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# RaY

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1 **Utilization of coal fly ash waste for effective recapture of phosphorus**  
2 **from waters**

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22

23 **Abstract**

24 Reutilisation of the waste by-products from industrial and agricultural activities is  
25 crucially important towards attainment of environmental sustainability and the  
26 'circular economy'. In this study, we have developed and evaluated a sustainably-  
27 sourced adsorbent from coal fly ash, which was modified by a small amount of  
28 lanthanum (La-FA), for the recapture of phosphorous (P) from both synthetic and real  
29 natural waters. The prepared La-FA adsorbent possessed typical characteristic  
30 diffraction peaks similar to zeolite type Na-P1, and the BET surface area of La-FA was  
31 measured to be 10.9 times higher than that of the original FA. Investigation of P  
32 adsorption capability indicated that the maximum adsorption ( $10.8 \text{ mg P g}^{-1}$ ) was 6.14  
33 times higher than that ( $1.8 \text{ mg P g}^{-1}$ ) of the original fly ash material. The  $\zeta$  potentials  
34 measurement and P K-edge X-ray Absorption Near Edge Structure (XANES) spectra  
35 demonstrated that P was bonded on La-FA surfaces via an adsorption mechanism. After  
36 applying the proposed adsorbent to real lake water with La/P molar ratios in the range  
37 from 0.5:1 to 3:1, the La-FA adsorbent showed the highest phosphate removal ability  
38 with a La/P molar ratio 1:1, and the P adsorption was similar to that performance with  
39 the synthetic solution. Moreover, the La-FA adsorbent produced a negligible effect on  
40 the concentrations of total dissolved nitrogen (TDN),  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  in water.  
41 This study thus provides a potential material for effective P recapture and details of its  
42 operation.

43 **Keywords:** Circular economy; coal fly ash; eutrophication management, lanthanum  
44 modification; phosphorus adsorbent

## 45 **1. Introduction**

46 Along with the growth in global population and concurrent industrialization, the  
47 widespread application of phosphorus (P) as fertilizer and animal feed have resulted in  
48 substantially increased discharge of P into the environment and intensified episodes of  
49 eutrophication in natural waters (Conley et al., 2009; Pan et al., 2018; Smith et al.,  
50 1999). It has been reported that eutrophication could even occur at P concentrations as  
51 low as 0.02 mg P L<sup>-1</sup> (Fernandez et al., 2007). Traditional and enhanced processes for  
52 the biological removal of P during natural and waste water treatments are generally not  
53 able to sustainably achieve such low effluent P concentrations (Kumar et al., 2019). The  
54 dosing of aluminium- or iron-based salts is a common approach in sewage treatment  
55 plants in order to secure an ultra-low level effluent with respect to P (Nakarmi et al.,  
56 2020; White et al., 2021). However, as P is a non-renewable resource, not only removal,  
57 but also recovery and recapture of the discharged P is strategically important for  
58 environmental sustainability (Pan et al., 2020). Therefore, treatment by adsorption is  
59 often suggested, due to the multiple advantages of low carbon footprint, minimal waste  
60 generation and the further option for P recovery (Kang et al., 2003).

61 Various synthetic adsorbents for P have been developed, and the valorisation of waste  
62 by-products from industrial and agricultural activities has recently drawn substantial  
63 attention within the concept of the circular economy (Zamparas et al., 2020). Many raw  
64 solid wastes (Table 1), such as steel slag (Bowden et al., 2009), magnesite dust (Al-  
65 Mallahi et al., 2020), concrete powder (Liu et al., 2020), and fine-grained by-products  
66 (Kasprzyk et al., 2021), have been investigated for P removal. In addition to the

67 immediate advantage of low cost, some of these materials possess high porosity and  
68 mineral mixtures consisting of aluminium and other metal oxides, and have yielded P  
69 removal capabilities comparable to those of synthetic adsorbents. As coal combustion  
70 is still one of the most important sources of energy, the global generation of fly ash is  
71 estimated to be approximately 750 million tons, and thus the treatment/utilisation of  
72 these wastes is crucial (Blissett & Rowson, 2012). It is necessary to find a feasible way  
73 for the utilization of fly ash. Additionally, the complexity and variety of fly ash should  
74 also be taken into consideration since it comprised of hundreds of different individual  
75 minerals and mineral groups (Vassilev and Vassileva, 2005).

76 Currently, researchers have attempted to use the raw fly ash for P removal. Some  
77 approaches have been used to improve the removal ability of modified fly ash through  
78 pre-treatment of acid/alkaline solutions and modification by metal ions (Hermassi et al.,  
79 2020). Although the modified fly ash could achieve P adsorption from several to  
80 hundreds of mg P g<sup>-1</sup> (Li et al., 2006; Wang et al., 2016b), it is considered that the  
81 overall efficiency could be improved further. The use of lanthanum (La), an  
82 environmentally friendly and relatively abundant rare earth element, is currently being  
83 used commercially to synthesise the P adsorbent *Phoslock*<sup>®</sup>. As a modifier on bentonite  
84 for P removal, a small portion of La (*ca.* 5.6%) could lead to P adsorption up to 10.6  
85 mg P g<sup>-1</sup> due to its excellent P-binding ability (Haghseresht et al., 2009). A La-based P  
86 adsorbent could also overcome adverse effects of fluctuating pH and redox conditions  
87 in solution, attributable to strong P binding reactions (Wang et al., 2016b; Shin et al.,  
88 2005; Zhang et al., 2016), however, research into the use of La as modifier on fly ash

89 for P removal is still not sufficient. It is therefore hypothesised that fly ash doped with  
90 a relatively small amount of La would result in a superior, low cost, and  
91 environmentally-friendly P adsorbent.

