

From Wastes To Functions: Preparation of Layered Double Hydroxides From Industrial Waste And Its Removal Performance Towards Phosphates

Liping Xiao

Qingdao University of Technology

Yan Li

Liaoning Technical University

Qiaoping Kong (✉ kongqiaoping@qut.edu.cn)

Qingdao University of Technology

Yunlong Lan

Qingdao University of Technology

Research Article

Keywords: Layered double hydroxides, Industrial waste residue, Phosphate, Adsorption, Wastewater

Posted Date: July 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-633550/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on September 23rd, 2021. See the published version at <https://doi.org/10.1007/s11356-021-16563-x>.

1 **From wastes to functions: Preparation of layered double hydroxides from**
2 **industrial waste and its removal performance towards phosphates**

3 Liping Xiao^{a,*}, Yan Li^b, Qiaoping Kong^{a,*}, Yunlong Lan^a

4 ^a School of Environmental and Municipal Engineering, Qingdao University of
5 Technology, Qingdao 266033, PR China

6 ^b School of Civil Engineering, Liaoning Technical University, Fuxin 123000, PR
7 China

8 **Abstract**

9 To control eutrophication and recover phosphate from wastewater, a calcium
10 carbide slag and red mud composite material (CR-LDH) was prepared using industrial
11 waste as raw material for phosphorus adsorption. The morphology and structure of
12 synthesized CR-LDH was characterized by FT-IR, SEM, EDS and XRD
13 measurements. The experimental data can be well described by pseudo-second-order
14 kinetics and Langmuir isotherm models, suggesting that the adsorption process of
15 CR-LDH with respect to phosphate is a chemical and monolayer process. The
16 theoretical maximum adsorption capacity obtained by Langmuir isotherm model is
17 16.06 mg·g⁻¹ at 25 °C. The intra-particle diffusion model fitting results indicated that
18 the adsorption of phosphate by CR-LDH was controlled by both liquid membrane

* Corresponding author at: School of Environmental and Municipal Engineering,
Qingdao University of Technology, Qingdao 266033, PR China.

E-mail address: xxlpp11@126.com (L. P. Xiao); kongqiaoping@qut.edu.cn (Q. P. Kong)

19 diffusion and intra-particle diffusion. Phosphate was bound to CR-LDH via
20 synergistic effect of physical adsorption, ion exchange, anion intercalation and
21 chemical precipitation as evidenced from a combination of microscopic analysis and
22 adsorption mechanism study. The actual phosphate-containing wastewater
23 investigation showed that CR-LDH not only exhibited good removal effect on
24 phosphate, but also could greatly reduce turbidity, COD and ammonia nitrogen, which
25 was suitable for disposal of practical wastewater. These results indicate that CR-LDH
26 can be considered as potential adsorbent for the treatment of phosphate-containing
27 wastewater, which will be helpful to achieve the goal of "treating waste with waste
28 and turning waste into treasure".

29 **Keywords:** Layered double hydroxides; Industrial waste residue; Phosphate;
30 Adsorption; Wastewater

31

32 **1. Introduction**

33 As a non-renewable and irreplaceable resource, phosphorus is essential element
34 for cell growth in plants, animals or bacteria, and thus necessary for maintaining the
35 stability of the whole ecosystem (Jiang et al., 2019; Seftel et al., 2018). However,
36 excess of phosphorous ($\geq 0.02 \text{ mg}\cdot\text{L}^{-1}$) will cause eutrophication in widespread water
37 body (Yang et al., 2019), along with a series of issues such as the reduction of water
38 economic value and the the restriction of sustainable development of the society and
39 economy. Hence, it's of vital importance for controlling redundant phosphate to a low
40 level by cost-effective approaches (Zhang et al., 2019). Generally speaking,

41 phosphorus in wastewater usually exists in the main forms of organic phosphate,
42 orthophosphate and polymeric (condensed) phosphate (Bacelo et al., 2020), but the
43 total phosphorus content and the mass fraction of various forms of phosphorus vary
44 depending on the source of the wastewater. Therefore, the most critical step in
45 phosphorus removal of most wastewater is to consider how to remove
46 orthophosphate.

47 Until now, various approaches have been adopted for the treatment of
48 phosphorus-containing wastewater such as chemical precipitation, crystallization,
49 biological processes and adsorption method (Bacelo et al., 2020). Among them,
50 adsorption with the characteristic of simple operation, low cost and
51 environment-friendly (Kong et al., 2021; Kong et al., 2019) is generally considered to
52 be the most effective method for the treatment of phosphorus-containing wastewater.
53 The key to the popularization and application of adsorption method lies in the
54 research and development of cheap and efficient new adsorbents. Many kinds of
55 adsorbents such as layered double hydroxides (LDHs) (Dox et al., 2019; Liu et al.,
56 2019; Seftel et al., 2018; Zhang et al., 2019), zeolite (Li et al., 2021; Razmi and
57 Ghasemi-Fasaei, 2018), corn bracts (Jiang et al., 2019), lignite (Samaraweera et al.,
58 2021), aluminum-modified eggshells (Guo et al., 2017), sludge (Tie et al., 2013), MgO
59 nanoparticles biochar composites (Zhu et al., 2021) and paper mill sludge-based
60 calcium-containing porous biochar (Wang et al., 2021) have been reported for the
61 removal of phosphorus from wastewater.

62 LDHs, also known as anionic clays, include hydrotalcite and hydrotalcite like

63 compounds, and the main body of LDHs is generally composed of hydroxides of two
64 metals. LDHs have the properties of ion exchange between layers and permanent
65 positive charge. After calcination, the product of LDHs has a huge specific surface
66 area and can return to the original layered structure in a certain environment. LDHs is
67 deemed as an excellent adsorbent for the removal of organic and inorganic pollutants
68 from wastewater. In terms of phosphate removal, Zhang et al. successfully
69 synthesized layered double hydroxides with nitrate via co-precipitation method and
70 the experimental results showed that the multilayer structure of the synthesized LDHs
71 exhibited good adsorption ability towards phosphate (Zhang et al., 2021). Jia et al.
72 exfoliated and incorporated MgAlFe-LDHs in polyether sulfone membranes and the
73 adsorption rate of the obtained membranes was faster than the un-exfoliated one. The
74 adsorption capacity of obtained membranes with respect to phosphate was $5.61 \text{ mg}\cdot\text{g}^{-1}$
75 (Jia et al., 2018). Seftel et al. used modified ZnAl-LDHs to adsorb phosphate from
76 aqueous solutions. The results showed that anionic exchange was the main adsorption
77 mechanism for the phosphate adsorbed by non-calcined LDH, while the adsorption
78 process of LDO materials towards phosphate was attributed to structural
79 reconstruction and precipitation (Seftel et al., 2018). However, the LDHs used in most
80 of the above publications were synthesized using chemical agents. If LDHs can be
81 prepared from industrial waste, the production cost of adsorbent will be greatly
82 reduced and the industrial waste can be reused for recycling. To our best knowledge,
83 the literature focus on using industrial waste residue to prepare LDHs for the removal
84 of phosphate from wastewater had rarely been reported.

85 The purpose of this study is to make full use of industrial waste residues to
86 develop new adsorbent for the removal phosphate in wastewater, which can reduce
87 the environmental pollution caused by industrial waste residues, and achieve the
88 purpose of effective treatment of phosphate-containing wastewater. Herein, we
89 prepared a novel CR-LDH adsorbent with hydrocalumite and magnesite structure by
90 calcium carbide slag and red mud via a simple method. Calcium carbide slag is a
91 calcium-containing solid industrial waste residue produced during the hydride
92 process of chlor-alkali industry, and the main chemical components are CaO, Al₂O₃,
93 Fe₂O₃, SiO₂, MgO, etc. Red mud is a kind of solid waste residue in aluminum
94 industry formed from bauxite (Hu et al., 2017). The influencing factors of adsorbent's
95 dosage, pH and co-existing ions on the removal performance of phosphate were
96 discussed. The adsorption kinetics, isotherm and thermodynamics were systematically
97 studied. The adsorption mechanism was proposed by combining the experimental
98 investigation and characterization of CR-LDH before and after adsorption of
99 phosphate. In addition, the applicability of CR-LDH for the removal of phosphate in
100 practical phosphate-containing wastewater was also investigated.

