

1 **Enhanced Phosphorus Locking by Novel Lanthanum/Aluminum-Hydroxide**
2 **Composite: Implication for Eutrophication Control**

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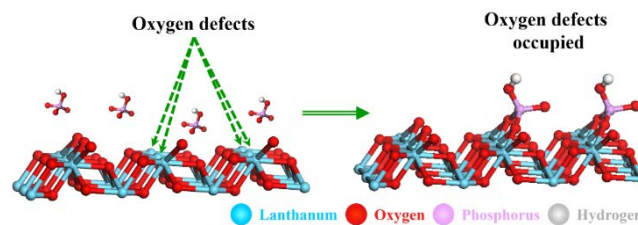
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26 **Abstract:** Lanthanum (La) bearing materials have been widely used to remove
27 phosphorus (P) in water treatment. However, it remains a challenge to enhance
28 phosphate (PO_4) adsorption capacity and La usage efficiency. In this study, La was co-
29 precipitated with aluminum (Al) to obtain a La/Al-hydroxide composite (LAH) for P
30 adsorption. The maximum PO_4 adsorption capacities of LAH (5.3% La) were 76.3 and
31 45.3 mg P g^{-1} at pH 4.0 and 8.5, which were 8.5 and 5.3 times higher than those of
32 commercially available La-modified bentonite (Phoslock[®], 5.6% La), respectively. P
33 K-edge X-ray absorption near edge structure analysis showed that PO_4 was
34 preferentially bonded with Al under weakly acid conditions (pH 4.0), while tended to
35 associate with La under alkaline conditions (pH 8.5). La L_{III}-edge extended X-ray
36 absorption fine structure analysis indicated that PO_4 was bonded on La sites by forming
37 inner sphere bidentate-binuclear complexes and oxygen defects exhibited on LAH
38 surfaces, which could be active adsorption sites for PO_4 . The electrostatic interaction,
39 ligand exchange and oxygen defects on LAH surfaces jointly facilitated PO_4 adsorption
40 but with varied contribution under different pH conditions. The combined contribution
41 of two-component of La and Al may be an important direction for the next generation
42 of commercial products for eutrophication mitigation.

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48 **Introduction**

49 Excessive phosphorus (P) discharge can trigger severe eutrophication in aquatic
50 environments,¹⁻³ which may further lead to harmful algal blooms, deterioration of water
51 quality, and eventually, ecosystem collapse.^{4, 5} Over recent decades, various materials
52 have been used for P removal in water bodies.² In particular, La-modified materials or
53 La-bearing compounds are often considered as effective geo-engineering tools to lock
54 P from aquatic ecosystems.^{6, 7} For instance, the commercial product Phoslock[®], a La-
55 modified bentonite clay, has been used for internal P loads control in 200 water bodies.^{2,}
56 ⁸

57 Previous studies suggest that the binding ability between La and PO₄ anions
58 dominates P locking by La-bearing materials.⁹⁻¹¹ Ligand exchange is generally
59 considered as the main mechanism of PO₄ affinity to La-bearing materials.^{9, 10} It is well
60 known that the ability of ligand exchange depends on the surface charge of the
61 adsorbent.¹² However, existing La-modified materials (including Phoslock[®]) often have
62 a negative surface charge in natural waters,^{10, 13} which is not favorable for attracting
63 H₂PO₄⁻ or HPO₄²⁻ from the viewpoint of electrostatic interaction. If the surface charge
64 of La-modified material could be made positive, it would attract more PO₄ anions.¹²
65 We hypothesize that synthesizing a La-bearing adsorbent with positive surface charge
66 would enable a two component mechanism involving both electrostatic interaction and
67 ligand exchange to improve PO₄ adsorption capacity and La use efficiency. This
68 requires a new host material for La in order to develop a more efficient PO₄ adsorbent.

69 Aluminum (Al) compounds are also widely used for P removal in water treatment.¹⁴
70 Al (hydro)oxide is effective at adsorbing P selectively in the presence of competing
71 anions such as Cl⁻, NO₃⁻, HCO₃⁻ and SO₄²⁻.¹⁵ It is also abundant in nature, low cost and
72 has a high point of zero charge (pH_{PZC}).¹⁴ Al compounds could potentially be a host

73 material for La in synthesizing a new adsorbent with positive surface charge. On the
74 other hand, it has been reported that the effectiveness of Al treatment depends on the
75 pH in waters,¹⁶ because Al compounds are prone to desorption of PO₄ under alkaline
76 conditions.^{17, 18} Moreover, the ecological effect of aluminum has become a concern in
77 aquatic research.^{17, 19} Owing to the high affinity between La and PO₄ anions, if an Al
78 compound is incorporated in the fabrication with La, the PO₄ adsorbed by La/Al
79 composite may be more stable over a wide pH range, which is important for practical
80 remediation engineering under field conditions.

81 As an element-specific and in situ method to detect the molecular structures of
82 reacting species, X-ray absorption fine structure (XAFS) spectroscopy, including X-ray
83 absorption near edge structure (XANES) and extended X-ray absorption fine structure
84 (EXAFS) spectroscopy, has been developed for determining the properties of PO₄
85 bonding on solid surfaces.^{11, 20, 21} P K-edge XANES has been used to study PO₄
86 adsorption in single or binary systems of Fe/Al-hydroxide materials, which can
87 distinguish PO₄ contents associated with Fe- or Al- hydroxide.^{20, 22, 23} EXAFS could
88 provide additional insights for PO₄ bonding mode by detecting the local structure of
89 metal elements reacted with PO₄.¹¹ By using La L_{III}-edge EXAFS spectroscopy, the PO₄
90 bonded on Phoslock[®] was proved to be an insoluble rhabdophane (LaPO₄·nH₂O, n ≤
91 3).¹¹ However, to the best of our knowledge, little information is available about the
92 effect of La local structure on PO₄ adsorption capacity and its transformation after
93 reaction with PO₄.