92 In many experiments demonstrating novel P adsorbents, adsorption capabilities are  
93 invariably tested using a synthetic P-contaminated solution with initial concentrations  
94 ranging from tens to hundreds mg P L<sup>-1</sup> (Xu et al., 2020). However, the P concentrations  
95 in natural waters or sewage effluent from upstream biological/chemical P removal  
96 treatments are usually much lower, for example in the range 0.1-1.0 mg P L<sup>-1</sup> (Wang et  
97 al., 2016a). Moreover, the removal efficiency of P from real waters could be affected  
98 by the presence of competing ions, such as SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> (Dithmer et al., 2016; Zhang  
99 et al., 2016). Previous studies, shown in Table 1, have reported a *ca.* 10% lower P  
100 removal ability from real wastewaters compared with that obtained from synthetic  
101 wastewater under the same condition. When targeting a real-life deployment, it should  
102 be realised that little is known about the behaviour and mechanisms of P removal by  
103 the proposed La-modified fly ash adsorbent from both synthetic and natural real waters.

104 In order to address these knowledge gaps, the aims of this study were to develop a La-  
105 modified adsorbent from solid waste coal fly ash and to investigate its performance for  
106 P recapture from examples of both synthetic and real waters. Adsorption capacity,  
107 kinetics and isotherm characteristics, and the effect of pH on P adsorption, were initially  
108 investigated with synthetic water samples. The P K-edge X-ray Absorption Near Edge  
109 Structure (XANES) technique was employed to explore and characterise the

110 microstructures formed when P bonded onto the proposed adsorbent. Moreover, the P  
111 removal performance of this material was also investigated with real lake waters, in  
112 order to provide an evidence, base that can be referenced regarding further  
113 implementations.

114 **Table 1.** Summary of the performance of various waste materials for P removal.

Material	Experiment solution	Dosage (g L <sup>-1</sup> )	pH	Initial P (mg P L <sup>-1</sup> )	P removal (%)	P adsorption capacity (mg P g <sup>-1</sup> )	Reference
Fly ash	Synthetic	2	3-11	30-300	100	-	(Shuai Gu et al., 2021)
	Real	2	-	51.5	100	-	
Steel slag	Synthetic	40	-	0-100	>90	1.14-2.49	(Barca et al., 2012)
	Real	40	-	0.41-1.11	>90	0.14-2.50	
	Synthetic	-	2-12	1-50, 100-300	62	8.39	(Bowden et al., 2009)
Eggshell	Synthetic	20	-	0.5-3.0	90	121	(Torit & Pihusut, 2019)
	Real	50	7.3	1.7	80	-	
	Synthetic	0.96	-	-	96.2	3.32	(Cy & Lpv, 2019)
Mussel shell	Synthetic	0-80	1.5-9.5	0-20	-	6.95	(Xiong et al., 2011)
Oyster shell	Synthetic	6	7.0-12	11.9	98	-	(Lee et al., 2009)
	Synthetic	400	-	6-80	-	32.9	(Wang et al., 2013)
Orange waste gel (loaded with zirconium)	Synthetic	1.67	1-9	-	-	57	(Biswas et al., 2008)
Magnesite dust	Synthetic	22.2	9	665	63%	-	(Al-Mallahi et al., 2020)
Concrete powder	Synthetic	-	10.5	20	-	4.96	(Liu et al., 2020)
Broken bricks	Synthetic	400	-	6-80	-	0.59	(Wang et al., 2013)
Iron humate	Synthetic	10-40	-	3.1-124	-	3.4-11.5	(Jano et al., 2011)
Fine-grained by-product	Synthetic	10	-	97.3	97.8	9.58	(Kasprzyk et al., 2021)

115

## 116 **2. Materials and methods**

### 117 **2.1. Material preparation and characterisation**

118 Raw coal fly ash (FA) was obtained from a power plant in Datong City (Shanxi province,  
119 China). The ash was washed three times with deionized water, dried at 105 °C, then  
120 passed through a 180 mesh sieve before use. La-modified fly ash (La-FA) was  
121 synthesized by the following process. The FA was first treated with 2.0 mol L<sup>-1</sup> NaOH  
122 solution at 95 °C for 24 h at a liquid/solid ratio of 360 mL alkali solution per 60 g FA,  
123 to obtain the zeolite and waste alkaline solution. After cooling to about 25 °C, a LaCl<sub>3</sub>  
124 solution (0.23 mol L<sup>-1</sup>, 100 mL) was added dropwise to the mixture with continuous  
125 stirring, and the mixture further stirred for another 4 h at 25 °C. Finally, the resulting  
126 solid was washed three times with deionized water and freeze-dried over 24 h.

127 To obtain the exact content of La in the prepared La-FA, samples were digested in HF-  
128 HClO<sub>4</sub>-HNO<sub>3</sub> solution and the chemistry of each resultant solution was determined by  
129 inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8300,  
130 PerkinElmer, USA). The morphologies of the raw FA and La-FA materials were  
131 observed by field emission scanning electron microscopy (FESEM, SU 8020, Hitachi,  
132 Japan). X-ray powder diffraction patterns were recorded on an X'Pert PRO MPD X-  
133 ray diffractometer (Malvern Panalytical, The Netherlands) with Cu-K radiation ( $\lambda =$   
134 1.5408) at 40 kV and 40 mA in the  $2\theta$  range of 5° to 90°. Brunauer-Emmett-Teller (BET)  
135 surface areas and pore size distributions were examined by a Micromeritics ASAP 2020  
136 static volumetric analyser (Micromeritics Instrument Corp., Norcross, USA). Zeta ( $\zeta$ )  
137 potential analysis of samples was performed by Zetasizer Nano ZS potential analyzer

138 (Malvern Panalytical Ltd., United Kingdom).