101

102 **2. Materials and methods**

103 **2.1. Chemicals and materials**

104 The carbide slag was taken from an acetylene plant in Fuxin City,
105 Liaoning Province. The red mud was provided by an aluminum plant in
106 Liaocheng City, Shandong Province. The red mud used in this study is "Bayer

107 red mud” which accounts for more than 90% of the world’s total red mud. The
108 raw carbide slag and red mud were crushed and ground through 200 mesh
109 sieve, and then dried to constant weight in 105 °C oven to remove the
110 moisture and maintain the original properties of the materials. The picture of
111 raw calcium carbide slag powder and red mud powder are presented in Fig.
112 S1a and Fig. S1b of Supplementary Material, respectively. The chemical
113 composition of raw calcium carbide slag powder and red mud powder are
114 provided in Table S1 and Table S2. Potassium dihydrogen phosphate
115 (KH_2PO_4) was purchased from Liaoning Quanrui Reagent Co., Ltd. 100
116 $\text{mg}\cdot\text{L}^{-1}$ phosphorus standard solution (GSB04-1741-2004a) was supplied by
117 China’s national center for analysis and testing of nonferrous metals and
118 electronic materials. Ascorbic acid were purchased from Liaoning Quanrui
119 Reagent Co., Ltd, China. The other chemicals were purchased from Shenyang
120 Huadong Reagent Factory, China. All chemicals were of analytic grade (or
121 higher), and were used without further purification.

122 **2.2. Preparation of CR-LDH**

123 The CR-LDH was prepared as the following steps: firstly, the raw material of
124 calcium carbide slag and red mud were roasted at 600 °C for 3 h in muffle furnace,
125 respectively. After cooling to room temperature, the obtained calcium carbide slag and
126 red mud with mass ratio of 1:1 were fully mixed and then added into 300 mL
127 deionized water. Under mechanical stirring of $700\text{ r}\cdot\text{min}^{-1}$, the resulting slurry was
128 stirred at 45 °C for 3 h. Subsequently, the above mixture was crystallized in 70 °C

129 water bath for 24 h and the residue was washed thoroughly with distilled water. After
130 drying at 105 °C to constant weight, the precipitate was ground to pass through
131 200-mesh sieve. Finally, carbide slag red mud composite powder was obtained,
132 denoted as CR-LDH. The picture of the prepared of CR-LDH was shown in Fig. S2.

133 **2.3. Physicochemical characteristic of CR-LDH**

134 The morphology and element distribution of CR-LDH was determined by a
135 S-4800 scanning electron microscopy (SEM) (Hitachi, Japan) and energy-dispersive
136 spectroscopy (EDS) mapping analysis. To determine the surface area of CR-LDH,
137 a ASAP2460 Brunauer-Emmett-Teller N₂ adsorption analysis (BET)
138 (Micromeritics, USA) was used. The functional groups and chemical bond types
139 of CR-LDH from 4000 to 400 cm⁻¹ was measured by a NICOLET iS5 fourier
140 transform infrared spectroscopy (FT-IR) (Thermo Nicolet Corporation, USA). A
141 x'pert pro X-ray diffraction (XRD) (Spectris, Holland) with Cu K^α radiation (40
142 kV, 40 mA) at a scan speed of 4°·min⁻¹ was used to detect the crystallographic
143 structure of CR-LDH.

144 **2.4. Batch adsorption experiments of CR-LDH**

145 A series of batch adsorption tests were conducted to evaluate the
146 adsorption performance of CR-LDH with respect to phosphate. The adsorption
147 experiments were carried out in 250 mL conical flasks with a certain amount of
148 CR-LDH and 100 mL of phosphate at 25 °C. After adsorption equilibrium, the
149 supernatants were collected and then filtered through 0.45 μm membrane filter and
150 diluted for further phosphate analysis by the UV spectrophotometer at a wavelength

151 of 700 nm using the molybdate colorimetric method (Zhang et al., 2019). The initial
152 pH values of the phosphate solutions were adjusted by 0.1 mol·L⁻¹ HNO₃ or NaOH.
153 The adsorption kinetics of phosphate were carried out by immersing 0.5 g of CR-LDH
154 into 100 mL phosphate solution with concentration of 30 mg·L⁻¹ (25 °C, 10 h). For the
155 adsorption isotherms study, 0.5 g of CR-LDH was added into 100 mL of phosphate
156 solution with initial concentration ranging from 5 to 210 mg·L⁻¹ by maintaining
157 reaction temperature at at 15, 25, 35 °C, respectively. The adsorption amount and
158 removal efficiency of CR-LDH towards phosphate were calculated by the following
159 equations:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$\text{Removal efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

160 where Q_t is adsorption amount of phosphate onto CR-LDH at time of t , mg·g⁻¹;
161 C_0 is the initial concentration of phosphate, mg·L⁻¹; C_t is the concentration of
162 phosphate at time of t ; m is the mass of CR-LDH, mg·L⁻¹; and V is the volume of
163 solution, mL.

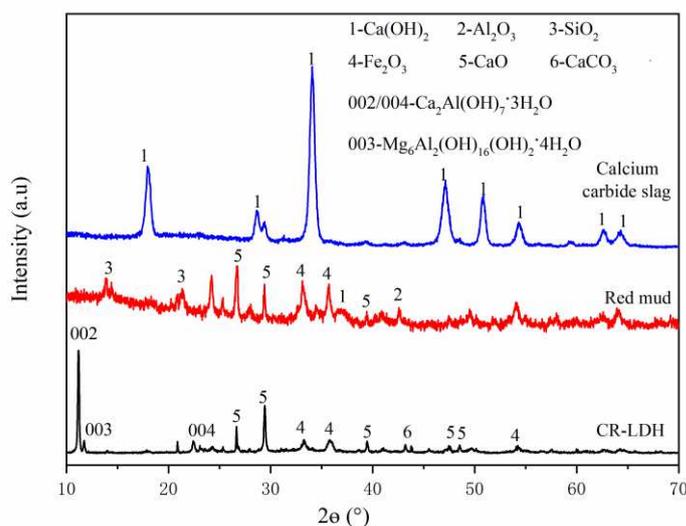
164 **3. Results and discussion**

165 **3.1. Characterization of CR-LDH composites**

166 The structural characteristics of calcium carbide slag, red mud and CR-LDH are
167 investigated by XRD patterns and the results are shown in Fig. 1. In the spectrum of
168 calcium carbide slag, the peaks at 2θ values of 18.107⁰, 28.728⁰, 34.169⁰, 47.249⁰,
169 50.896⁰ and 54.464⁰ suggested the presence of Ca(OH)₂. The component of Ca(OH)₂

170 would be conducive for the removal of phosphate by forming phosphide precipitation
171 through the reaction between Ca^{2+} and phosphate at high pH environmental
172 conditions. However, phosphate removal by calcium carbide slag would lead to
173 higher pH value of effluent. The XRD pattern of red mud presented the absorption
174 peaks of Fe_2O_3 ($2\theta=33.117^\circ$ and $2\theta=35.604^\circ$), CaO ($2\theta=24.749^\circ$ and $2\theta=29.756^\circ$) and
175 SiO_2 ($2\theta=21.662^\circ$). The abundant metal elements in red mud, especially for Al and Fe,
176 could interact with phosphate during the adsorption process. For XRD patterns of
177 CR-LDH composite, the characteristic peaks corresponding to the (002) and (004)
178 crystal planes of hydrocalumite were appeared, which was consistent with the PDF
179 card of the International Diffraction Data Center (PDF#16-0333). The CR-LDH
180 composite exhibited hydrocalumite structure. Hydrocalumite was an ordered layered
181 inorganic compound of LDHs with excellent removal ability for phosphate. The
182 diffraction peaks corresponding to the hydrocalumite (002) crystal plane had the
183 characteristics of sharp peaks, good peak type, low and flat base line, high
184 crystallinity and a relatively complete monoclinic symmetrical layered structure. In
185 addition, the characteristic peaks corresponding to the (003) crystal face of boehmite
186 were appeared in the XRD patterns of CR-LDH. The peaks of CaCO_3 ($2\theta=43.14^\circ$)
187 and Fe_2O_3 ($2\theta=33.24^\circ$, $2\theta=35.73^\circ$ and $2\theta=54.21^\circ$) were also detected in the XRD
188 patterns of CR-LDH. The reason for the existence of these metal oxides was that their
189 raw materials are industrial waste slag, and the metal oxides were not fully reacted in
190 the process of preparing the composites, and there were still some metal oxides in the
191 CR-LDH composite. All these findings indicated that calcium carbide slag and red