94 Here, a La/Al-hydroxide composite (LAH) with high PO₄ adsorption efficiency was
95 synthesized by a co-precipitation method. Three LAH composites with different La:Al
96 molar ratios of 1:30, 1:20 and 1:10 were prepared in order to investigate the role of La
97 in LAH for PO₄ adsorption. Batch experiments were conducted to determine the

98 adsorption and desorption properties of PO₄ on LAH. P K-edge XANES spectroscopy
99 was used to investigate the proportions of PO₄ associated with Al relative to La. La L_{III}-
100 edge EXAFS spectroscopy was used to detect the local atomic structure changes around
101 the La (III) ion before and after PO₄ adsorption to elucidate the adsorption mechanism
102 of PO₄ on LAH surfaces. The objective of this study is to synthesize a highly efficient
103 PO₄ adsorption material and to investigate its mechanism at the molecular level, so that
104 the methodology could be used to guide new development of geo-engineering materials
105 for eutrophication management.

106 **Materials and methods**

107 **LAH synthesis and characterization.** Predetermined amounts of analytical grade
108 LaCl₃·7H₂O and AlCl₃ were dissolved into 200 mL deionized water to obtain La/Al
109 molar ratios of 1:30, 1:20 and 1:10 (LAH-1/30, LAH-1/20 and LAH-1/10). Under
110 stirring, 2 mol L⁻¹ NaOH aqueous solution was added dropwise to the mixed solutions
111 at 333 K until pH 9.0. Then the mixture was stirred for 2 h and aged for 24 h at 333 K.
112 Precipitates were washed three times with deionized water and freeze-dried for 24 h.
113 Powders of Al(OH)₃ and La(OH)₃ were synthesized by the same process to act as
114 controls (Details are provided in the Supporting Information).

115 To obtain the exact content of La and Al in the LAH, samples were digested in 6 mol
116 L⁻¹ HCl and the chemistry of the resultant solutions was determined using an
117 inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8300,
118 PerkinElmer, USA). Brunauer-Emmett-Teller (BET) surface areas and pore size
119 distributions were examined by a Micromeritics ASAP 2020 static volumetric analyzer.
120 LAH morphologies were observed using field emission scanning electron microscopy
121 (FESEM, SU 8020, Hitachi, Japan). X-ray powder diffraction (XRD) data of the LAH
122 were recorded on an X'Pert PRO MPD X-ray diffractometer (PANalytical, The

123 Netherlands) with a Cu-K radiation ($\lambda = 1.5408$) at 40 kV and 40 mA in the 2θ range
124 of 5° to 90° . Electron paramagnetic resonance (EPR) spectrum of LAH-1/10 was
125 recorded on a JEOL JES-FA200 EPR spectrometer (Japan) at room temperature. Zeta
126 (ζ) potential analysis of LAH was measured by a Zetasizer Nano ZS potential analyzer
127 (Malvern Instrument Ltd., United Kingdom). Phoslock[®] (Phoslock[®] Water Solutions
128 Ltd, Australia) was also characterized by the same procedures described above.

129 **Adsorption and desorption experiments.** In order to identify the influence of pH
130 on the equilibrium adsorption capacity, adsorption experiments of PO_4 on LAH were
131 conducted in polypropylene tubes at pH 4.0 ~ 10.0. LAH (1 g L^{-1}) were added to 50 mL
132 polypropylene tubes with initial P concentration 80 mg P L^{-1} in 0.01 mol L^{-1} NaCl
133 background and shaken at 170 rpm at 298 K for 48 h. The solution pH was maintained
134 constant with 0.01 mol L^{-1} HCl and NaOH.

135 Adsorption isotherm experiments were conducted in 50 mL polypropylene tubes by
136 mixing various concentrations of KH_2PO_4 solutions with 1 g L^{-1} adsorbents in 0.01 mol
137 L^{-1} NaCl background. The mixture was stirred at 298 K for 48 h allowing the adsorption
138 to reach equilibrium. pH 4.0 (pH for maximum PO_4 adsorption in this study, Figure S3)
139 and pH 8.5 (up limit pH for lakes)²⁴ were chosen to determine the adsorption and
140 desorption behaviors of PO_4 . At the end of adsorption isotherm experiments, the
141 exhausted solutions of LAH samples which had initial P concentration 80 mg P L^{-1} were
142 centrifuged to preserve 10 mL suspension at the bottom, and then 0.01 mol L^{-1} NaCl
143 solution was added to keep the same ionic strength. The experimental conditions of
144 desorption experiments were conducted following adsorption studies.

145 The PO_4 concentration was measured by ascorbic acid method to monitor the
146 absorbance at 880 nm with spectrophotometer (UV-756 PC, Shanghai Sunny Hengping
147 Scientific Instrument CO. LTD, China). The concentrations of released Al^{3+} and La^{3+}

148 were analyzed by ICP-OES (Optima 8300, PerkinElmer, USA).