## 139 **2.2. P adsorption experiment**

### 140 **2.2.1. Adsorption isotherm**

141 P adsorption isotherm experiments were conducted in 50 mL polypropylene tubes.

142 Samples of FA and La-FA (1.0 g L<sup>-1</sup>) were mixed with solutions containing various

143 concentrations of KH<sub>2</sub>PO<sub>4</sub> each with 0.01 mol L<sup>-1</sup> NaCl ionic background. The solution

144 pH was adjusted to 8.50 ± 0.05 with 0.01 mol L<sup>-1</sup> HCl and NaOH. The suspensions were

145 shaken at 25 °C for 48 h. The suspensions were then centrifuged, filtered through 0.45

146 µm membrane filters, and the clear supernatants used to determine P concentrations by

147 the ascorbic acid method, using a UV-756 PC spectrophotometer at 880 nm (Shanghai

148 Sunny Hengping Scientific Instrument Co. Ltd., China).

149 In order to model the adsorption results, Langmuir (Eq. 1) and Freundlich (Eq. 2)

150 isotherms were used in this study, respectively.

$$151 \quad q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (1)$$

$$152 \quad q_e = K_F C_e^{1/n} \quad (2)$$

153 *Where  $q_e$  is the equilibrium adsorption capacity (mg g<sup>-1</sup>),  $q_m$  refers to the maximum adsorption*

154 *capacity (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration after adsorption (mg L<sup>-1</sup>),  $K_L$  is the*

155 *constant in Langmuir model (L mg<sup>-1</sup>),  $K_F$  is the constant in Freundlich model (mg g<sup>-1</sup>),  $n$  is the*

156 *constant in Freundlich isotherm model representing adsorption intensity.*

### 157 **2.2.2. Adsorption kinetics and desorption experiments**

158 Adsorption kinetic experiments were carried out in 1000 mL flasks containing 500 mL

159 P solution with concentrations of 10 and 30 mg P L<sup>-1</sup>, and 0.5 g adsorbent samples  
160 added. The flasks were shaken at 25 °C for 48 h at 170 rpm. About 0.5 mL of each  
161 supernatant was sampled at various time intervals in order to determine P concentration.  
162 The pH was maintained at 8.50 ± 0.05 during the 48 h equilibration time.

163 Pseudo-second order kinetics (Eq. 3) and intra-particle diffusion (Eq. 4) models were  
164 used to model the experimental data, respectively.

$$165 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

$$166 \quad q_t = k_i t^{1/2} \quad (4)$$

167 *Where  $q_e$  and  $q_t$  represents the equilibrium capacity (mg g<sup>-1</sup>) and adsorption amount versus*  
168 *time  $t$  (min),  $k_2$  is the equilibrium rate constant of pseudo-second-order adsorption (g mg<sup>-1</sup> h<sup>-1</sup>),*  
169  *$k_i$  is the rate constant of intra-particle diffusion model (mg g<sup>-1</sup> h<sup>-1/2</sup>).*

170 At the conclusion of the adsorption kinetics experiment, the exhausted solutions of La-  
171 FA samples with initial P concentration 30 mg P L<sup>-1</sup> were first centrifuged, and 10 mL  
172 of the suspension at the bottom were preserved, then NaCl solution (0.01 mol L<sup>-1</sup>) was  
173 added in order to maintain the same ionic strength. The suspensions were then shaken  
174 at 25 °C for 48 h. After that, the P concentrations of the clear supernatants were  
175 measured in order to determine the P desorption ability of the adsorbent.

### 176 **2.3. The effect of pH on P removal**

177 In order to assess the effect of pH on the equilibrium adsorption capacity, adsorption of  
178 P onto La-FA was conducted at pH 4, 5, 6, 7, 8, 9, and 10. La-FA (1.0 g L<sup>-1</sup>) was added  
179 to 50 mL polypropylene tubes with an initial P concentration of 30 mg P L<sup>-1</sup> with NaCl

180 (0.01 mol L<sup>-1</sup>) ionic background, and shaken at 170 rpm at 25 °C for 48 h. The solution  
181 pH was maintained with 0.01 mol L<sup>-1</sup> HCl and NaOH.

#### 182 **2.4. P K-edge XANES data collection and analysis**

183 The P K-edge XANES data were collected in fluorescence yield mode on Beamline  
184 4B7A at the Beijing Synchrotron Radiation Facility (BSRF), China. Measurements  
185 were acquired at energies between -30 to +90 eV relative to P K-edge energy of 2152  
186 eV with a minimum step size of 0.3 eV over the range 2140 and 2180 eV. XANES  
187 spectra of samples were normalized by the ATHENA software program (Ravel &  
188 Newville, 2005).

#### 189 **2.5. P binding experiments in real lake water**

190 Real lake water was collected from Meiliang Bay of Taihu Lake (Jiangsu province,  
191 China) in November 2017. Taihu Lake is a mild eutrophic surface water and  
192 experiences periodic algal blooms every few years (Pan et al., 2019). In total, 5.0 L  
193 sample was collected by a plexiglass water sampler (Bei Jing Gresp Co., Ltd, China)  
194 from 0.5 m deep below the surface in the centre of Meiliang Bay (31°43'N, 120°14'E).  
195 The water sample was first screened by a 180 µm mesh to remove large zooplankton  
196 grazers and then stored under 4 °C before being used for the following experiment. The  
197 chemical characteristics of the lake water are listed in Table 2. Stock suspensions of La-  
198 FA were prepared by continuous mixing of the adsorbent materials (50 mg) with  
199 deionized water (500 mL). Subsamples of 0.3, 0.6, 1.2, 1.8 and 2.4 mL were taken from  
200 these suspensions to obtain the desired adsorbent dosages, and then transferred to 50

201 mL polypropylene tubes containing lake water samples (40 mL) previously filtered  
 202 through 0.45  $\mu\text{m}$  membrane filters. The final volume of each solution was maintained  
 203 at 45 mL by addition of aliquots of real lake water. The suspensions were shaken at  
 204 25 °C for 48 h at 170 rpm and then filtered for the measurement of total dissolved  
 205 phosphorus (TDP), orthophosphate ( $\text{PO}_4^{3-}\text{-P}$ ), total dissolved nitrogen (TDN),  
 206 ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ ) and nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ ). Each experiment was  
 207 carried out in triplicate.