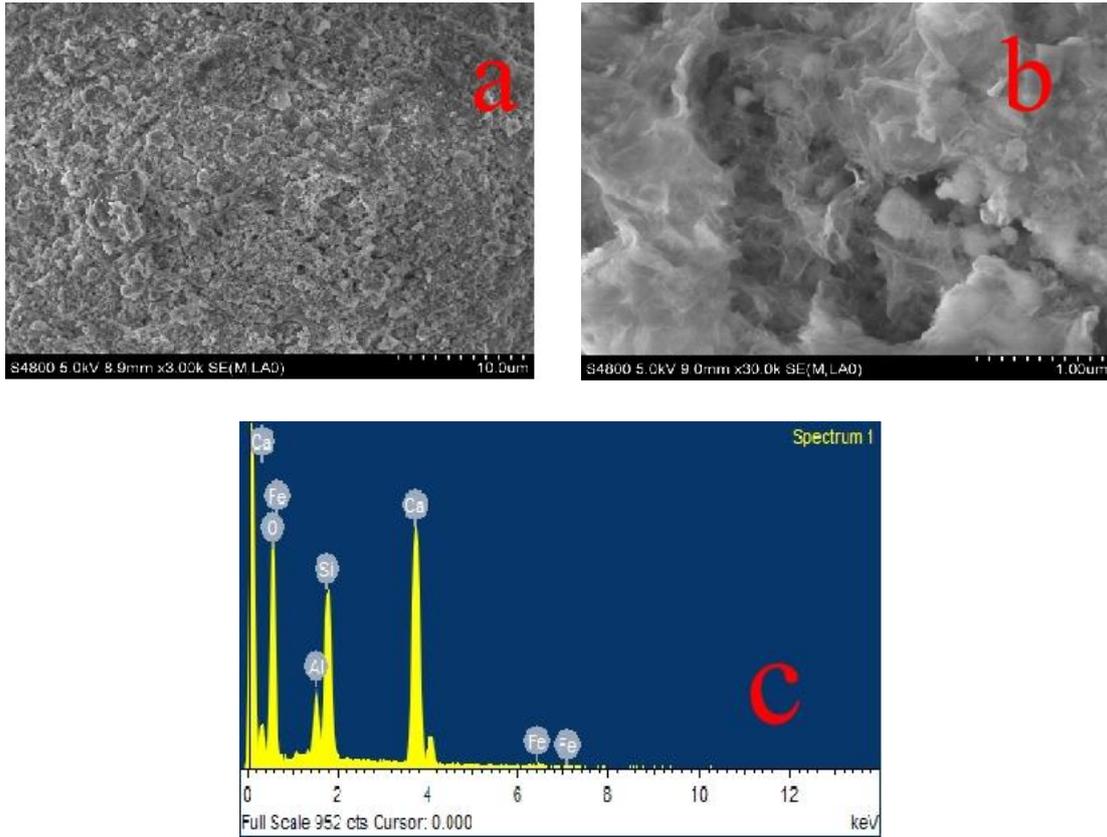
192 mud ha been successfully compounded to form CR-LDH.



193

194 Fig. 1 XRD pattern of calcium carbide slag, red mud and CR-LDH.

195 SEM and EDS are used to investigate the surface morphology and element
196 content distribution of CR-LDH, respectively. As shown in Fig. 2a and Fig. 2b,
197 CR-LDH presented a typical plate-like morphology of LDHs (Cheng et al., 2019). The
198 surface of CR-LDH was relatively rough and there are a large number of gaps, which
199 was conducive to the adsorption process. The BET surface area of CR-LDH was
200 $42.46 \text{ m}^2 \cdot \text{g}^{-1}$, providing a large number of surface active sites for the adsorption of
201 phosphate in the aqueous solutions. According to the EDS results (Fig. 2c and Table
202 1), the content ratio of main elements of CR LDHs mainly contained O, Al and Ca,
203 and the content of Ca was much higher than that of other metal elements, which were
204 consistent with the XRD results that CR-LDH had the characteristic adsorption peaks
205 of hydrocalumite and boehmite.



206 Fig. 2 SEM of CR-LDH (a, b) and EDS of CR-LDH (c).

207 Table 1 The elemental content changes of CR-LDH before and after adsorption of
 208 phosphate.

Element	CR-LDH (Before adsorption)		CR-LDH-phosphate (After adsorption)	
	wt%	at%	wt%	at%
O	62.35	78.42	47.30	69.23
Al	3.26	2.43	7.49	6.50
Si	9.30	6.67	4.54	3.79
Ca	24.24	12.17	14.89	8.70
Fe	0.85	0.31	20.82	8.73

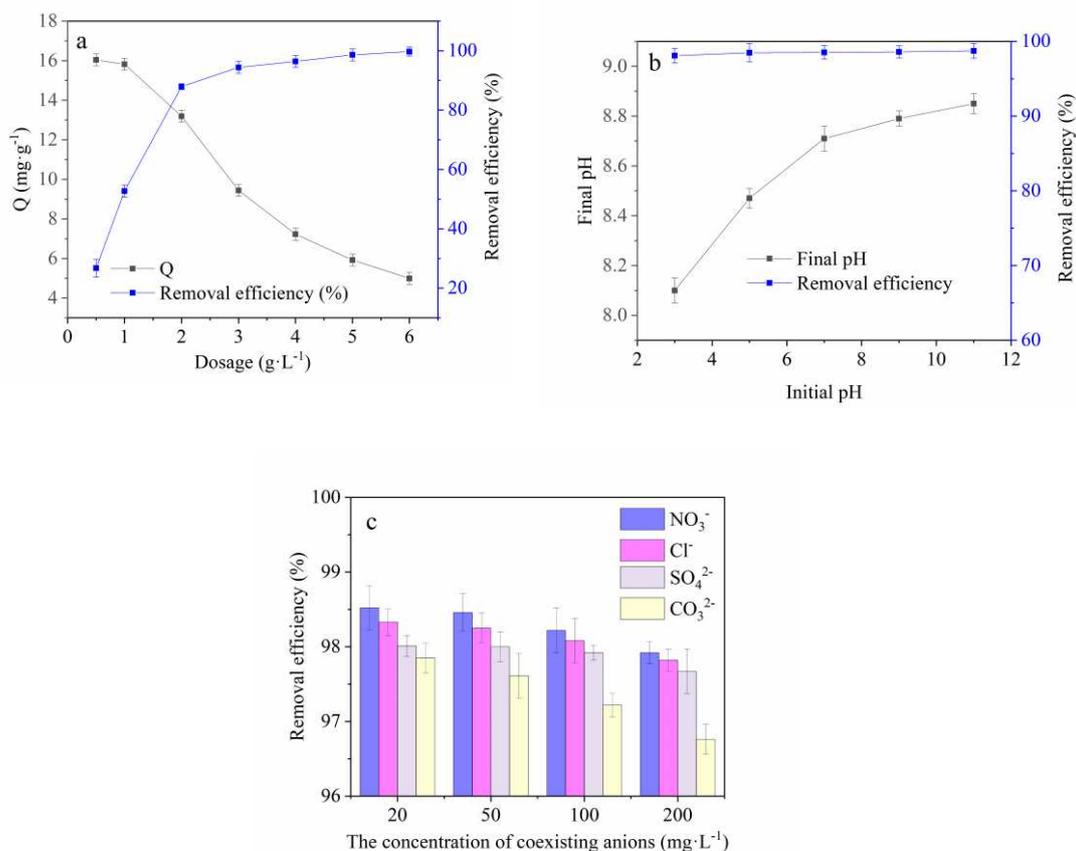
P	—	—	1.20	0.91
---	---	---	------	------

209 **3.2. Optimization of the batch adsorption conditions**

210 **3.2.1. Effect of CR-LDH dosage on phosphate adsorption**

211 To investigate the effect of dosage on the adsorption performance of CR-LDH
 212 with respect to phosphate, 0.5, 1, 2, 3, 4, 5 and 6 g·L⁻¹ CR-LDH were added into 100
 213 mL phosphate ion solution with a concentration 30 mg·L⁻¹. Adsorption experiments
 214 conducted for 24 h at 25 °C with pH of 7 and shaking speed of 180 r·min⁻¹. The
 215 results are shown in Fig. 3a. It can be seen from Fig. 3a that the removal rate of
 216 phosphate was first gradually increased and then basically approached 100%, while
 217 the adsorption ability of per unit mass CR-LDH was gradually decreased. The
 218 increase of phosphate removal rate was due to the increase of adsorbent dosage,
 219 which increases the number of available adsorption sites on the material surface and
 220 the contact probability with adsorption sites in the solution, providing favorable
 221 conditions for phosphate adsorption removal. Under the condition that the initial
 222 concentration of phosphate is 30 mg·L⁻¹, the amount of phosphate in solution was
 223 fixed and more phosphate were removed with the increasing dosage of CR-LDH,
 224 while the per amount phosphate adsorbed by CR-LDH was decreased relatively.
 225 Considering the phosphate removal performance and meeting the first-level discharge
 226 standard (≤ 0.5 mg·L⁻¹) in the comprehensive sewage discharge standard of China
 227 (GB8978-1996), the optimal dosage of 5 g·L⁻¹ was selected in the following study
 228 when the phosphate concentration was 30 mg·L⁻¹. Under this condition, the phosphate
 229 removal rate was 98.6% and the phosphate concentration in the effluent was 0.42

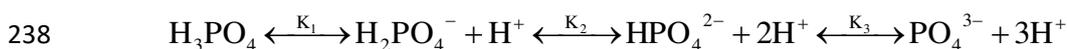
230 $\text{mg}\cdot\text{L}^{-1}$.