149 **XAFS data collection and analysis.** Phosphorus K-edge XANES data were
150 collected on Beamline 4B7A at the Beijing Synchrotron Radiation Facility (BSRF),
151 China. The storage ring was operating at 2.5 GeV with current from 250 to 150 mA. A
152 double crystal Si (111) monochromator offered an energy resolution of about 0.6 eV
153 with a beam size of $1.0 \times 3.0 \text{ mm}^2$. The incident X-ray energy was calibrated by using
154 the white line of K_2SO_4 (S K-edge) at 2482.4 eV before spectra collection. Spectra were
155 collected in the fluorescence yield (FLY) mode between -30 to +90 eV relative to P K-
156 edge energy at 2152 eV with a minimum step size of 0.3 eV between 2140 and 2180
157 eV. The P1s peak position of KH_2PO_4 was used to calibrate the P K-edge XANES
158 spectra. La L_{III} -edge EXAFS data were collected on beamline 1W2B at the BSRF,
159 China. The monochromator energy calibration was monitored to 5483 eV using a
160 vanadium foil as an internal standard with a transmission chamber detector. The moist
161 samples were fixed in a Teflon cell and sealed with Mylar film during EXAFS
162 measurement.²⁵ An average of three scans was performed to achieve suitable
163 single/noise, and no obvious change in spectral data was observed during the three
164 scans. The spectral data were processed following the standard procedures of
165 background absorption removal, normalization, k-space conversion and Fourier
166 transformation. Details for data collection and analysis were given in the Supporting
167 Information.

168 **Results**

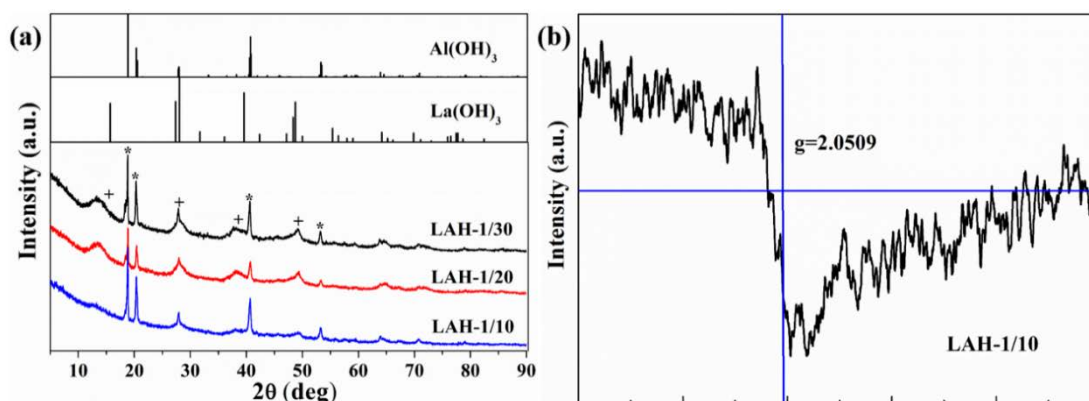
169 **Characterization.** The physiochemical properties of the three synthesized LAH
170 materials, commercial product Phoslock[®] and $\text{Al}(\text{OH})_3$ were summarized in Table 1.
171 The La mass proportion of LAH-1/30 was 5.3%, which was close to that of Phoslock[®]
172 (5.6%). The La mass proportions of LAH-1/20 and LAH-1/10 were 7.8% and 13.1%,

173 respectively. The BET surface areas of LAH-1/30, LAH-1/20 and LAH-1/10 were
 174 107.1, 121.0 and 99.3 m² g⁻¹, respectively, which were much higher than those of
 175 Phoslock[®] (38.2 m² g⁻¹) and Al(OH)₃ (51.2 m² g⁻¹).

176 **Table 1. General characteristics of LAH, Phoslock[®] and Al(OH)₃**

Adsorbent	La (wt %)	Al (wt %)	surface area	pore volume
			(m ² g ⁻¹)	(cm ³ g ⁻¹)
LAH-1/30	5.3	31.7	107.1	0.34
LAH-1/20	7.8	31.4	121.0	0.39
LAH-1/10	13.1	26.5	99.3	0.31
Phoslock [®]	5.6	7.8	38.2	0.14
Al(OH) ₃	-	34.6	51.2	0.06

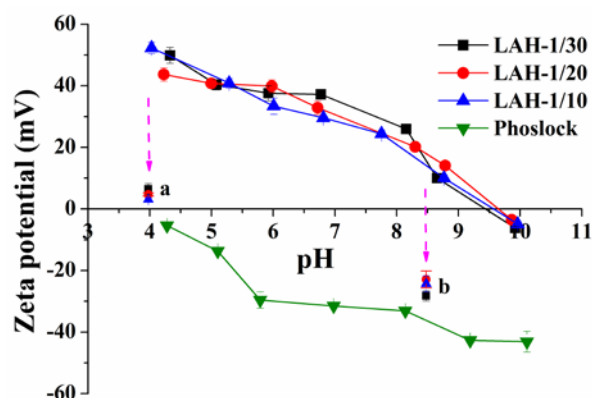
177 The XRD analysis suggested that LAH were mainly composed of Al(OH)₃ (PDF NO.
 178 74-1119) and La(OH)₃ (PDF NO. 36-1481) (Figure 1a). The characterization peaks of
 179 La(OH)₃ were weaker with increasing La contents, indicating that more amorphous
 180 La(OH)₃ was formed. The EPR spectrum of LAH-1/10 showed a clear signal at g =
 181 2.0509 (Figure 1b) corresponding to oxygen defects on the surfaces.^{26, 27} FESEM
 182 images showed that the average particle size of LAH composite was about 8-16 μm and
 183 thin flakes appeared on LAH surfaces with increasing La contents (Figure S1).



184

185 **Figure 1.** (a) XRD patterns of LAH, in comparison with model compounds of $\text{Al}(\text{OH})_3$
186 and $\text{La}(\text{OH})_3$. Asterisks (*), $\text{Al}(\text{OH})_3$; Plus (+), $\text{La}(\text{OH})_3$. (b) EPR spectrum of LAH-
187 1/10 at room temperature.

