Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2021

Supporting information

Highly regenerative and efficient adsorption of phosphate by restructuring natural palygorskite clay via alkaline activation and co-calcination

Yanfu Wei^{*a}, Kexin Guo^a, Honghai Wu^{*a}, Peng Yuan^b, Dong Liu^b, Peixin Du^b,

Pengcheng Chen^c, Longmeng Wei^c, and Wei Chen^d

^a Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental

Safety & MOE Key Laboratory of Theoretical Chemistry of Environment, School of

Environment, South China Normal University, Guangzhou 510006, China.

^b CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key

Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry,

Chinese Academy of Sciences (CAS), Guangzhou 510640, China

^c School of Environmental Science and Engineering, Analysis and Test Center,

Guangdong University of Technology, Guangzhou 510006, China.

^d Chongqing Key Laboratory of Environmental Materials & Remediation

Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, China

E-mail address: yanfuwei@m.scnu.edu.cn (Yanfu Wei), wuhonghai@scnu.edu.cn

(Honghai, Wu)

03 March 2021

Note added after first publication:

This Supplementary Information file replaces that originally published on 08 Jan 2021. The incorrect TEM image of the LO nanoparticles was previously given in figure S11. This has now been updated with the correct version of figure S11.

Materials and methods	3
Chemicals	3
Synthesis of LO-Pal	3
Adsorbent regeneration test	3
Batch adsorption experiments	4
Phosphate removal from sewage effluent	5
Characterization	5
Supplementary Results	6
Analysis of porosity of LO-Pal sample	6
Analysis of proportions of phosphate in different states in LO-Pal	7
Discussion of the efficiency and energy-saving of the LO-Pal regeneration	7
Supplementary Fig.s	9
Fig. S1	9
Fig. S2	9
Fig. S3	10
Fig. S4	
Fig. S5	11
Fig. S6	
Fig. S8	13
Fig. S9	13
Fig. S10	15
Fig. S11	15
Supplementary Tables	16
Table S1	
Table S2	
Table S3	21
Table S4	21

Table of contents

Materials and methods

Chemicals

The sample of pristine Pal originated from Mingguang, Anhui province, China, and was treated by grinding and sieving through a 200-mesh sieve. The mass composition of the Pal sample is listed in Table S1. Lanthanum nitrate hydrate (99.9%) was obtained from Macklin Inc. (Shanghai, China), and glycine (99.9%) and KH₂PO₄ (99%) were purchased from Damao Chemical Co. (Tianjin, China). These chemicals were used as received without further purification. Deionized water was used in the phosphate adsorption tests unless otherwise specified.

Synthesis of LO-Pal

In a typical procedure, defined amounts of La(NO₃)₃· $6H_2O$ and C₂H₅NO₂ were added to a 50 mL beaker, dissolved in deionized water, and sonicated for 15 min. To this mixture was added the ground and sieved Pal in a Pal/La mass ratio of 1:0.45, which was previously found to be the optimal ratio during our synthesis of an LO–clay phosphate adsorbent *via* co-calcination ¹. The resulting mixture was further dispersed *via* sonication for 30 min, and the obtained suspension was heated in an oven (130°C) for 5 h. The dry sample was then further calcined in a furnace (450°C) for 2 h. LO nanoparticles are produced according to the following glycine–nitrate combustion reaction:

 $6La(NO_3)_3 \cdot 6H_2O + 10C_2H_5NO_2 \rightarrow 3La_2O_2CO_3 + 17CO_2 + 14N_2 + 31H_2O$ (1) After cooling, the sample was ground and sieved through a 200-mesh screen to obtain the final composites composed of LO nanoparticles anchored to the Pal surface. For the purposes of comparison, samples of Pal calcined at 450°C and pure LO without Pal addition were also prepared under the same synthetic conditions used to obtain LO-Pal.

Adsorbent regeneration test

The regeneration of LO-Pal (4 g·L⁻¹) was evaluated by mixing the adsorbent with KH₂PO₄ solution (100 mg P·L⁻¹) for 24 h. The adsorbent was then centrifuged (4,000 rpm, 10 min) and the obtained solid was washed three times in 6 M NaOH solution (100 mL) for 24 h each time to remove the adsorbed phosphate. The sample was then centrifuged (4,000 rpm, 10 min), washed with deionized water until a pH value of 7.0 was attained, and dried at 65°C for 1 d. The recycled LO-Pal was then used in the subsequent cycle of phosphate capture.

