In contrast, two new reflections are observed at  $2\theta \approx$ 32° and 51° for the Zr modified LDH (Zr0.1-HT, Zr0.5-HT), which are assigned to ZrO<sub>2</sub> formed by dehydroxylation of Zr(OH)<sub>4</sub>. This is supported by the conversion of amorphous Zr(OH)<sub>4</sub> to crystalline ZrO<sub>2</sub>, when hydrothermally treated similar to the LDH samples. To identify the presence of Zr(OH)<sub>4</sub> in 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 typical LDH bands including hydroxides (3500 - 3600 cm<sup>-1</sup>), interlayer water (1600 - 1650 cm<sup>-1</sup>), and 360 the metal oxides bands, MO<sub>6</sub>, (696 - 717 cm<sup>-1</sup>) and OMO bands (500 - 400 cm<sup>-1</sup>); M = metal cation 361 362 (Goh et al., 2008; Staal et al., 2017). Minor carbonate contamination is also observed at 1350-1380 cm<sup>-</sup> <sup>1</sup> due the high affinity of LDH for carbonate (Forano et al., 2006; Goh et al., 2008). When the Zr(IV) 363 content is increased from 0.1 to 0.5 the intensity of the AlO<sub>6</sub> stretching mode (850-950 cm<sup>-1</sup>) decreased 364 365 strongly for both the aged and hydrothermally treated LDH samples. This indicates depletion of Al in the LDH cation layer corresponding to the reduced reactant concentration (Table 2). 366

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



Figure 3. A representative deconvolution of a single pulse <sup>27</sup>Al MAS NMR spectrum using two phases:  $\delta_{iso}(^{27}Al) \approx 10 \text{ ppm} \text{ (LDH, pink)} \text{ and } \delta_{iso}(^{27}Al) \text{ centered at} \approx 7 \text{ ppm} \text{ (AOH, green)}. The <sup>27</sup>Al MAS NMR$ spectra of the other samples, which are similar, are shown in Figures S6 and S7.

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TGA (Figure S8) and <sup>1</sup>H MAS NMR (Figure 4, Figures S9-11) probed the thermal 384 degradation and water content: Zr0.5-A exhibited a mass loss of 22(2)% and Zr0.5-HT of only 11(2)% 385 below 200°C implying a higher water or hydroxide content in the aged sample compared to the 386 hydrothermally treated. Moreover, <sup>1</sup>H MAS NMR showed an increased intensity around 5 ppm, which 387 is ascribed to the overlap of the <sup>1</sup>H NMR resonances from  $Zr(OH)_4$  ( $\delta_{iso}(^{1}H) = 4.8$  ppm; Figure S9) and 388 water in the LDH ( $\delta_{iso}(^{1}H) = 4.5 - 5.0$  ppm; Table S4 and Figures S10-11). Deconvolution of the <sup>1</sup>H 389 MAS NMR spectra showed resonances at  $\delta_{iso}(^{1}\text{H}) \approx 4.8(2)$  ppm for Zr0.5-HT (26(5)%) and for Zr0.5-A 390 (37(5)%) (Figure 4). 391

This intensity difference is ascribed to the presence of <sup>1</sup>H NMR resonance of  $Zr(OH)_4$ , which overlap with H<sub>2</sub>O (see also Figure S9). Thus,  $Zr(OH)_4$  must be present in Zr0.5-A. To further probe this, SEM provided insight into particle size, morphology, and homogeneity (Figure S12).



**Figure 4.** Deconvolution of the <sup>1</sup>H MAS NMR spectra of a) Zr0.5-A and b) Zr0.5-HT with the experimental (black), simulated (red), and difference between the experimental and simulated spectrum (dark blue), as well as the individual sites AOH (green), H<sub>2</sub>O (turquoise),  $Zr(OH)_4$ , orange for Mg<sub>2</sub>Al-OH, pink for Mg<sub>3</sub>-OH and black is an unknown site needed for the satisfactory simulation of the 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<sub>2</sub> and Zr(OH)<sub>4</sub> for Zr0.5-HT and Zr0.5-A respectively). Their presence is 406 also supported by TGA and <sup>1</sup>H 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). Hydrothermal treatment prevents aggregation and favors a face-to-face orientation of individual 410 411 hexagonal platelets while for Zr0.1-A the particles are in dense, disordered agglomerates. EDX analysis (Figure S13) reveal an increase in the Mg:Al ratio in the LDH from 2.0 to 2.5, for Zr0.1-A and Zr0.1-412 HT respectively.. ZrO<sub>2</sub> nanoparticles (≈10 nm) are clearly observed on the surface of Zr0.1-HT 413 platelets as well as dispersed black spots (Figure 5B). The absence of these dark spots on the TEM 414 415 images of Zr0.1-A confirms the formation of amorphous Zr(OH)<sub>4</sub> nanoclusters most likely covering the LDH surface as also observed by <sup>1</sup>H MAS NMR, TGA, and SEM analysis. 416