188 The ζ potential of Phoslock[®] and LAH samples before and after PO_4 adsorption were
189 shown in Figure 2. The LAH had positive surface charge from pH 4.0 to 9.7, while
190 Phoslock[®] had negative potential from -5.4 to -43.1 mV in the pH range of 4.0 to 10.0.
191 The ζ potential of all LAH materials decreased after PO_4 adsorption at initial P
192 concentration 50 mg P L^{-1} . For LAH-1/30, the ζ potential decreased significantly from
193 about +50 mV (pH 4.0) and +10 mV (pH 8.5) to +11 mV (Figure 2, dot a) and -21 mV
194 (Figure 2, dot b) ($p < 0.001$, paired t-test, SPSS 19.0) after PO_4 adsorption, respectively.
195 The ζ potential of $\text{La}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ were also determined, and the pH_{pzc} value of
196 $\text{La}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ was approximately 9.4 (Figure S2).

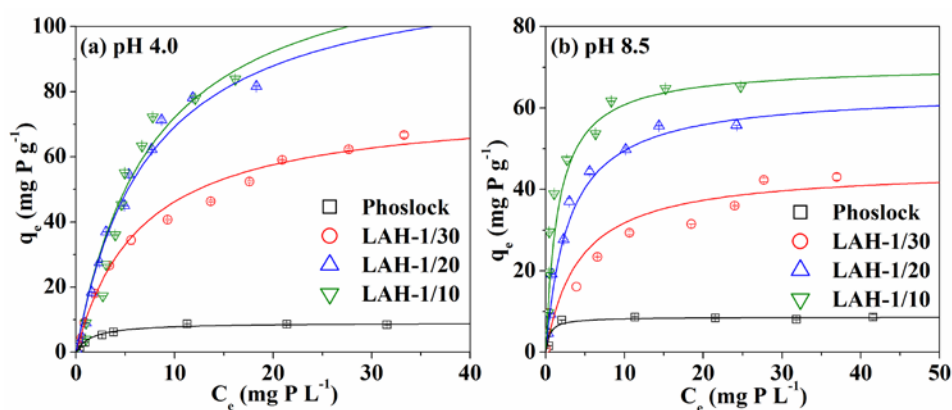


197
198 **Figure 2.** ζ potential of LAH and Phoslock[®] as a function of pH (solid line), and that of
199 LAH with adsorbed PO_4 at pH 4.0 (dot a) and 8.5 (dot b).

200 **Phosphate adsorption and desorption.** The effect of pH on PO_4 adsorption to LAH
201 was investigated in the pH range of 4.0 ~ 10.0 (Figure S3). LAH-1/10 had the highest
202 PO_4 adsorption capacity of 71.6 mg P g^{-1} at pH 4.0 and decreased to 26.1 mg P g^{-1} at
203 pH 10.0. The data showed LAH exhibited a maximum PO_4 adsorption capacity at pH
204 4.0 and dropped with increasing pH values. Consequently, pH 4.0 (pH for maximum

205 PO₄ adsorption in this study) and pH 8.5 (up limit pH for lakes)²⁴ were chosen in
206 following experiments to investigate the macro phenomena and micro mechanisms of
207 PO₄ adsorption on LAH.

208 Phosphate adsorption isotherms for LAH were L-curves (Figure 3) and were fitted
209 with the Langmuir model (Table S1). LAH-1/10 had the maximum PO₄ adsorption
210 capacities (Q_m) of 128.2 and 70.4 mg P g⁻¹ at pH 4.0 and pH 8.5 (Table S1). The Q_m of
211 LAH-1/30 (5.3% La, Table 1) were 8.5- and 5.3-fold higher than those of Phoslock[®]
212 (5.6%, Table 1) at pH 4.0 and pH 8.5, respectively. The PO₄ specific adsorptions on
213 Phoslock[®] and LAH were calculated on the basis of Q_m (Table S1) and BET surface
214 area (Table 1). LAH-1/10 exhibited higher PO₄ specific adsorptions of 1.29 and 0.71
215 mg m⁻² than those of LAH-1/20 (1.00 and 0.53 mg m⁻²) and LAH-1/30 (0.71 and 0.42
216 mg m⁻²) at pH 4.0 and 8.5 (Table S1), respectively. The PO₄ desorption rates of LAH-
217 1/30, LAH-1/20 and LAH-1/10 were 2.54%, 2.01% and 4.05% at pH 4.0, which were
218 reduced to 0.28%, 0.22% and 0.29% at pH 8.5 (Figure S4), respectively.

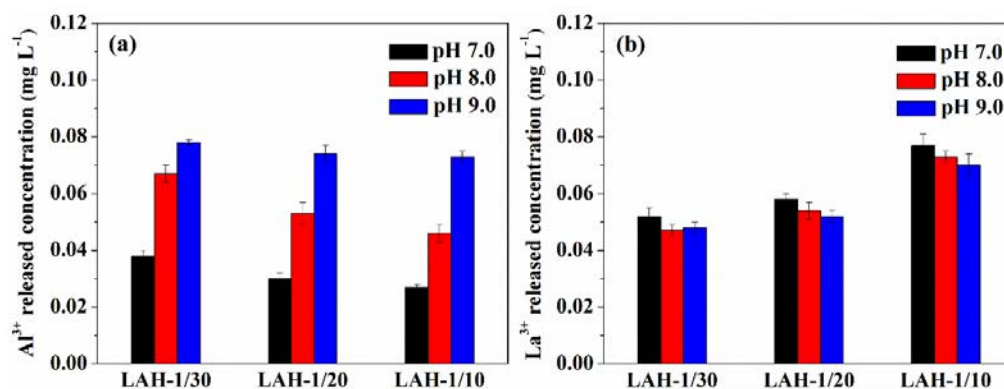


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220 **Figure 3.** Langmuir isotherm fitting plots of LAH and Phoslock[®] at pH 4.0 (a) and pH
221 8.5 (b). The experimental condition: temperature = 298 K, adsorbent dosage = 1 g L⁻¹,
222 reaction time = 48 h.