231 Fig. 3 Adsorption performance of CR-LDH towards phosphate as a function of
 232 CR-LDH dosage (a), initial pH (b) and of coexisting anions (c).

233 3.2.2. Effect of initial pH values on phosphate adsorption

234 pH is deemed as an important factor influencing the physico-chemical adsorption
 235 reaction process of adsorbent towards adsorbate because pH will influence the
 236 phosphate dissociation equilibria in aqueous solutions (Cheng et al., 2009; Kong et al.,
 237 2020; Zhang et al., 2019):



239 where $\text{p}K_1=2.15$, $\text{p}K_2=7.20$ and $\text{p}K_3=12.33$, respectively. In this study, the effect
 240 of initial pH values on phosphate adsorption by CR-LDH were investigated at pH

241 ranging from 3.0 to 11.0 and the results were shown in Fig. 3b. As shown in Fig. 3b,
242 with the increase of initial pH, the phosphate removal rate increased gradually, but the
243 change range was relatively small. When the pH was in the range of 3.0-11.0 (the
244 main species of phosphate was H_2PO_4^- and HPO_4^{2-}), CR-LDH maintained a high
245 phosphate removal rate. Due to the adsorption free energy of H_2PO_4^- was lower than
246 that of HPO_4^{2-} (Yang et al., 2014), so CR-LDH was more likely to adsorb H_2PO_4^- . At
247 pH 3.0 and 11.0, the phosphate removal rate were 98.1% and 98.7%, respectively.
248 This phenomenon is mainly due to that CR-LDH have a certain regulating effect on
249 the pH of the solution. The final pH values were gradually increased after reaction
250 equilibrium and remained ranging from 8.1 to 8.9, indicating that OH^- were released
251 by CR-LDH in the adsorption process under lower pH. While at higher pH values,
252 OH^- was consumed in the transformation process of calcium phosphate precipitation
253 into hydroxyapatite. Considering that the actual water samples are mostly in the
254 neutral range, pH of 7.0 was selected in the follow-up experiments.

255 **3.2.3. Effect of co-existing inorganic anions on phosphate adsorption**

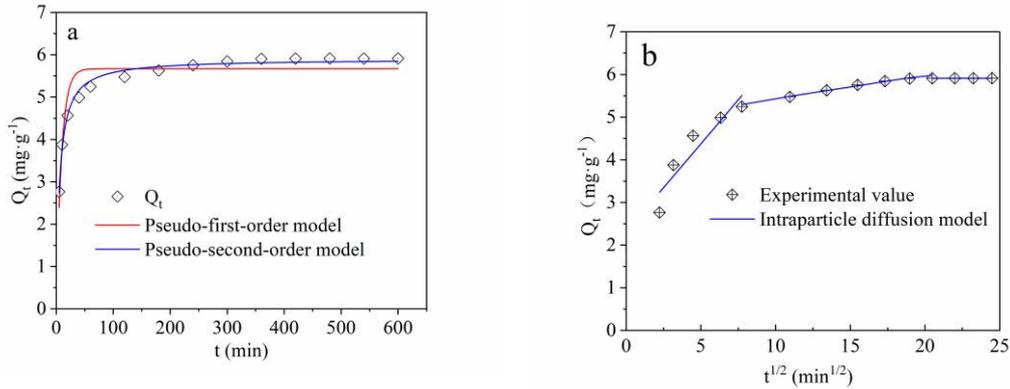
256 Phosphate is not existed alone in wastewater, but may be coexisted with CO_3^{2-} ,
257 SO_4^{2-} , NO_3^- , Cl^- and other inorganic anions. In this study, the effect of CO_3^{2-} , SO_4^{2-} ,
258 NO_3^- , Cl^- on the adsorption performance of CR-LDH towards phosphate were
259 investigated within co-existing inorganic anions concentration of 20, 50, 100 and 200
260 $\text{mg}\cdot\text{L}^{-1}$, respectively. As shown in Fig. 3c, when CO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- were
261 con-existed in solution, the removal rate of phosphate was decreased in varying
262 degrees. The inhibition effect of co-existing inorganic anions was increased with the

263 increase of its concentration. Under the same initial concentration of CO_3^{2-} , SO_4^{2-} ,
264 NO_3^- , Cl^- , the inhibition order of the above four co-existing ions was as follows:
265 $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. When the concentration of CO_3^{2-} was $200 \text{ mg}\cdot\text{L}^{-1}$, the
266 removal rate of CR-LDH towards phosphate was reduced to 96.77% and the effluent
267 phosphate concentration was $0.97 \text{ mg}\cdot\text{L}^{-1}$. The inhibition effect of co-existing
268 inorganic anions was mainly due to the fact that these anions would compete with
269 phosphate to enter the interlayer structure of CR-LDH in adsorption process, resulting
270 in decrease adsorption sites of the interlayer. The interaction between the inorganic
271 anions with higher valence and the positively charged laminates was stronger, which
272 made it easier to enter the interlayer channels of CR-LDH. As a result, the inhibitory
273 effect of bivalent anion (CO_3^{2-} and SO_4^{2-}) were stronger than that of monovalent anion
274 (NO_3^- and Cl^-), which was consistent with the research results reported in previous
275 publications (Seftel et al., 2018).

276 **3.2.4. Adsorption kinetics**

277 The process of phosphate adsorbed by CR-LDH is a time-dependent reaction.
278 The adsorption behavior of CR-LDH with respect to phosphate as a function of time
279 was studied and the results were shown in Fig. 4. It can be seen that the adsorption of
280 phosphate by CR LDHs can be roughly divided into three stages, namely, the rapid
281 adsorption reaction stage of 0-60 min, the slow adsorption reaction stage of 60-480
282 min, and the adsorption equilibrium stage after 480 min. At the initial stage of
283 adsorption, the surface of CR-LDH possessed abundant adsorption sites and a large
284 number of phosphate were existed in the solution, leading to the faster adsorption rate

285 of phosphate by CR-LDH. With the progress of the reaction, the concentration of
 286 phosphate was decreased in the solution and numerous adsorption site on the surface
 287 of CR-LDH were occupied by phosphate. As a result, the available adsorption sites of
 288 CR-LDH were less and the adsorption rate of phosphate was decreased accordingly.



289 Fig. 4 Fitting results of pseudo-first-order, pseudo-second-order kinetic model (a) and
 290 intra-particle diffusion model (b).

291 To better describe the adsorption process of CR-LDH towards phosphate,
 292 pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models
 293 were adopted in this study. The pseudo-first-order and pseudo-second-order equations
 294 are expressed as Eq. (3) and Eq. (4), respectively.

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \quad (4)$$

295 where t (min) represents the adsorption time; Q_t is the adsorption amount of
 296 phosphate adsorbed by CR-LDH at time t , mg·g⁻¹; Q_e represents the equilibrium
 297 adsorption capacity, mg·g⁻¹; k_1 (min⁻¹) and k_2 (g·mg⁻¹·min⁻¹) donate the
 298 pseudo-first-order and pseudo-second-order rate constants, respectively. As illustrated

299 in Fig. 4a and Table 2, the pseudo-second-order kinetic model ($R^2=0.989$) better fitted
 300 than the pseudo-second-order kinetic model ($R^2=0.896$) for phosphate adsorption on
 301 CR-LDH, suggesting that the adsorption of phosphate onto CR-LDH was mainly
 302 controlled by chemical adsorption through sharing or exchanging electrons, thus
 303 forming valence force for adsorption (Cao et al., 2020).

304 To determine the adsorption rate limiting step, intra-particle diffusion model was
 305 used to fitting the adsorption experimental results. The intra-particle diffusion model
 306 can be expressed as follows:

$$Q_t = k_3 t^{1/2} + C \quad (5)$$

307 where k_3 represents the intra-particle diffusion rate constant ($\text{mg} \cdot (\text{g min}^{1/2})^{-1}$) and C is
 308 the constant related to the thickness of the boundary layer ($\text{mg} \cdot \text{g}^{-1}$).