It is clear that the hydrothermal treatment converts these highly dispersed  $Zr(OH)_4$ nanoclusters into  $ZrO_2$  nanoparticles, which are very evident in the TEM images, as illustrated for Zr0.5-A (Figure S14c and d). The sorption of phosphate on both the Zr0.1-A and Zr0.1-HT samples forces the collapse of individual particles into densely packed aggregates most likely due to the change in surface charge properties and inversion of the zeta potential. These Zr-based nanoparticles are still observed after P sorption (Figures S14c and d). The presence of Al hydroxides or boehmite rods in addition to Zr0.1-A and Zr0.1-HT-P particles (Figures14) supported the results from <sup>27</sup>Al MAS NMR
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, <sup>25</sup>Mg MAS NMR spectra supported a higher Mg:Al ratio in the LDH than the 429 targeted 2:1 (Figure S15), in agreement with <sup>27</sup>Al-, <sup>1</sup>H MAS NMR, and ICP-OES, as the second order 430 quadrupolar line shape is more undefined as the Mg:Al ratio increases (<u>Sideris et al., 2012</u>).

431 To summarize, Zr is segregated as amorphous  $Zr(OH)_4$  for Zr0.1- and Zr0.5-A and as crystalline ZrO<sub>2</sub> for ZrO.1-HT and ZrO.5-HT, i.e., Zr is not incorporated into the LDH structure. The 432 433 presence of  $ZrO_2$  and  $Zr(OH)_4$  is expected to influence the phosphate sorption capacity. Therefore, the theoretical sorption capacity can be estimated using the Mg:Al ratio from <sup>27</sup>Al MAS NMR and ICP-434 435 OES (Table S1) combined with the AOH and Zr(IV) content from ICP-OES. From the detailed characterization, it can be unambiguously concluded that the samples contain three phases: 1) MgAl-436 LDH 2) AOH, and 3) Zr(OH)<sub>4</sub> (aged samples) or ZrO<sub>2</sub> (hydrothermally treated). Based on <sup>27</sup>Al MAS 437 438 NMR and ICP-OES the contribution from each phase can be calculated. The adjusted Mg:Al ratio in the MgAl-LDH and their removal capacities are summarized in Table S1. The LDH phase represents 439 90-98 mass% of the sample. The AOH and Zr (hydr)oxide content corresponds to 1-10 mass%, with 440 Zr(OH)<sub>4</sub>/ZrO<sub>2</sub> contribution 2-6 mol% based on ICP-OES. Thus, based on the Zr (hydr)oxide content, 441 this phase accounts for less than 5 mgP/g (Table 1). Therefore, mainly the LDH and the AOH 442 contribute to the sample's phosphate removal capacity. Finally, the decreased sorption capacity is a 443 direct consequence of the decrease in Al content. 444

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

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

As expected, phosphate sorption on the surface of aged and hydrothermally treated samples reversed the charge of the platelets. Thus, the zeta potential value changes from 29 - 27 mV (MgAl-A and MgAl-HT) to -17 mV (MgAl-A-P and MgAl-HT-P) (Table 3). No significant different is observed between the MgAl-LDH and the lowest Zr-doping level. Increasing the Zr(IV) content to 0.5 in the aged LDH leads to a clear change of surface charge from +29 mV to -12 mV. Hydrothermal treatment leads to phase segregation and formation of ZrO<sub>2</sub>, which has limited effect on the mean (bulk) zeta potential (Table 3).