223 In order to assess the ecological risk of LAH to natural water bodies, concentrations
224 of released Al³⁺ and La³⁺ were measured in natural water pH ranges from 7.0 to 9.0

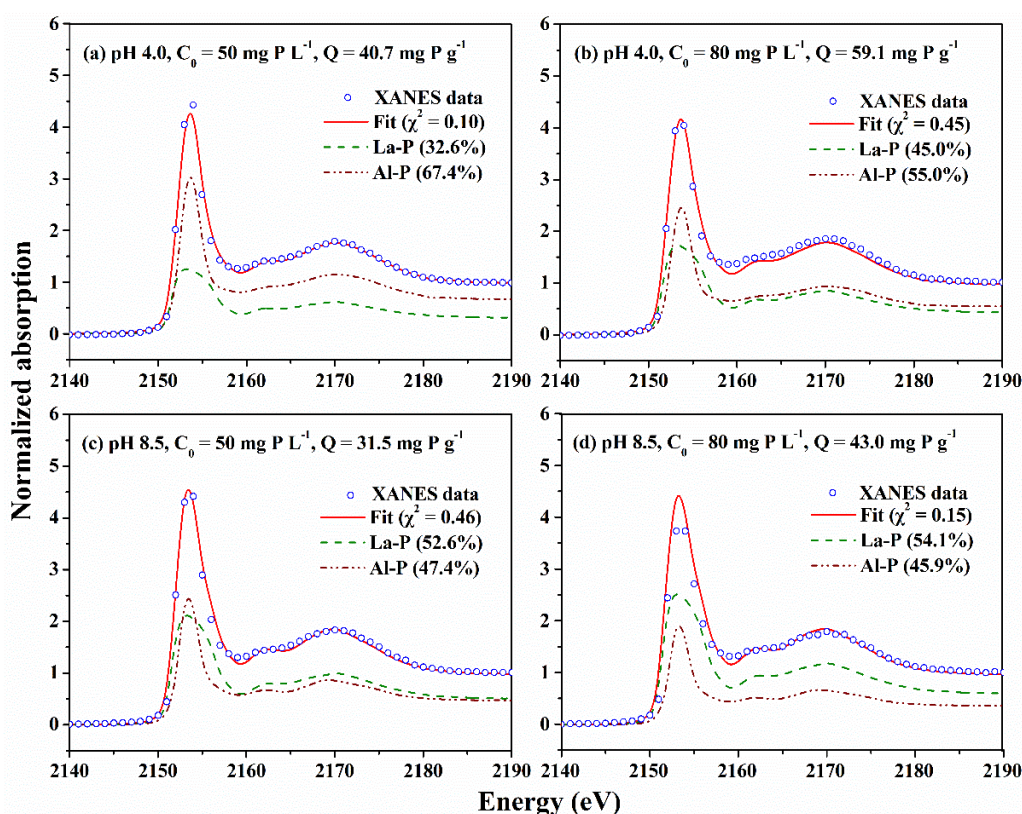
225 (Figure 4). The maximum concentration of released Al^{3+} was 0.078 mg L^{-1} by LAH-
 226 1/30 at pH 9.0 (Figure 4a). LAH-1/10 had the highest released La^{3+} concentration of
 227 0.077 mg L^{-1} at pH 7.0 (Figure 4b). The dissolutions of Al and La from LAH at pH 4.0
 228 to 10.0 were also determined (Figure S5). The maximum Al and La dissolved
 229 proportions were 0.58% by LAH-1/30 and 0.55% by LAH-1/10 at pH 4.0, respectively.



230

231 **Figure 4.** Concentrations of released Al^{3+} and La^{3+} from pH 7.0 to 9.0. The
 232 experimental condition: temperature = 298 K, adsorbent dosage = 1 g L^{-1} , reaction time
 233 = 48 h.

234 **P K-edge XANES.** Normalized P K-edge XANES spectra for LAH-1/30 samples
 235 after PO_4 adsorption with initial P concentrations (C_0) 50 and 80 mg P L^{-1} at pH 4.0 and
 236 8.5 were shown in Figure 5. LCF results showed that the proportions of PO_4 bonded
 237 with La-hydroxide (La-P) for LAH-1/30 with adsorbed PO_4 at pH 4.0 were 32.6% and
 238 45.0%, which were less than those with Al-hydroxide (Al-P) of 67.4% and 55.0%
 239 (Figure 5a, b). However, for LAH-1/30 with adsorbed PO_4 at pH 8.5, the proportions
 240 of PO_4 bonded with La-hydroxide (La-P, 52.6% and 54.1%) were higher than those with
 241 Al-hydroxide (Al-P, 47.4% and 45.9%) (Figure 5c, d).