309 Table 2 Fitting results of kinetic model.

Kinetic model	Parameter	Value
Pseudo-first-order kinetic model	Q_e	5.67
	k_1	0.10967
	R^2	0.896
Pseudo-second-order kinetic model	Q_e	5.90
	K_2	0.0293
	R^2	0.989
Intra-particle diffusion	C_1	2.3151
	R_1^2	0.8689
	k_{31}	0.4119

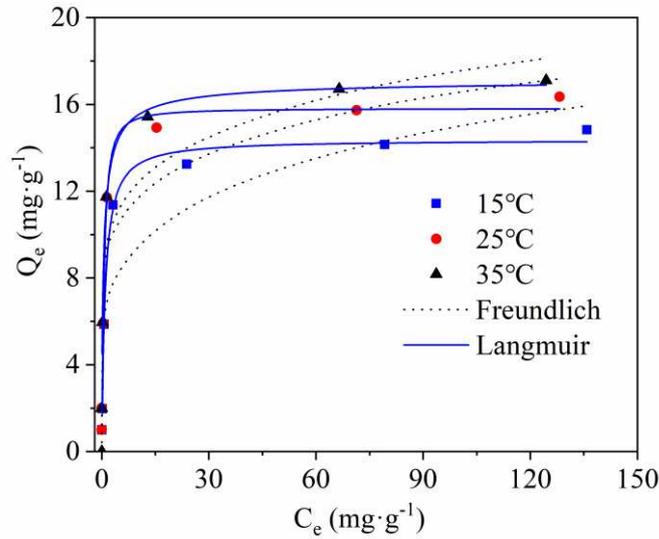
C2	4.8779
k ₃₂	0.0538
R ₂ ²	0.970
C3	5.9009
k ₃₃	0.0005
R ₃ ²	0.6439

310 According to intra-particle diffusion kinetic model, if the adsorption rate is only
311 determined by the intra-particle diffusion, the $Q_t-t^{1/2}$ curve will be a straight line with
312 C value of zero. As shown in Fig. 4b and Table 2, the adsorption experimental results
313 of CR-LDH towards phosphate presented a linear relationship in three stages and
314 value of C was not zero, suggesting that intra-particle diffusion was not the solely
315 speed limiting step. The adsorption process of CR-LDH with respect to phosphate
316 could be divided into three stages: film diffusion stage, intra-particle diffusion stage
317 and adsorption equilibrium stage. The film diffusion stage which occurred on the
318 initial of the reaction of 0-60 min was a rapid adsorption stage. Phosphate could
319 transfer to the abundant adsorption sites on the surface of CR-LDH through film
320 diffusion to achieve rapid adsorption. The intra-particle diffusion stage happened on
321 60-480 min was a gradual adsorption stage. In this stage, phosphate reached the
322 adsorption sites inside the pores of the CR-LDH with the happening of intra-particle
323 diffusion. The third stage was adsorption equilibrium stage (>480 min) and the
324 adsorption driving force was relatively weak due to the fact that there were fewer
325 adsorption sites in the solution and the number of free phosphate radicals was very

326 limited. The obtained C value followed the sequence of $C_1 < C_2 < C_3$, indicating that the
327 boundary layer thickness of CR-LDH was increased with the proceed of adsorption
328 reaction of CR-LDH towards phosphate.

329 **3.2.5. Adsorption isotherms**

330 Adsorption isotherms of phosphate removed by CR-LDH were investigated
331 within different concentration of phosphate ranging from 0 to 150 mg·L⁻¹ at three
332 different temperatures (15, 25 and 35 °C) and the results were shown in Fig. 5. As
333 exhibited in Fig. 5, with the increasing of phosphate's initial concentration, the
334 adsorption capacity of CR-LDH towards phosphate was increased. When the initial
335 concentration of phosphate was at a relatively low level, the adsorption sites on
336 CR-LDH could ensure that most of the phosphate in the solution was removed, and
337 the corresponding phosphate adsorption capacity of CR-LDH showed a linear upward
338 trend. With the further increase of the initial phosphate concentration, more and more
339 adsorption sites were occupied by phosphate radicals, and the number of free
340 adsorption sites was decreased, leading to the decrease in the tangent slope of the
341 phosphate adsorption curve.



342

343

Fig. 5 Isotherms of phosphate adsorption on CR-LDH.

344

Langmuir and Freundlich isotherm models were conducted to simulate the

345

adsorption experimental data of phosphate adsorbed by CR-LDH. The equation of

346

Langmuir (chemical adsorption model of single molecular layer) and Freundlich

347

(empirical model) isotherm models can be expressed as (Kong et al., 2019):

$$Q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (8)$$

$$Q_e = K_F C_e^{1/n} \quad (9)$$

348

where C_e represents equilibrium concentration of phosphate, $\text{mg}\cdot\text{L}^{-1}$; Q_{\max} is the

349

maximum adsorption capacity, $\text{mg}\cdot\text{g}^{-1}$; b is the affinity coefficient, $\text{L}\cdot\text{mg}^{-1}$; K_F and n

350

represent the constants of Freundlich isotherm model.

351

The fitting results of experimental data of Langmuir and Freundlich isotherm

352

models are exhibited in Fig. 5 and Table 3. Compared to Freundlich isotherm model,

353

Langmuir isotherm model ($R^2 > 0.98$) was more suitable to fit the adsorption process of

354

phosphate adsorbed onto CR-LDH which indicated that the adsorbed phosphate had

355 no interaction with each other and were distributed on the surface of CR-LDH as a
 356 molecular layer. The maximum adsorption capacity values calculated by Langmuir
 357 isotherm were close to the experimental data. When the temperature increased from
 358 15 to 35 °C, the maximum adsorption capacity of CR-LDH towards phosphate were
 359 enhanced from 14.41 to 16.59 mg·g⁻¹, indicating that high temperature had a
 360 beneficial effect on adsorption of phosphate. Comparison of the adsorption ability of
 361 different adsorbents towards phosphate is provided in Table 4. It can be seen that the
 362 maximum adsorption capacity of CR-LDH was in the middle level. In light of the cost
 363 of the adsorbent and the reuse of industrial waste-carbide slag, CR-LDH is still
 364 considered as a potential environmental friendly adsorbent. The n values of
 365 Freundlich isotherm model were all higher than 1, suggesting that the adsorption
 366 process of CR-LDH with respect to phosphate was easily implemented.

367 Table 3 Isotherm fitting results of phosphorus removal by CR-LDH.

Temperature (°C)	Q _{max} (mg·g ⁻¹)	Langmuir b	R ²	K _F	Freundlich n	R ²
15	14.41	1.06	0.994	6.87	5.83	0.889
25	16.06	1.53	0.989	9.45	8.12	0.941
35	16.59	2.19	0.993	9.97	8.07	0.955

368 Table 4 Comparison of the adsorption ability of different LDHs towards phosphate.

Adsorbents	Maximum adsorption amount (mg·g ⁻¹)	References
Zn-Al LDH	41.26	(Cheng et al., 2010)

Mg-Al LDH	31.30	(Yang et al., 2014)
Zn-Al LDH	68.40	(Yang et al., 2014)
Calcined MgMn-LDHs	7.30	(Chitrakar et al., 2005)
Mg-Al LDH (granular)	47.30	(Kuzawa et al., 2006)
CR-LDH	16.06	This study

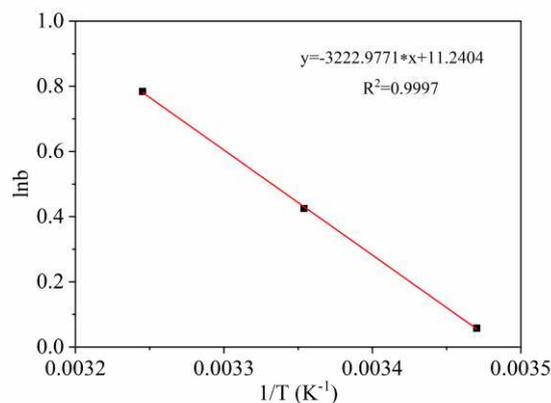
369 3.2.6. Adsorption thermodynamics

370 Adsorption thermodynamics analysis were also carried out to describe the
 371 adsorption process of phosphate adsorbed by CR-LDH. The adsorption
 372 thermodynamics formula can be expressed as follows:

$$\Delta G^0 = -RT \ln K^0 \quad (10)$$

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

373 where ΔG^0 is the Gibbs free energy, $\text{KJ} \cdot \text{mol}^{-1}$; R represents the is the constant of
 374 perfect gas and $R=8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T is the absolute temperature of solution, K; ΔS^0
 375 represents the entropy change, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; ΔH^0 is the enthalpy change, $\text{KJ} \cdot \text{mol}^{-1}$ and
 376 K^0 is the standard equilibrium constant. Because the adsorption process of CR-LDH
 377 with respect to phosphate fitted Langmuir isotherm model well with $R^2 > 0.98$, so the
 378 Langmuir constant of b could be calculated as K^0 .



379

380 Fig. 6 ln b and 1/T relationship curve of CR-LDH adsorption phosphorus.

381 As shown in Fig. 6 and Table 5, the values of ΔG^0 were all less than zero which
 382 suggested the adsorption process of phosphate by CR-LDH were spontaneous reaction.
 383 The absolute values of ΔG^0 became more positive with the increasing of temperature,
 384 suggesting that higher temperature was more conducive to the adsorption of
 385 CR-LDH towards phosphate. The positive ΔH^0 of 26.21 KJ·mol⁻¹ implied that the
 386 adsorption of phosphate by CR-LDH were endothermic and this finding was in
 387 agreement with the results that the adsorption capacities of CR-LDH were enhanced
 388 with the increasing of temperature. The positive ΔS^0 of 91.45 J·mol⁻¹·K⁻¹ indicated
 389 that the randomness at the solid-solution interface was increased which was due to the
 390 adsorption reaction of phosphate adsorbed by CR-LDH.