208 **Table 2** Characteristics of the natural water used in the P adsorption experiment.

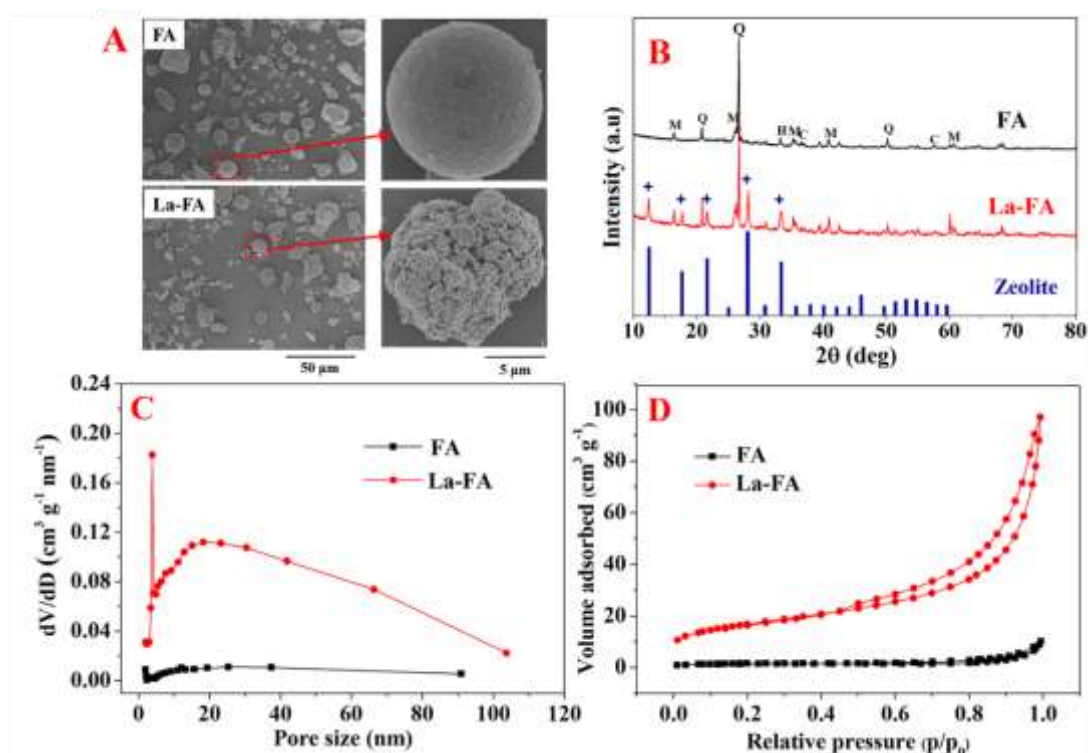
Parameter	Average value
pH	7.85
Dissolved oxygen (DO, $\text{mg O}_2 \text{ L}^{-1}$ )	8.50
Electrical conductivity ( $\mu\text{S cm}^{-1}$ )	180
Total phosphorus (TP, $\text{mg P L}^{-1}$ )	0.067
Total dissolved phosphorus (TDP, $\text{mg P L}^{-1}$ )	0.030
Orthophosphate ( $\text{PO}_4^{3-}\text{-P}$ , $\text{mg P L}^{-1}$ )	0.011
Total nitrogen (TN, $\text{mg N L}^{-1}$ )	2.09
Total dissolved nitrogen (TDN, $\text{mg N L}^{-1}$ )	2.02
Nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ , $\text{mg N L}^{-1}$ )	1.54
Ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ , $\text{mg N L}^{-1}$ )	0.13
Dissolved organic carbon (DOC, $\text{mg L}^{-1}$ )	10.25

### 209 3. Results and discussion

#### 210 3.1. Characterisation of the La-modified coal fly ash

211 The original FA particles were characterised by spherical morphologies and smooth  
 212 surfaces, whereas particles of La-FA exhibited more irregular structures and much  
 213 rougher surfaces (Fig. 1A). FESEM images indicated that particle size distributions of  
 214 La-FA adsorbents were not uniform, with most average particle sizes of approximately  
 215 20  $\mu\text{m}$ . The proportion of La in La-FA was approximately 5.0% (w/w), which was  
 216 slightly lower than that contained in the commercial La based P adsorbent, *Phoslock*<sup>®</sup>

217 (5.6%; Xu et al., 2017). These differences could be ascribed mainly to the formation of  
 218 zeolite crystal clusters during the La modification process. XRD analysis (Fig. 1B)  
 219 suggested that the original FA possessed crystalline phases of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  or  
 220  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), quartz ( $\text{SiO}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and corundum ( $\text{Al}_2\text{O}_3$ ), which were also  
 221 observed in the structures of La-FA. In addition, La-FA particles showed typical  
 222 characteristic diffraction peaks similar to zeolite type Na-P1 ( $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ ,  
 223 JCPDS code 39-0219) at  $2\theta = 12.455^\circ$ ,  $17.649^\circ$ ,  $21.657^\circ$ ,  $28.072^\circ$ , and  $33.356^\circ$ .  
 224 However, the characteristic diffraction peaks of La-(hydro)oxide were not detected in  
 225 La-FA, possibly owing to its existence in an amorphous phase (Wang et al., 2016b).



226  
 227 **Fig. 1.** (A) SEM images of original FA and La-FA. (B) XRD patterns of original FA, La-FA,  
 228 and zeolite identifying selected peaks of minerals quantified by Rietveld analysis (M = mullite,  
 229 Q = quartz, H = hematite, C = corundum). (C) Pore size distribution of original FA and La-FA.