Batch adsorption experiments

For the batch phosphate-removal experiments, LO-Pal (10 mg) and KH₂PO₄ solution (20 mL) were mixed in a 50 mL centrifuge tube, which was then placed on a shaker operating at 150 rpm at 25°C. The adsorption kinetics of LO-Pal were investigated over adsorption times ranging from 20 min to 48 h using a phosphate solution with a concentration of 200 mg P·L⁻¹. To evaluate the adsorption performances of LO-Pal, pristine Pal, Pal calcined at 450°C, and pure LO, the phosphate adsorption isotherms were measured using various phosphate concentrations. The adsorption isotherm samples were placed on a rotary shaker at 150 rpm and 25°C for 1 d. A solution pH of 5.0 ± 0.1 was used in the kinetic and adsorption isotherm experiments.

To examine the influence of pH on phosphate capture, LO-Pal (0.5 g·L⁻¹) was mixed with KH₂PO₄ solution (300 mg P·L⁻¹, 20 mL). The pH value of the original solution was adjusted to between 2.0 and 11.0 *via* the addition of NaOH or HCl solution. The influence of potential interferences, *i.e.* organic matter and inorganic species, on the phosphate removal was investigated by separately adding Cl⁻, NO₃⁻, HCO₃⁻, or SO₄²⁻ (1 and 10 mM) and fulvic acid or humic acid (1 and 10 mg·L⁻¹) to the samples. The phosphate adsorption performance was also evaluated for various LO-Pal dosages of 0.025–1.0 g·L⁻¹. In addition, the leaching of La³⁺ and Al³⁺ from LO-Pal was examined using inductively coupled plasma mass spectrometry.

After phosphate removal, all samples were centrifuged (8,000 rpm, 5 min) and the supernatants were then passed through 0.22 μ m filter membranes and diluted prior to measuring the phosphate concentration *via* the molybdenum blue/ascorbic acid method on a UV spectrophotometer at 680 nm². All experiments were performed in duplicate. To assess the adsorption performance of LO-Pal, the removal capacity (*q*), *i.e.* the amount of phosphate adsorbed per unit mass of adsorbent, was calculated using the following equation:

$$q = (C_{\rm i} - C_{\rm e}) \times V/M \quad (2)$$

where *q* denotes the phosphate removal capacity (mg $P \cdot g^{-1}$), C_i is the initial phosphate concentration (mg $P \cdot L^{-1}$), C_e is the equilibrium phosphate concentration (mg $P \cdot L^{-1}$), *M* is the adsorbent mass (g), and *V* is the solution volume (L).

The kinetic data for the removal of phosphate from aqueous solutions were fitted using the following pseudo-second-order kinetic model:

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

where k_2 denotes the removal rate constant of the pseudo-second-order model $(g \cdot mg^{-1} \cdot min^{-1})$, q_t is the amount of phosphate removal at time t (h) (mg P \cdot g^{-1}), and q_e is the phosphate removal capacity at dynamic equilibrium (mg P \cdot g^{-1}).

The maximum removal capacity is the most important index for evaluating adsorption, where a higher maximum value indicates more efficient phosphate adsorption. The Langmuir model was used to fit the phosphate adsorption isotherm to obtain the maximum phosphate removal capacity:

$$\frac{c_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm m} \times K_{\rm L}} + \frac{c_{\rm e}}{q_{m}} \quad (4)$$

where C_e denotes the equilibrium phosphate concentration (mg P·L⁻¹), q_e denotes the corresponding phosphate removal capacity (mg P·g⁻¹), q_m is the fitted maximum adsorbed amount (mg P·g⁻¹), and K_L is the Langmuir constant (L·mg⁻¹).

Phosphate removal from sewage effluent

Sewage effluent from a subsurface flow constructed wetland on the campus of the Guangzhou Institute of Geochemistry, Guangzhou, China, was collected into a plastic bottle and stored in a refrigerator at 4°C. The phosphorus concentration in the effluent was 2.1 mg $P \cdot L^{-1}$. The adsorption effectiveness of LO-Pal for phosphate removal from the effluent was evaluated for various adsorbent dosages. After adsorption, the mixed solutions were centrifuged (8,000 rpm, 5 min), the resulting supernatants were passed through 0.22 µm filter membranes, and the residual phosphate concentrations after adsorption were measured.