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

The *c* unit cell parameters, i.e., the interlayer spacing, increases ca 0.5 Å after P sorption, which combined with the increase in the FWHM of the (001) reflections (Table 3) reflects the intercalation of phosphate into the LDH as previously observed (Costantino et al., 1997; Hou et al., 2003; Lundehøj et al., 2019a). Moreover, the  $v_3(PO_4^{3-})$  vibration (Badreddine et al., 1999) observed by FT-IR (Figure S5) also proves phosphate related to the material and the negative surface charge (-9 to -19 mV; Table 3) indicates surface complexation. To summarize, characterization show no changes in the sample composition (i.e., limited dissolution and degradation) of the LDH layer after phosphateexposure but strong surface modifications.

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476 *3.4. Quantification of the different phosphate removal pathways by* <sup>31</sup>*P MAS NMR spectroscopy* 



Figure 6. Experimental <sup>31</sup>P MAS NMR spectra of the LDH samples after phosphate sorption (a, b, e, f), Zr(OH)<sub>4</sub> (c), and ZrO<sub>2</sub> (d) and the respective deconvolutions with experimental (black), simulation (red), error (blue) and the individual sites: 1: turquoise, 2: orange, 3: green and site 4 and 5: grey.

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

Sites 4 (10 - 26%) and site 5 (20 - 28%) are assigned to phosphate removed by AOH, and the Zr phase(s),  $Zr(OH)_4$  for aged samples and  $ZrO_2$  for hydrothermally treated samples, respectively. This was based on a comparison with <sup>31</sup>P MAS NMR spectra recorded for  $Zr(OH)_4$ -P and  $ZrO_2$ -P (Figure 6c and d) combined with previous studies (Lundehøj et al., 2019a; Lundehøj et al., 2019b). Differentiation between the AOH,  $Zr(OH)_4$ , and  $ZrO_2$  cannot be done because of broad and overlapping resonances and is beyond the scope of this work.

Finally, Site 1 (4 - 12%;  $\delta_{iso}({}^{31}P) = 6.8$  to 7.8 ppm) has the lowest intensity and is not 504 detected for Zr0.5-A or Zr0.5-HT. Furthermore, this site is most prominent for aged samples, 505 Therefore, this site is tentatively assigned to dissolution of the LDH, as the smaller particles are less 506 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. 507 Phosphate sorbed to impurities (AOH,  $Zr(OH)_4$ , and  $ZrO_2$ ) is the major pathway (41 – 508 54%) for aged samples in accordance with <sup>27</sup>Al- and <sup>1</sup>H MAS NMR. For a comparison, the impurities 509 contribute 34 – 38% for hydrothermally treated samples. Thus, the impurity content in the LDH must 510 511 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.





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

(blue), H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup> removed by the LDH (orange and green) and the contribution from impurities, i.e.,
AOH, ZrO<sub>2</sub>, Zr(OH)<sub>4</sub> (grey).

519

#### 520 **4.** Conclusions

Detailed insight into the phosphate removal capacity and stability of a series of MgAl-521 LDH with different Zr(IV) modifications was achieved using global and local characterization 522 523 techniques. Our results clearly demonstrate, that Zr(IV) cannot be incorporated into the LDH lattice and thereby improve the phosphate removal capacity. Instead separate phase of Zr(OH)<sub>4</sub> or ZrO<sub>2</sub> were 524 present for the aged and hydrothermal treated samples, respectively. Especially detection of the X-ray 525 amorphous  $Zr(OH)_4$  in the aged samples required advanced characterization techniques (<sup>1</sup>H- and <sup>27</sup>Al 526 MAS NMR, SEM, TEM and TGA). The unsuccessful incorporation of Zr(IV) together with the 527 decreased Al doping resulted in a drastic decrease in the phosphate removal capacity (45 - 54 to 16 - 20 528 mgP/g). Single pulse <sup>31</sup>P MAS NMR showed that 42 - 62% of the ortho-phosphate was intercalated in 529 the LDH by ion-exchange. However, <sup>31</sup>P MAS NMR also showed that up to 54% of phosphate was 530 removed by impurity phases or dissolution of the LDH. Thus, phosphate has a high affinity towards the 531 532 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 minimized. Moreover, it is emphasized that phosphate removal pathways cannot be reliably assessed 535 based on sorption studies only. Detailed characterization of the LDH sorbent before and after 536 537 phosphate exposure is paramount for reliable assessment of the LDH sorbent performance and stability.

538

# **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 PXRD, Le Bail refinement, 553 FT-IR, SEM, <sup>1</sup>H, <sup>25</sup>Mg, <sup>31</sup>P, <sup>27</sup>Al 1D MAS NMR together with 2D MAS NMR (<sup>27</sup>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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