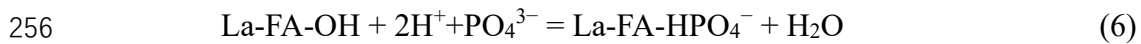
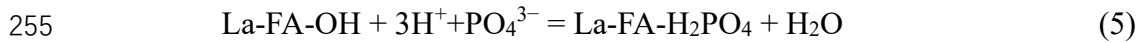
230 (D) N<sub>2</sub> adsorption/desorption isotherm of original FA and La-FA.

231 It has been reported that zeolite and hydrous La-oxide possesses a narrow pore size  
232 distribution around 4.0 nm (Wang et al., 2016b). This data supports findings from this  
233 study of a pore size distribution around 3.9 nm in La-FA (Fig. 1C), which was mainly  
234 dependant on the pore structure of La-(hydro)oxide. The N<sub>2</sub> adsorption-desorption  
235 isotherm of La-FA could be represented by a typical curve of type II (Fig. 1D). The  
236 BET surface area of La-FA was measured at 59.9 m<sup>2</sup> g<sup>-1</sup>, which was 10.9 times larger  
237 than that of the original FA (5.5 m<sup>2</sup> g<sup>-1</sup>), and in turn, was higher than that determined  
238 for a lanthanum-doped coal fly ash-blast furnace cement composite with a surface area  
239 of 11.4 m<sup>2</sup> g<sup>-1</sup> (Asaoka et al., 2020). Additionally, the pore volume of La-FA was  
240 calculated to be 0.11 cm<sup>3</sup> g<sup>-1</sup>, which was 11.0-fold larger than that of the original FA  
241 material, with a pore volume of 0.01 cm<sup>3</sup> g<sup>-1</sup>. Compared with the original FA, the  
242 obvious increases in BET surface area and pore volume of La-FA have further  
243 demonstrated the potential enhanced capabilities for P adsorption of the latter material.

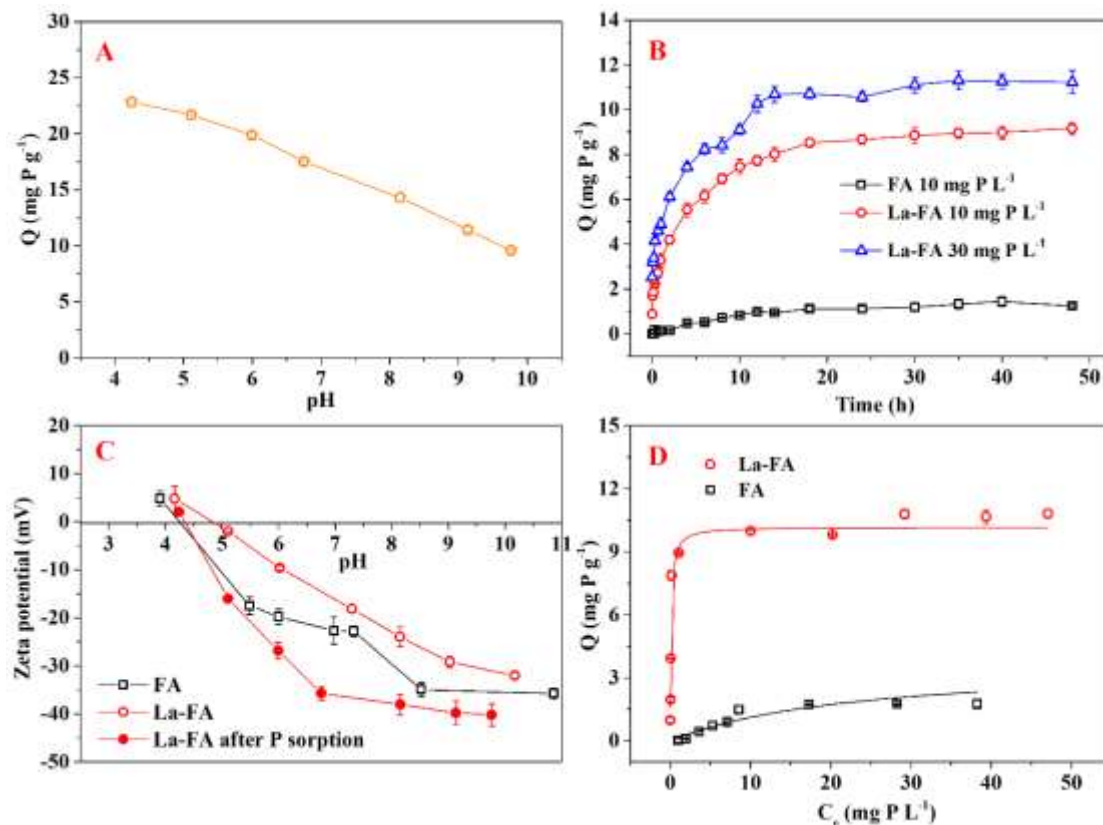
### 244 **3.2 P adsorption behaviours and mechanism**

245 At an initial P concentration of 30 mg P L<sup>-1</sup>, La-FA exhibited the highest P adsorption  
246 capacity of 22.8 mg P L<sup>-1</sup> at pH 4.25, which gradually decreased to 9.6 mg P L<sup>-1</sup> along  
247 with increasing pH to 9.76 (Fig. 2A). The negative correlation between the P adsorption  
248 capacity and pH was supported by previous relevant studies (Awual et al., 2011a;  
249 Goscianska et al., 2017), and which may have been due to the increased hydroxide  
250 concentration that might potentiate interference with the hard Lewis acid anion in water,

251 thus affecting P adsorption (Awual et al., 2011c). Moreover, hydrogen ions might  
252 transfer to the surface of La-FA for capturing the dominant species of  $\text{H}_2\text{PO}_4^-$  and  
253  $\text{HPO}_4^{2-}$  according to the following reactions (Eq. 5) and (Eq. 6) (Awual et al., 2011b;  
254 Hiemstra and Van Rimsdijk, 1996).