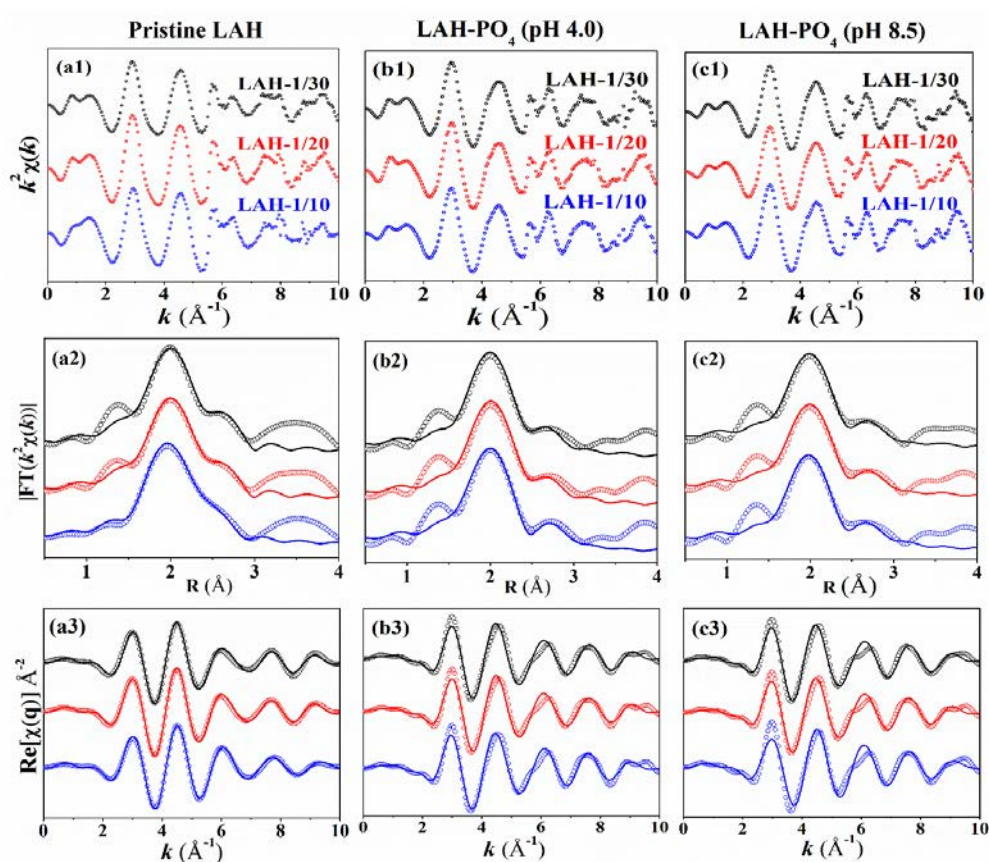


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243 **Figure 5.** Linear combination fitting for LAH-1/30 samples after PO₄ adsorption with
 244 weighted components of La-P and Al-P. The experimental condition: (a) pH 4.0 with
 245 C₀ 50 mg P L⁻¹, (b) pH 4.0 with C₀ 80 mg P L⁻¹, (c) pH 8.5 with C₀ 50 mg P L⁻¹ and (d)
 246 pH 8.5 with C₀ 80 mg P L⁻¹.

247 **La L_{III}-edge EXAFS.** In order to investigate the La local coordination environment,
 248 the La L_{III}-edge EXAFS spectra analysis was conducted (Figure 6). Spectra of
 249 commercial La(OH)₃ and Phoslock[®] were also collected (Figure S6, S7). The first shell
 250 La-O of LAH was at a distance of 2.55 ~ 2.60 Å (Table S2), which was very close to
 251 that of the La-O shell of La(OH)₃ (2.5 ~ 2.6 Å).²⁸ The La-O CN of LAH-1/30, LAH-
 252 1/20 and LAH-1/10 were 6.8 ± 0.7, 6.5 ± 0.4 and 6.1 ± 0.3 (Table S2), respectively. Al
 253 atoms were detected at 3.10 ~ 3.11 Å with La-Al CN of 2.6 ± 0.9, 2.2 ± 0.5 and 1.4 ±
 254 0.5 to LAH-1/30, LAH-1/20 and LAH-1/10 (Table S2), respectively. The La-O CN of
 255 LAH samples after PO₄ adsorption were 7.3 ~ 7.6 (Table S3). A new La-P shell in LAH
 256 samples with adsorbed PO₄ was detected at a distance of 3.20 ~ 3.31 Å and the average

257 CN of La-P shell were about 2.5 (Table S3). Additionally, the original CN of La-O shell
 258 in Phoslock[®] was 8.9 ± 0.8 (Table S2), which was about 8.8 after PO₄ adsorption (Table
 259 S3). With increased La loading, the intensity of La-O peak became weaker in LAH
 260 composite (Figure S8b). Besides, the attenuation rate of $\chi(k)$ of LAH was faster than
 261 that of La(OH)₃ (Figure S8a). In accordance with XRD spectra (Figure 1a), La L_{III}-edge
 262 EXAFS spectra also proved that amorphous La(OH)₃ was formed in LAH during the
 263 La/Al co-precipitation process.



264
 265 **Figure 6.** Normalized k^2 -weighted La L_{III}-edge EXAFS spectra (a1, b1, c1), the
 266 corresponding Fourier transformed magnitude (a2, b2, c2) and real (q) part of Fourier
 267 transform (c1, c2, c3) of pristine LAH, LAH with adsorbed PO₄ at pH 4.0 (LAH-PO₄,
 268 pH 4.0) and LAH with adsorbed PO₄ at pH 8.5 (LAH-PO₄, pH 8.5). Samples of LAH-
 269 1/30 (black), LAH-1/20 (red) and LAH-1/10 (blue). The dotted lines were observed
 270 spectra and the solid lines were fitting curves.