391 Table 5 Thermodynamic results of phosphorus adsorbed by CR-LDH.

Temperature (K)	ΔG (KJ·mol ⁻¹)	ΔH (KJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K ⁻¹)
288.15	-0.140		
298.15	-1.054	26.21	91.45
308.15	-2.008		

392

393 3.2.7. Application of CR-LDH to practical phosphate-containing wastewater

394 To investigate the applicability of CR-LDH for the removal of phosphate in
395 practical phosphate-containing wastewater, the untreated wastewater in the sewage
396 well of a machinery factory in Shenyang is selected and analyzed. Phosphating is an
397 important process in the pretreatment process of coating surface in mechanical
398 processing plants. A large number of phosphorus-containing agents are needed in the
399 phosphating process, and the phosphate content of phosphating wastewater often
400 exceeds the standard. The soluble orthophosphate forms in phosphating wastewater
401 account for about 87.8% of total soluble phosphorus, which is comparable with the
402 use of simulated phosphorus containing wastewater as experimental water. The photos
403 and water quality parameters of practical phosphate-containing wastewater before
404 CR-LDH adsorption and after CR-LDH adsorption were given in Fig. S3 and Table 6,
405 respectively.

406 Table 6 Water quality parameters of practical phosphate-containing wastewater before
407 and after CR-LDH adsorption ($\text{mg}\cdot\text{L}^{-1}$, except for pH).

Process	pH	COD _{cr}	Turbidity (NTU)	NH ₄ ⁺ -N	PO ₄ ³⁻ -P
Before CR-LDH adsorption	7.32	92.0	30.7	62	9.8
After CR-LDH adsorption	7.89	53	7	49.16	0.48

First-class standard of

national discharge

6-9

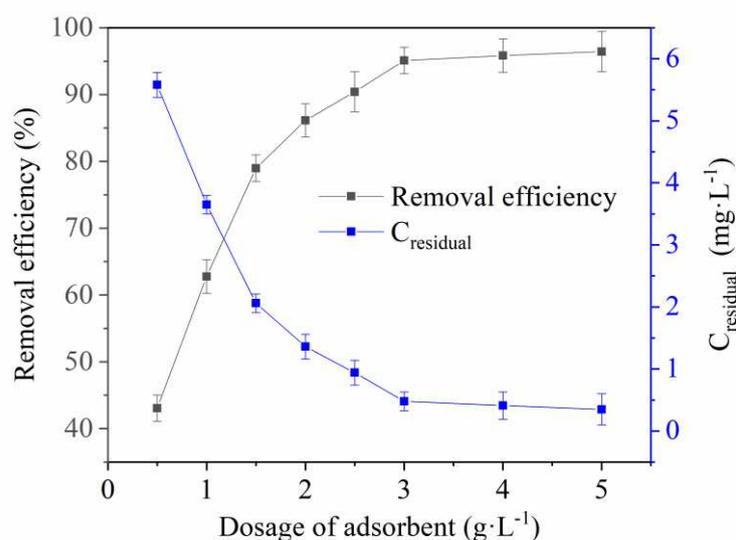
60

1

5

0.5

standards



408

409

Fig. 7 Effect of dosages on the removal of phosphate from practical

410

phosphate-containing wastewater.

411

In the applicability of CR-LDH test, 0.5, 1, 1.5, 2, 3, 4 and 5 g/L of CR-LDH

412

were added into the 100 mL practical phosphate-containing wastewater for the

413

adsorption experiments, respectively. After adsorption for 8 h at 25 °C, the samples

414

were filtered through 0.45 μm cellulose filtered membrane and then diluted for further

415

phosphate analysis. As exhibited in Fig. 7 and Table 5, the residual phosphate of

416

practical wastewater was decreased gradually as the increase of CR-LDH dosage,

417

while the phosphate removal rate was increased first and then stabilized. When the

418

dosage of CR-LDH was 3 g/L, the residual phosphate concentration was 0.48 mg·L⁻¹

419

and the corresponding removal rate was 95.1%, which met the first class discharge

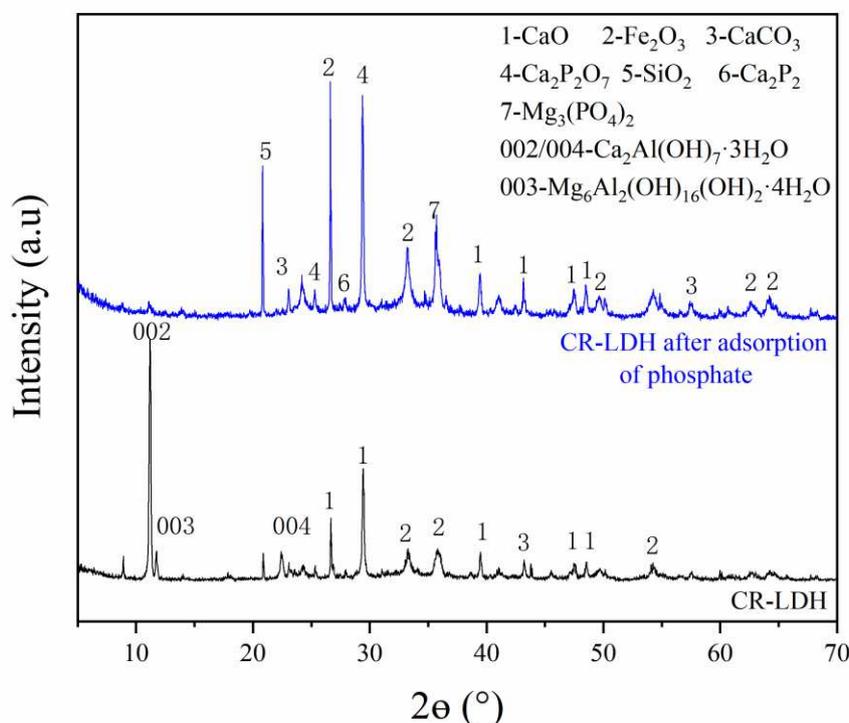
420 standard ($\leq 0.5 \text{ mg}\cdot\text{L}^{-1}$) in the integrated wastewater discharge standard
421 (GB8978-1996). The effluent pH met the discharge standard and the COD, turbidity
422 and $\text{NH}_4^+\text{-N}$ were reduced by 42.39%, 77.20% and 20.71%, respectively. The above
423 results indicated that CR-LDH had great potential for adsorbing phosphate from
424 practical phosphate-containing wastewater.

425 3.3. Adsorption mechanism

426 In order to clarify the adsorption mechanism, FT-IR was used to find out the
427 functional groups' changes of CR-LDH before and after adsorption of phosphate. As
428 shown in Fig. S4, the peak at 3415.75 cm^{-1} and 1637.79 cm^{-1} were assigned to the
429 stretching and bending vibration of the -OH in the CR-LDH and interstitial water
430 molecules, respectively. After adsorbed phosphate, the peaks at 1003.28 cm^{-1} and 548
431 cm^{-1} appeared which were attributed to the stretching and bending vibration of
432 phosphate. The band at 874 cm^{-1} belonged to the vibration of P-O in HPO_4^{2-} ,
433 indicating that effective adsorption of phosphate by CR-LDH was existed.

434 The XRD spectra of CR-LDH after adsorption of phosphate is shown in Fig. 8.
435 Compared to XRD pattern of CR-LDH before adsorption of phosphate, the diffraction
436 peak intensity of boehmite was decreased and the characteristic diffraction peak of
437 brucite was disappeared. New diffraction peaks of $\text{Ca}_2\text{P}_2\text{O}_7$, Ca_2P_2 , $\text{Mg}_3(\text{PO}_4)_2$ were
438 appeared which might be due to that phosphate entered into the layered structure of
439 CR-LDH after the adsorption process and Ca^{2+} dissolved on the surface combined
440 with HPO_4^{2-} hydrolyzed to form CaHPO_4 . After that, CaHPO_4 was polymerized and
441 dehydrated to form $\text{Ca}_2\text{P}_2\text{O}_7$ precipitation. The peaks at 2θ of 26.47° and 39.49° were

442 attributed to CaO. The adsorption peak of CaCO_3 was appeared at 2θ of 43.14° . The
 443 appearance of peaks at 2θ of 33.24° , 35.73° and 54.21° identified the existence of
 444 Fe_2O_3 . The reason for the existence of the above metal oxides in the XRD pattern of
 445 CR-LDH after adsorption of phosphate was due to that the raw material of carbide
 446 slag was industrial waste and the metal oxide didn't fully react during the preparation
 447 process of CR-LDH.