257 In order to simulate the scenario of P removal from eutrophic natural waters, a pH of  
258 8.50 was chosen in the following experiments (Xiong & Peng, 2008). The capacities  
259 for P adsorption, by the original FA and La-FA materials, increased with contact time  
260 at initial P concentrations of 10 and 30  $\text{mg P L}^{-1}$  and attained equilibrium after about 30  
261 h (Fig. 2B). The pseudo-second order kinetics model better fitted the results ( $r^2$  of  
262 0.992-0.997) compared with those ( $r^2$  of 0.886-0.936) obtained from the intra-particle  
263 diffusion model (Table 3). The rate constants ( $k_2$ ) of the original FA and La-FA were  
264 calculated at 2.756 and 0.058  $\text{g mg}^{-1} \text{h}^{-1}$ , under an initial P concentration of 10  $\text{mg L}^{-1}$ ,  
265 respectively. The rate constant for La-FA further decreased to 0.035  $\text{g mg}^{-1} \text{h}^{-1}$  when the  
266 initial P concentration increased to 30  $\text{mg P L}^{-1}$ .



267

268 **Fig. 2.** (A) Effect of pH on P adsorption efficiency for La-FA. (B) Kinetic studies for P  
 269 adsorption by original FA and La-FA. (C) The  $\zeta$  potentials of original FA, La-FA and La-FA  
 270 after P adsorption. (D) Langmuir adsorption isotherms of P by original FA and La-FA.

271 **Table 3.** Pseudo-second order and intra-particle diffusion model parameters of P adsorption by  
 272 original FA and La-FA.

Adsorbent	Initial P concentration (mg P L <sup>-1</sup> )	Pseudo-second order model			Intra-particle diffusion model	
		$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	$q_e$ (mg P g <sup>-1</sup> )	$r^2$	$k_i$ (mg g <sup>-1</sup> h <sup>-1/2</sup> )	$r^2$
FA	10	2.756	0.378	0.992	0.236	0.936
La-FA	10	0.058	9.390	0.997	1.256	0.891
La-FA	30	0.035	13.141	0.992	1.354	0.886

273 The  $\zeta$  potentials of original FA and La-FA materials exhibited decreasing trends with  
 274 increasing pH value (Fig. 2C). The  $\zeta$  potentials of La-FA were higher than those of the  
 275 original FA under similar conditions of pH, possibly owing to the presence of La-

276 modified compounds (Goscianska et al., 2017). Additionally, the  $\zeta$  potentials of La-FA  
 277 after P adsorption all decreased compared to the initial values. For example, the initial  
 278  $\zeta$  potential of La-FA was -24.0 mV at pH 8.15 and decreased to -38.1 mV after P  
 279 adsorption. These results suggested that P might be bonded onto the surface of La-FA  
 280 by formation of inner sphere complexes (Antelo et al., 2005; Wan et al., 2016).

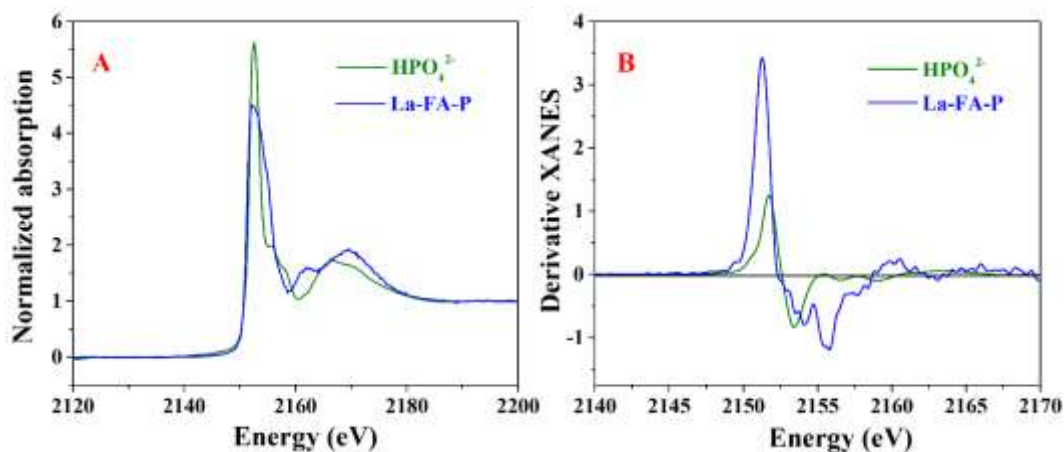
281 When evaluating the P adsorption capacity by La-FA compared to the original FA, a  
 282 Langmuir isotherm model presented clearly better fittings ( $r^2$  of 0.994-0.999) compared  
 283 with those ( $r^2$  of 0.713-0.831) fitted by the Freundlich model (Table 4). The better  
 284 Langmuir isotherm simulation is visualised in Fig. 2D, and the maximum adsorption  
 285 capacity of La-FA was determined to be 10.8 mg P g<sup>-1</sup>, some 6.1 times higher than that  
 286 of the original FA (1.8 mg P g<sup>-1</sup>). In accordance with previous studies, the molar ratio  
 287 of adsorbed P to La was used to calculate the efficiency of La usage in La-modified  
 288 materials (Emmanuelawati et al., 2013; Yang et al., 2012; Yang et al., 2011). In the  
 289 present study, the molar ratio of adsorbed P to La in La-FA was 0.96, by the ratio of the  
 290 maximum amount of P adsorbed, calculated by the Langmuir model (10.8 mg P g<sup>-1</sup>), to  
 291 the total La content in La-FA (5.0%). The molar ratio of P to La (1:1) in the La-FA  
 292 material was also in agreement with previous studies (Yasseri & Epe, 2015).

293 **Table 4.** Langmuir and Freundlich isotherms parameters of P adsorption by original FA and La-  
 294 FA.