271 **Discussion**

272 **Electrostatic attraction and ligand exchange.** The ζ potential data showed that the
273 pH_{PZC} value of LAH-1/30, LAH-1/20 and LAH-1/10 was approximately 9.7 (Figure 2).
274 When solution pH was lower than 9.7, LAH were protonated and positively charged.
275 Compared to negatively charged Phoslock[®], the positively charged surfaces of LAH
276 could attract more negatively charged PO_4 anions by electrostatic interaction over a
277 wide pH range. The results showed that the ζ potential of LAH decreased with
278 increasing pH values (Figure 2). Lower pH is beneficial for the protonation of LAH
279 surfaces, which could enhance the electrostatic attraction between LAH and PO_4 anions.
280 Owing to the higher surface charge and more protonated active sites, LAH-1/30 showed
281 a higher PO_4 adsorption capacity (76.3 mg P g^{-1} , Table S1) at pH 4.0 than that (45.3 mg
282 P g^{-1} , Table S1) at pH 8.5. Although $\text{La}(\text{OH})_3$ is also positively charged under natural
283 lake pH conditions (Figure S2),²⁹ the utility of La (hydro)oxide alone in eutrophication
284 restoration is not recognized as an economic way in view of its high price and relative
285 scarcity. The incorporation of Al hydroxide with La in LAH materials not only
286 maintains high pH_{PZC} values, but also reduces costs compared to using La (hydro)oxide
287 alone.

288 Changes of solution pH during PO_4 adsorption on LAH-1/30 at initial pH 4.0 and 8.5
289 were monitored (Figure S9). The solution pH increased from initial pH 4.0 to nearly
290 6.5 after 24 h and it increased little when initial pH was 8.5 (Figure S9). The increase
291 in pH value was due to the release of OH^- after ligand exchange interaction, indicating
292 that ligand exchange played a primary role in PO_4 adsorption.^{9, 10} The surface charges
293 of pristine LAH-1/30 decreased significantly after PO_4 adsorption (Figure 2),
294 suggesting that PO_4 was bonded on LAH surfaces by forming inner-sphere complexes
295 via ligand exchange.³⁰ In order to demonstrate ligand exchange interaction at the

296 molecular level, we measured P K-edge XANES spectra of LAH-1/30 samples with
297 adsorbed PO₄ (Figure 5). According to LCF analysis, the proportions of PO₄ bonded
298 with Al-hydroxide were 2.07 and 1.22 times higher than those with La-hydroxide at pH
299 4.0 (Figure 5a, b). On the contrary, the proportions of PO₄ bonded with Al-hydroxide
300 (Al-P, 47.4% and 45.9%) were less than those with La-hydroxide (La-P, 52.6% and
301 54.1%) at pH 8.5 (Figure 5c, d). The fitting data showed PO₄ was preferentially bonded
302 with Al in weakly acidic conditions (pH 4.0), while most PO₄ tended to associate with
303 La under alkaline conditions (pH 8.5). The results showed that both La-hydroxide and
304 Al-hydroxide in LAH composite could bind with PO₄ anions by forming inner-sphere
305 complexes.^{31, 32} In this study, the XANES measurement provided strong evidence that
306 a ligand exchange mechanism played a role both at pH 4.0 and 8.5.

307 It was reported that higher alkaline condition (pH 9.5) might result in the dissolution
308 of Al(OH)₃ and the release of PO₄ concomitantly.¹⁷ However, the Al³⁺ and PO₄ released
309 proportions in LAH were both very low at alkaline conditions (Figure S4, S5).
310 According to La L_{III}-edge EXAFS analysis, a La-Al shell was formed in LAH samples
311 (Table S2). As the addition of La to alumina could generate new-type Lewis acid site
312 on the surface,³³ the increased La loading in LAH might affect the properties of Al-
313 hydroxide in LAH composite. The Al³⁺ and La³⁺ ions all showed a higher dissolution
314 proportions at lower alkalinity (Figure S5).³⁴ It has been hypothesized that natural
315 organic matter can impact PO₄ adsorption via the formation of OM-Fe(III)-PO₄ or OM-
316 Al(III)-PO₄ ternary complexes.^{35, 36} Hence, we induced that the ternary LAH-Al³⁺/La³⁺-
317 PO₄ complex might also be formed when pH changed to the low value of 4.0.

318 **The oxygen defects on La compound.** EXAFS analysis showed that La-O CN of
319 LAH-1/30, LAH-1/20 and LAH-1/10 were 6.8 ± 0.7, 6.5 ± 0.4 and 6.1 ± 0.3 (Table S2),
320 respectively. The average La-O CN of LAH composite were approximately 6.5, which

321 were all less than the saturated La-O CN of 9.0 in La(OH)₃.²⁸ It is generally recognized
322 that lower CN of surface ions may depend on oxygen defects on the surfaces of metal
323 compound.³⁷⁻³⁹ Among LAH materials, LAH-1/10 with highest La content (13.1%,
324 Table 1) might had the most amounts of oxygen defects on the surfaces. Additionally,
325 EPR spectrum demonstrated the presence of oxygen defects on the surfaces (Figure 1b).
326 It was reported that the surface defect sites were more reactive than the perfect
327 surfaces.^{40, 41} LAH-1/10 with more La loading exhibited higher PO₄ specific
328 adsorptions of 1.29 (pH 4.0) and 0.71 mg m⁻² (pH 8.5) than those of LAH-1/20 and
329 LAH-1/30 (Table S1), respectively, which might be also attributed to more amounts of
330 oxygen defects on the surfaces. Compared to the mixture of pure La(OH)₃ and pure
331 Al(OH)₃ to a La/Al molar ratio 1:30, the PO₄ specific adsorption on LAH-1/30 at pH
332 8.5 (0.42 mg m⁻², Table S1) was 1.6 times higher than the mixture (0.26 mg m⁻², Figure
333 S10), further supporting that the oxygen defects on LAH surfaces provided special
334 adsorption towards PO₄ anions. The La-O CN of Phoslock[®] with PO₄ bonded was 8.8
335 (Table S3), which was similar to its original CN of 8.9 (Table S2). While, the average
336 La-O CN of LAH after PO₄ adsorption increased to 7.5 (Table S3) compared to its
337 original average value of 6.5 (Table S2). The change of La-O in LAH before and after
338 PO₄ adsorption proved the role of oxygen defects on LAH to facilitate PO₄ adsorption.
339 It was reported that the oxygen defects on Al compound were not observed until the
340 material was calcined at above 473 K.⁴² Therefore, the role of oxygen defects on La
341 compound for PO₄ adsorption, not Al compound, was the major consideration in
342 present study since the prepared temperature of LAH was 333 K.