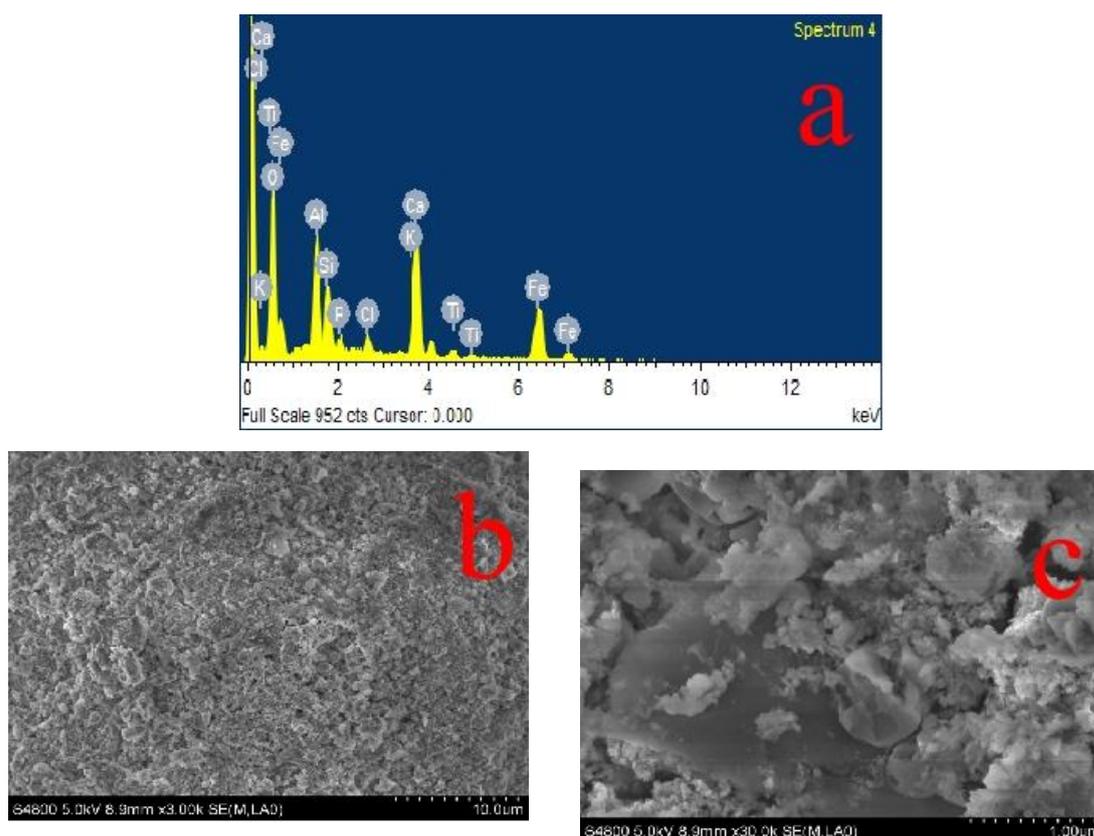


448

449 Fig. 8 XRD pattern of CR-LDH and after adsorption of phosphate.

450 According to the EDS results (Fig. 9a and Table 1), non-metallic P element was
 451 appeared in CR-LDH after adsorption of phosphate, indicating that the surface of the
 452 CR-LDH composite could adsorb phosphate by surface adsorption, surface
 453 complexation, electrostatic attraction and chemical precipitation. The SEM images of
 454 CR-LDH after adsorption of phosphate (Fig. 9b and Fig. 9c) exhibited a relatively flat,

455 irregular block morphology and the surface gap of CR-LDH was filled, leading to the
456 increase in the specific surface area which was conducive for the adsorption process.
457 During the adsorption process, the free metal cations might be combined with PO_4^{3-}
458 and hydroxyl groups to form phosphate or other metal oxides and then deposited on
459 the surface of the adsorbent. e



460 Fig. 9 EDS of CR-LDH after adsorption of phosphate (a) and SEM of CR-LDH after
461 adsorption of phosphate (b and c).

462 Based on the adsorption experimental results and characterization analysis, we
463 could infer that the adsorption of phosphate by CR-LDH might be through the
464 following four interactions: (1) physical adsorption; The strength of physical
465 adsorption mainly depends on the specific surface area and pore size distribution of
466 adsorbent. Generally, the larger the specific surface area of adsorbent, the higher the

467 adsorption capacity of physical adsorption. CR-LDH with surface area of $42.46 \text{ m}^2 \cdot \text{g}^{-1}$
468 had a lamellar structure due to the large number of gaps on the surface and the
469 relatively rough surface (Fig. 2), providing a great quantity of active adsorption sites
470 for the adsorption of phosphate. Thus, part of phosphate could be adsorbed on the
471 surface of CR-LDH by van der Waals force of physical adsorption. (2) ion exchange;
472 The exchangeability of interlayer anions is one of the important properties of LDHs.
473 Some anions in the aqueous solution will enter the material ion layer, while the anions
474 originally in the ion layer will transfer to the aqueous solution. The interlayer anions
475 in the layered structure of CR-LDH in solution might be replaced by anions with
476 stronger exchange performance to achieve partial adsorption of phosphate. (3) anion
477 intercalation; Since CR-LDH laminates are positively charged, the anions in the
478 solution will enter the layers of CR-LDH to balance the structure and electrical
479 properties of the laminates, so anion intercalation plays an important role in the
480 process of phosphate removed by CR-LDH. This inference was consistent with XRD
481 results that the intensity of the hydrocalumite diffraction peak was decreased after the
482 adsorption of phosphate, the characteristic diffraction peak of magnesia was
483 disappeared, and the diffraction peak of $\text{Ca}_2\text{P}_2\text{O}_7$ was appears, indicating that part of
484 phosphate entered into the interlayer structure of CR-LDH. The phosphate on the
485 surface of CR-LDH would form phosphorus-containing precipitate with dissolved
486 Mg^{2+} and Ca^{2+} . (4) chemical precipitation. The free metal cations (Ca^{2+} , Al^{3+} , Fe^{3+} , etc)
487 produced by CR-LDH would be combined with phosphate to form various
488 precipitates and then deposited on the surface of adsorbent, leading to the flat surface

489 of CR-LDH after adsorption of phosphate (Fig. 9b). The appearance of $\text{Ca}_2\text{P}_2\text{O}_7$ in the
490 XRD pattern of CR-LDH after adsorption of phosphate suggested that Ca^{2+} dissolved
491 from CR-LDH was combined with HPO_4^{2-} to form CaHPO_4 and then polymerize,
492 dehydrated to obtain $\text{Ca}_2\text{P}_2\text{O}_7$ precipitate (Fig. 8). The detection of P element in the
493 EDS of CR-LDH after adsorption of phosphate also indicated that chemical
494 precipitation was occurred in the process of phosphate adsorbed by
495 CR-LDH (Fig. 9a).

496 **4. Conclusion**

497 In this study, adsorbent of CR-LDH were successfully designed via a simple
498 method by using calcium carbide slag and red mud as raw materials. Characterization
499 results showed that the synthesized CR-LDH had typical properties of LDH. The
500 experimental data of phosphate adsorbed by CR-LDH could be well fitted by
501 pseudosecond-order model and Langmuir isotherm model with theoretical maximum
502 adsorption capacity of $16.06 \text{ mg}\cdot\text{g}^{-1}$ at $25 \text{ }^\circ\text{C}$, suggesting that it's a chemical and
503 monolayer adsorption process. Based on the adsorption experimental results and
504 characterization analysis, the adsorption of phosphate by CR-LDH was assumed to be
505 through physical adsorption, ion exchange, anion intercalation and chemical
506 precipitation. In brief, the CR-LDH prepared from calcium carbide slag and red mud
507 was a effective adsorbent for treating practical phosphate-containing wastewater,
508 which is helpful for the reuse of industrial waste resources, the reduction of
509 environmental pollutants of phosphate and the protection of the environment.

510 **Ethics approval and consent to participate**

511 Not applicable.

512 **Consent for publication**

513 Not applicable.

514 **Authors Contributions**

515 Liping Xiao: Resources, Methodology, Investigation, Supervision, Conceptualization,

516 Project administration, Writing - review & editing. Yan Li: Methodology,

517 Investigation, Resources, Writing - review & editing. Qiaoping Kong: Writing -

518 original draft, Writing - review & editing, Methodology, Investigation, Resources.

519 Yunlong Lan: review & editing.

520 **Availability of data and materials**

521 Not applicable.

522 **Competing Interest**

523 The authors declare that they have no known competing financial interests or personal

524 relationships that could have appeared to influence the work reported in this paper.