Adsorbent	Langmuir			Freundlich		
	$q_m$ (mg P g <sup>-1</sup> )	$k_L$ (L mg <sup>-1</sup> )	$r^2$	n	$k_F$ (mg P g <sup>-1</sup> )	$r^2$

FA	1.752	1.675	0.994	0.895	0.002	0.831
La-FA	10.753	2.981	0.999	4.417	50.188	0.713

295 In order to investigate and demonstrate the mechanism at the molecular level, the P K-  
296 edge XANES spectra of the La-FA sample containing bonded P was measured (Fig.  
297 3A). As P has only one valance state, it can be perfectly characterised by the derivative  
298 analysis of the XANES spectra (Khare et al., 2007). It has been reported that aqueous  
299 Fe(III)–PO<sub>4</sub><sup>3-</sup> solutions increased in the degree of bidentate compared to monodentate  
300 bonding with increasing Fe/P ratio by using ferrihydrite adsorbent (Filatova et al., 1976).  
301 However, in this study, there was no obvious change of white line energy from the La-  
302 FA bonded P sample, compared to the derivative spectra for HPO<sub>4</sub><sup>2-</sup> (Fig. 3B), possibly  
303 indicating that P was bound on La-FA surfaces by adsorption (Khare et al., 2007).  
304 Although XANES is recognized as an element-specific and in-situ method for the  
305 detection of the molecular structures of reacting species (Khare et al., 2005; Xu et al.,  
306 2017), it is beneficial to explore molecular mechanisms by combining the results from  
307 multiple-characterisation methods, such as X-ray photoelectron spectroscopy (XPS),  
308 and Fourier transform infrared spectroscopy (FTIR), which could be conducted in a  
309 future study.



310

311 **Fig. 3.** (A) Normalized XANES spectra of  $\text{HPO}_4^{2-}$  and La-FA bonded with P. (B) First-

312 derivative XANES spectra for  $\text{HPO}_4^{2-}$  and La-FA bonded with phosphate.

### 313 3.3. La-FA application in real natural waters

314 Previous studies have investigated the vertical distribution of La in-lake sediments for

315 each experimental site, in order to explore the impact of *Phoslock*<sup>®</sup> being applied for

316 remediation of eutrophic water bodies (Yasseri & Epe, 2015). Although the theoretical

317 binding ratio of a La/P material was 1:1 based on the reaction equation ( $\text{La}^{3+} + \text{PO}_4^{3-} =$

318  $\text{LaPO}_4$ ), the application of materials with La/P molar ratios greater than 1:1 could

319 increase P removal by up to 60% (Yasseri & Epe, 2015). Hence, it is suggested that

320 more studies should be carried out in order to investigate the amount of La-modified

321 material required in a real environmental application. Fig. 4 illustrates that the La-FA

322 had a relatively efficient removal ability to  $\text{PO}_4^{3-}$ -P at different La/P molar ratios

323 compared with TDP. With La/P molar ratios of 0.5:1, 1:1, 1.5:1 and 2:1,  $\text{PO}_4^{3-}$ -P

324 removal efficiencies were  $54.5 \pm 2.4\%$ ,  $72.8 \pm 2.7\%$ ,  $62.2 \pm 2.9\%$  and  $63.6 \pm 1.8\%$ ,

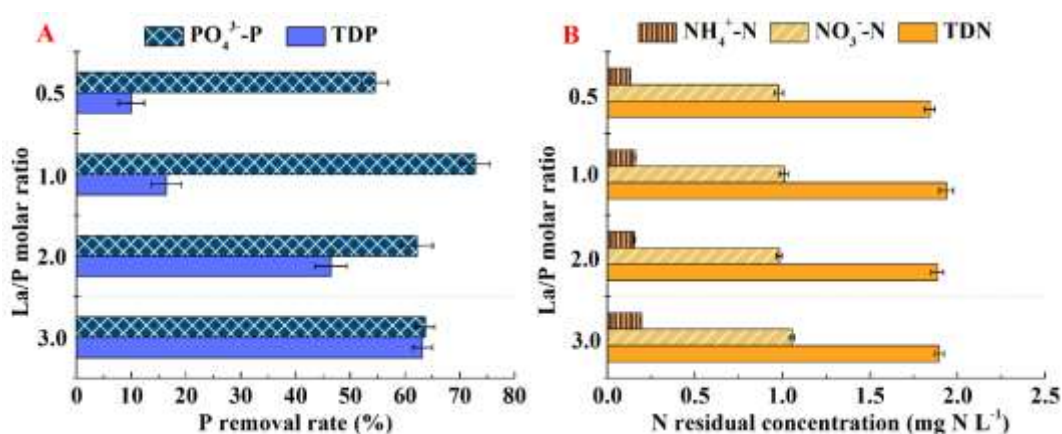
325 respectively. The La-FA material exhibited noticeably higher  $\text{PO}_4^{3-}$ -P removal ability

326 with a La/P molar ratio of 1:1 compared with that a La/P molar ratio of 0.5:1, which

327 might suggest that this La/P molar ratio equalled the best theoretical value. Increasing  
328 the La/P to 1.5:1 and further to 2:1 did not produce significant differences in the  $\text{PO}_4^{3-}$   
329 -P removal abilities, which might have been caused by saturation of adsorption sites in  
330 the material. It should be noted that the current experiment was conducted in aqueous  
331 solution without the presence of sediment. Taking into consideration P liberated from  
332 sediments, higher dosage of La-modified materials might be applied in lake restoration  
333 geo-engineering (Huang & Zhang, 2010). Nevertheless, the removal efficiency of TDP  
334 by La-FA increased with increasing La/P molar ratio. In detail, the removal rate of TDP  
335 was determined to be only  $10.0 \pm 2.4\%$  with La/P molar ratio 0.5:1, but  $63.2 \pm 1.8\%$   
336 when the La/P molar ratio increased to 3:1 (Fig. 4A). In this study, La-FA exhibited  
337 better selectivity to  $\text{PO}_4^{3-}$ -P than to TDP, possibly owing to presence of many other P  
338 species (e. g. hexakisphosphate) in the latter (Wan et al., 2016).