343 After PO₄ adsorption, a new La-P shell was detected in LAH samples (Table S3).
344 The distance of La-P shell was at 3.20 ~ 3.31 Å (Table S3), which was shorter than that
345 of LaPO₄•1.4H₂O (3.52 Å) and LaPO₄ (4.16 Å).¹¹ With the bond distance and the

346 average CN (~ 2.5, Table S3) of La-P shell, the PO₄ surface configuration was in
347 agreement with previous EXAFS studies of PO₄ adsorption on goethite/water
348 interface.⁴³ Hence, the most likely configuration of PO₄ on La site was a bidentate-
349 binuclear complex.⁴³ The La-PO₄ bonding was a direct evidence to demonstrate the
350 formation of inner-sphere complex of P on La site.

351 **Toxicity analysis.** The release of metal ions is a major concern when using lake
352 restoration materials, which may induce potentially environmental risk and limit their
353 usage as P removers in some environments.² It has been demonstrated that excessive
354 concentrations of Al³⁺ and La³⁺ may be toxic to the sensitive species in waters.^{2, 17}
355 *Daphnia magna* has been used to indicate eco-toxicity potential when using geo-
356 engineering materials.⁴⁴ According to previous studies, the median effect
357 concentrations (EC₅₀) of Al³⁺ and La³⁺ to *Daphnia magna* were above 3.9 and 23 mg
358 L⁻¹.^{45, 46} In this study, the maximum concentrations of released Al³⁺ and La³⁺ after
359 adsorption procedure were 0.078 mg L⁻¹ by LAH-1/30 and 0.077 mg L⁻¹ by LAH-1/10
360 under natural water pH conditions (Figure 4), which were much lower than the reported
361 thresholds of 3.9 and 23 mg L⁻¹, respectively. Moreover, it has been reported that La³⁺
362 and Al³⁺ ions could also bind with CO₃²⁻ and humics in aquatic environments thus
363 possibly reducing their toxicity to some extent.⁴⁷⁻⁴⁹ Although further investigation is
364 needed under a wide range of environmental conditions, the initial findings suggest that
365 it is possible to use LAH materials at their optimal dosage for control of internal P loads
366 without causing substantial adverse effects to aquatic ecosystem.

367 **Environmental implications.** In recent decades, cost-efficient and ecologically
368 benign P locking materials have been in urgent demand in geo-engineering for
369 eutrophication control.^{6, 7, 50} This study may promote the development of novel La-
370 modified materials for highly efficient P removal from water bodies. To remove one Kg

371 P in water bodies, the cost of LAH is 18.5 - 25.6 \$/Kg P, which is less than that of
372 Phoslock[®] (27.9 \$/Kg P) (Table S4). The LAH composite has the potential to save up
373 to ~ 34% cost compared to that of Phoslock[®]. Moreover, LAH have much higher P
374 adsorption capacity and La use efficiency than other La-modified materials reported
375 before (Table S5). After LAH are applied in natural waters (pH 8.5), the composition
376 of La-hydroxide in LAH may play a primary role in locking P than Al-hydroxide
377 (Figure 5). The combined contribution of two-component of La and Al may be an
378 important direction to improve the P removal efficiency for the next generation of
379 commercial products. LAH exhibited great practical potential due to its low PO₄
380 desorption rates and low metal ions released concentrations under natural lake pH
381 conditions. The positively charged LAH may also have the potential in removing other
382 negatively charged pollutants in waters, such as algal cells, arsenate and chromate. With
383 the combination of LAH and modified local soil,⁵¹ the toxic algae and P in waters may
384 be removed, and the floc resuspension and P release from lake sediments can also be
385 capped and blocked as well.⁵⁰ Considering the challenge of understanding long-term
386 effects, further studies are needed to evaluate its impacts on aquatic ecological
387 responses. With additional research, LAH may be a compelling candidate as a geo-
388 engineering tool for P control.

389 **ASSOCIATED CONTENT**

390 **Supporting Information**

391 Details on the synthesis of La(OH)₃ and Al(OH)₃, equations used in this study and
392 XAFS data collection and analysis. Figures showing the FESEM images of LAH, ζ
393 potential of La(OH)₃ and Al(OH)₃, effect of pH on phosphate adsorption efficiency,
394 phosphate desorption rates of LAH, Al/La dissolutions from LAH at varying pH 4.0-
395 10.0, EXAFS experimental and fitted spectra, changes of solution pH and Langmuir

396 adsorption isotherm on mixture of La(OH)₃ and Al(OH)₃. Tables showing Langmuir
397 isotherm parameters and phosphate specific adsorptions, EXAFS data of La(OH)₃,
398 LAH and Phoslock[®], cost of LAH and Phoslock[®] and comparison of La-modified
399 materials. This information is available free of charge via the Internet at
400 <http://pubs.acs.org>.

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405 **Notes**

406 The authors declare no competing financial interest.

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