525 **Acknowledgments**

526 This work was supported by the National Natural Science Foundation of China (NO.

527 51474122 and NO. 51174267) and the Key projects of scientific research fund of

528 Liaoning Provincial Department of Education (NO. ZL002)

529

530 **References:**

531 Bacelo, H., Pintor, A.M.A., Santos, S.C.R., Boaventura, R.A.R., Botelho, C.M.S., 2020.

532 Performance and prospects of different adsorbents for phosphorus uptake and recovery

533 from water. *CHEMICAL ENGINEERING JOURNAL*, 381, 122566.

534 Cao, H., Wu, X., Syed-Hassan, S.S.A., Zhang, S., Mood, S.H., Milan, Y.J.,
535 Garcia-Perez, M., 2020. Characteristics and mechanisms of phosphorous adsorption by
536 rape straw-derived biochar functionalized with calcium from eggshell.
537 *BIORESOURCE TECHNOLOGY*, 318.

538 Cheng, S., Shao, L., Ma, J., Xia, X., Liu, Y., Yang, Z., Yang, C., Li, S., 2019.
539 Simultaneous removal of phosphates and dyes by Al-doped iron oxide decorated MgAl
540 layered double hydroxide nanoflakes. *ENVIRONMENTAL SCIENCE. NANO*, 6,
541 2615-2625.

542 Cheng, X., Huang, X., Wang, X., Sun, D., 2010. Influence of calcination on the
543 adsorptive removal of phosphate by Zn-Al layered double hydroxides from excess
544 sludge liquor. *JOURNAL OF HAZARDOUS MATERIALS*, 177, 516-523.

545 Cheng, X., Huang, X., Wang, X., Zhao, B., Chen, A., Sun, D., 2009. Phosphate
546 adsorption from sewage sludge filtrate using zinc-aluminum layered double hydroxides.
547 *JOURNAL OF HAZARDOUS MATERIALS*, 169, 958-964.

548 Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2005.
549 Adsorption of phosphate from seawater on calcined MgMn-layered double hydroxides.
550 *JOURNAL OF COLLOID AND INTERFACE SCIENCE*, 290, 45-51.

551 Dox, K., Pareijn, R., Everaert, M., Smolders, E., 2019. Phosphorus recycling from
552 urine using layered double hydroxides: A kinetic study. *APPLIED CLAY SCIENCE*,
553 182, 105255.

554 Guo, Z., Li, J., Guo, Z., Guo, Q., Zhu, B., 2017. Phosphorus removal from aqueous

555 solution in parent and aluminum-modified eggshells: thermodynamics and kinetics,
556 adsorption mechanism, and diffusion process. *ENVIRONMENTAL SCIENCE AND*
557 *POLLUTION RESEARCH*, 24, 14525-14536.

558 Hu, P., Zhang, Y., Lv, F., Tong, W., Xin, H., Meng, Z., Wang, X., Chu, P.K., 2017.
559 Preparation of layered double hydroxides using boron mud and red mud industrial
560 wastes and adsorption mechanism to phosphate. *WATER AND ENVIRONMENT*
561 *JOURNAL : WEJ*, 31, 145-157.

562 Jia, Z., Hao, S., Lu, X., 2018. Exfoliated Mg-Al-Fe layered double
563 hydroxides/polyether sulfone mixed matrix membranes for adsorption of phosphate
564 and fluoride from aqueous solutions. *JOURNAL OF ENVIRONMENTAL SCIENCES*,
565 70, 63-73.

566 Jiang, Y., Chen, Y., Du, Q., Shi, J., 2019. Adsorption of different forms of phosphorus
567 on modified corn bracts. *WATER ENVIRONMENT RESEARCH*, 91, 748-755.

568 Jiang, Y., Li, A., Deng, H., Ye, C., Li, Y., 2019. Phosphate adsorption from wastewater
569 using ZnAl-LDO-loaded modified banana straw biochar. *ENVIRONMENTAL*
570 *SCIENCE AND POLLUTION RESEARCH*, 26, 18343-18353.

571 Kong, Q., Preis, S., Li, L., Luo, P., Hu, Y., Wei, C., 2020. Graphene oxide-terminated
572 hyperbranched amino polymer-carboxymethyl cellulose ternary nanocomposite for
573 efficient removal of heavy metals from aqueous solutions. *INTERNATIONAL*
574 *JOURNAL OF BIOLOGICAL MACROMOLECULES*, 149, 581-592.

575 Kong, Q., Shi, X., Ma, W., Zhang, F., Yu, T., Zhao, F., Zhao, D., Wei, C., 2021.
576 Strategies to improve the adsorption properties of graphene-based adsorbent towards

577 heavy metal ions and their compound pollutants: A review. *JOURNAL OF*
578 *HAZARDOUS MATERIALS*, 415, 125690-125690.

579 Kong, Q., Wei, J., Hu, Y., Wei, C., 2019. Fabrication of terminal amino hyperbranched
580 polymer modified graphene oxide and its prominent adsorption performance towards
581 Cr(VI). *JOURNAL OF HAZARDOUS MATERIALS*, 363, 161-169.

582 Kuzawa, K., Jung, Y., Kiso, Y., Yamada, T., Nagai, M., Lee, T., 2006. Phosphate
583 removal and recovery with a synthetic hydrotalcite as an adsorbent. *CHEMOSPHERE*,
584 62, 45-52.

585 Li, X., Xie, Q., Kuang, Y., Wu, D., 2021. Coupled influence of pH and dissolved
586 organic carbon on the immobilization of phosphorus by lanthanum-modified zeolite.
587 *CHEMOSPHERE*, 274.

588 Liu, C., Zhang, M., Pan, G., Lundehoj, L., Nielsen, U.G., Shi, Y., Hansen, H.C.B., 2019.
589 Phosphate capture by ultrathin MgAl layered double hydroxide nanoparticles.
590 *APPLIED CLAY SCIENCE*, 177, 82-90.

591 Razmi, B., Ghasemi-Fasaei, R., 2018. Investigation of Taguchi optimization,
592 equilibrium isotherms, and kinetic modeling for phosphorus adsorption onto natural
593 zeolite of clinoptilolite type. *ADSORPTION SCIENCE & TECHNOLOGY*, 36,
594 1470-1483.

595 Samaraweera, H., Sharp, A., Edwards, J., Jr. Pittman, C.U., Zhang, X., Hassan, E.B.,
596 Thirumalai, R.V.K.G., Warren, S., Reid, C., Mlsna, T., 2021. Lignite,
597 thermally-modified and Ca/Mg-modified lignite for phosphate remediation. *SCIENCE*
598 *OF THE TOTAL ENVIRONMENT*, 773.

599 Seftel, E.M., Ciocarlan, R.G., Michielsen, B., Meynen, V., Mullens, S., Cool, P., 2018.
600 Insights into phosphate adsorption behavior on structurally modified ZnAl layered
601 double hydroxides. *APPLIED CLAY SCIENCE*, 165, 234-246.

602 Tie, J., Chen, D., Wan, Y., Yan, C., Zhang, X., 2013. Adsorption removal of phosphorus
603 from aqueous solution by heat-activated alum sludge. *ASIAN JOURNAL OF*
604 *CHEMISTRY*, 25, 9129-9134.

605 Wang, Z., Miao, R., Ning, P., He, L., Guan, Q., 2021. From wastes to functions: A paper
606 mill sludge-based calcium-containing porous biochar adsorbent for phosphorus
607 removal. *JOURNAL OF COLLOID AND INTERFACE SCIENCE*, 593, 434-446.

608 Yang, F., Zhang, S., Sun, Y., Tsang, D.C.W., Cheng, K., Ok, Y.S., 2019. Assembling
609 biochar with various layered double hydroxides for enhancement of phosphorus
610 recovery. *JOURNAL OF HAZARDOUS MATERIALS*, 365, 665-673.

611 Yang, K., Yan, L., Yang, Y., Yu, S., Shan, R., Yu, H., Zhu, B., Du, B., 2014. Adsorptive
612 removal of phosphate by Mg-Al and Zn-Al layered double hydroxides: Kinetics,
613 isotherms and mechanisms. *SEPARATION AND PURIFICATION TECHNOLOGY*, 124,
614 36-42.

615 Zhang, J., Xia, Q., Hong, X., Chen, J., Liu, D., 2021. Synthesis of layered double
616 hydroxides with nitrate and its adsorption properties of phosphate. *WATER SCIENCE*
617 *AND TECHNOLOGY*, 83, 100-110.

618 Zhang, Z., Yan, L., Yu, H., Yan, T., Li, X., 2019. Adsorption of phosphate from aqueous
619 solution by vegetable biochar/layered double oxides: Fast removal and mechanistic
620 studies. *BIORESOURCE TECHNOLOGY*, 284, 65-71.

621 Zhu, D., Yang, H., Chen, X., Chen, W., Cai, N., Chen, Y., Zhang, S., Chen, H., 2021.
622 Temperature-dependent magnesium citrate modified formation of MgO nanoparticles
623 biochar composites with efficient phosphate removal. *CHEMOSPHERE*, 274.
624

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterial.docx](#)