339 Previous studies have demonstrated that some La-modified materials (e. g. La-  
340 modified bentonite) could lead to adverse effects on the concentrations of nitrogen-  
341 containing compounds in water (Reitzel et al., 2013). The nutrients, including  $\text{NH}_4^+$ -N,  
342  $\text{NO}_3^-$ -N, and  $\text{NO}_2^-$ -N could attributed to the soluble fraction in the bentonite-based  
343 material and to the nitrification process, as occurs in anaerobic sediments (Van  
344 Oosterhout and Lüring, 2013; Gibbs et al., 2011). Such consequences might pose a risk  
345 to the surface waters, as N is also one of the key causes of eutrophication (Wang et al.,  
346 2016a; Zhang et al., 2018). In order to investigate the effect of La-FA material to  
347 nitrogen in natural water system, we also determined the concentrations of  $\text{NH}_4^+$ -N,  
348  $\text{NO}_3^-$ -N and TDN in water under different La-FA dosage regimes, which indicated that

349 La-FA had little effect on the nitrogen concentrations in water (Fig. 4B). With increase  
 350 in La/P molar ratio, TDN content of the solution did not change significantly, compared  
 351 with the initial concentration of 2.02 mg N L<sup>-1</sup> prior to adsorption (Table 2).  
 352 Concentrations of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in the lake water was not noticeably affected by  
 353 the addition of La-FA.



354  
 355 **Fig. 4.** (a) Removal rates of PO<sub>4</sub><sup>3-</sup>-P and TDP by La-FA. (b) Residual concentrations of NH<sub>4</sub><sup>+</sup>-  
 356 N, NO<sub>3</sub><sup>-</sup>-N and TDN after using La-FA.

### 357 3.4 Environmental implications

358 Laboratory experiments on La-FA have provided the theoretical basis and a technical  
 359 reference for its further application in a natural aquatic environment. The key purpose  
 360 of lake geological engineering is to control a eutrophication problem quickly and  
 361 effectively (Reitzel et al., 2013). The maximum amount of P adsorbed by La-FA (10.8  
 362 mg P g<sup>-1</sup>, Fig. 4) was similar to that obtained by use of the commercially available  
 363 material *Phoslock*<sup>®</sup> (10.6 mg P g<sup>-1</sup>) (Haghseresht et al., 2009). However, as a material  
 364 for the recapture of P for eutrophication control, the stability of the La-FA adsorbent  
 365 should be considered when applied into natural waters. Here, La-FA showed great

366 ability to combine with P, exhibiting a desorption rate of 0.81% without taking into  
367 consideration possible interference by submerged macrophytes in shallow waters  
368 (Zhang et al., 2018). To the best of our knowledge, there exist many ionic species in  
369 natural waters such as chloride, sulfate, calcium, magnesium, arsenic and nitrite (Shahat  
370 et al., 2018; Awual, et al., 2019), which might act as potential antagonists for efficient  
371 P adsorption. It has been reported that some hydrophobic materials, such as anion  
372 exchange fibres prefer lowly hydrated anions ( $\text{H}_2\text{PO}_4^-$ ) compared with highly hydrated  
373 ones ( $\text{H}_2\text{AsO}_4^-$ ) with the same electronic charge (Awual et al., 2008). In this study, as  
374 an effective P adsorption material, La-FA showed better selectivity and sensitivity to  
375 different P species for both synthetic and natural water systems (Fig. 4). However, the  
376 effects of multiple different ions on efficiency of P removal by La-modified materials  
377 should be further considered when applying these to natural waters. Based on the  
378 current results of this study, longer-term experiments in large-scale systems should be  
379 further conducted in order to better investigate the selectivity to different ions and to  
380 evaluate the full cost-benefit of feasibility of waste utilization.

381 This study suggested that the proposed La-based material could provide a suitable  
382 approach for the reuse of this type of industrial wastes. In addition to removal of P, La-  
383 FA could provide a sediment covering function, possibly improving the anaerobic  
384 environment of sediment and effectively slowing down the release of nutrients in  
385 sediment. Practically, it would be necessary to determine the optimum dosage and  
386 proportion of La-modified materials used for a project, according to the different  
387 sediment environments present. As a natural lake system is very complex, investigation

388 into the specific effects of different dosages of La-modified materials on natural aquatic  
389 organisms such as *Daphnia magna* and fish should be carried out. According to the  
390 different water quality conditions and the types of aquatic organisms, the ecological  
391 security of the aquatic organisms should be evaluated.

#### 392 **4. Conclusions**

393 In this study, we have developed a La-modified adsorbent using solid waste coal fly ash  
394 (La-FA) as raw material and investigated its performance for removal of phosphorus  
395 from both synthetic and natural waters. The adsorption equilibrium data followed well  
396 the Langmuir model with maximum adsorption capacity 10.8 mg P g<sup>-1</sup> of La-FA, some  
397 6 times higher than that obtained from the original FA material. The pseudo-second-  
398 order kinetic model was identified as the best model to describe the adsorption process.  
399 Both the measurement of  $\zeta$  potentials and P K-edge XANES spectra indicated that P  
400 was probably bonded onto the La-FA by surface adsorption. The La-FA showed the  
401 highest PO<sub>4</sub><sup>3-</sup>-P removal ability at a La/P molar ratio of 1:1. The application of La-FA  
402 had negligible effects on the concentrations of TDN, NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in water. With  
403 these results, La-FA may be a potential material for the removal of P from polluted  
404 natural waters for the mitigation of eutrophication.

#### 405 **Declaration of competing interest**

406 The authors declare no conflicts of interest in this research.

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