Characterization

The crystalline phases present in LO-Pal and the control samples were determined via XRD on a Bruker D8 Advance diffractometer using Cu Ka radiation ($\lambda = 0.15406$ nm), an accelerating voltage of 40 kV, and a current of 40 mA. Spectra were recorded from 5° to 80° with a scan rate of 1° $2\theta \cdot \text{min}^{-1}$. The control samples included Pal, Pal calcined at 450°C, and pure LO. The mass and molar contents (including the elemental La content) of LO-Pal were determined using and XRF spectrometer (Thermo Scientific Niton XL3t-800). The morphology, structure, and elemental distribution of LO-Pal were examined via TEM (FEI Titan Themis 200) and EDS imaging at 200 kV. During the TEM test, we used ultrasound treatment to disperse 1 mg of LO-Pal or R-LO-Pal sample in 1 ml of water for 15 minutes to get the disaggregated hybrid. Then the sample was doped and deposited on 200-mesh copper TEM grids bearing carbon films. The morphology of the LO-Pal sample without dispersion was observed using a field emission scanning electron microscope (SEM, GEMINI300, ZEISS) after coated with a gold film. The TG-MS analyses were conducted from ambient temperature to 750 °C using a Thermo Mass Photo TG-DTA-PIMS 410/S (Rigaku Corporation, Tokyo, Japan). The intensity of gases released from the heating of LO-Pal were determined with pure N₂ at 300 mL/min. The mass detection range was 1-400 atomic mass unit. The N₂ adsorption/desorption isotherms of Pal, LO-Pal, and regenerated LO-Pal (R-LO-Pal) were measured using a Micromeritics ASAP-2000 nitrogen adsorption apparatus to determine

the specific surface area and PSD curves of the Pal-based adsorbents. The samples were mixed with KBr and prepared as discs. The various functional groups of the samples were characterized using FTIR spectroscopy (Bruker Vertex 70) from 4000 to 400 cm⁻¹ at room temperature using dry potassium bromide for background subtraction. The surface interactions between LO and Pal and between LO-Pal and phosphate were analysed *via* XPS (Thermo-VG Scientific, USA) using 300 W Al K α radiation. The particle size distribution of LO-Pal in water was determined using the Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire).

The R-LO-Pal after six cycles of adsorption was further characterized by XRD. The morphology, structure, and elemental distribution of R-LO-Pal and a phosphate-adsorbed R-LO-Pal sample (P@R-LO-Pal) were investigated via TEM (FEI Titan Themis 200) and EDS imaging at 200 kV. The surface interactions of R-LO-Pal and P@R-LO-Pal were analysed via XPS. Phosphorus K-edge XANES analysis of P@LO-Pal was conducted at beamline 4B7A of the Beijing Synchrotron Radiation Facility, China. Data were obtained in the fluorescence yield mode between -10 and +40 eV, relative to the P K-edge energy of 2,151 eV, with a step size of 0.2 eV. All of the XANES spectra were first subjected to baseline correction and normalization using the ATHENA software ^{3,4}. The adsorbed phosphate contents of the LO, Fe₂O₃, MgO, and Al₂O₃ components in the P@LO-Pal sample were determined via LCF analysis. The saturated P@LO-Pal sample used for the XPS, FTIR, TEM, and XANES analysis was obtained by mixing LO-Pal (0.5 mg \cdot L⁻¹) with KH₂PO₄ (500 mg P \cdot L⁻¹) for 1 d at pH 5. Similarly, phosphate-adsorbed samples of LO (P@LO) and the metal oxides (P@Al₂O₃, P@Fe₂O₃, and P@MgO) were prepared by mixing the corresponding oxides (0.5 mg \cdot L⁻¹) with phosphate solution (500 mg P \cdot L⁻¹) for 1 d at pH 5, and these were used as reference samples in the LCF analysis.

Supplementary Results

Analysis of porosity of LO-Pal sample

The nitrogen adsorption/desorption isotherms of LO-Pal and pristine Pal (Fig. 1d) both indicated typical type-II isotherms with H3 hysteresis loops according to the International Union of Pure and Applied Chemistry classification. This suggests that both LO-Pal and pristine Pal contained a large proportion of mesopores. The Brunauer– Emmett–Teller (BET) specific surface area and total pore volume of LO-Pal (33.59 $m^2 \cdot g^{-1}$ and 0.09 cm³ · g⁻¹, respectively) were considerably lower than those of Pal (138.02 m² · g⁻¹ and 0.24 cm³ · g⁻¹, respectively), indicating that hybridizing with LO decreased the porosity of Pal. The pore size distribution (PSD) curves (inset of Fig. 1d) for Pal and LO-Pal revealed relatively broad pore populations centred at 2 and 10.2 nm, which were ascribed to the mesopores between layers of Pal. The decreased pore volume for LO-Pal indicated the coating of the La species the inner and outer surfaces of Pal.

Analysis of proportions of phosphate in different states in LO-Pal

The LCF results (Fig. 4) indicated that the amounts of P taken up by the LO nanoparticles and the other metal oxide (Fe₂O₃, Al₂O₃, and MgO) nanoparticles accounted for 72% and 28%, respectively, of the total P content in the P@LO-Pal sample. The XRF analysis indicated that the total amount of P in the phosphateadsorbed LO-Pal sample was 10.05 mol%. Therefore, on the basis of the combined LCF and XRF results, it can be concluded that the contents of P adsorbed to LO and the metal oxides were 7.236 and 2.814 mol%, respectively. The XRF data for P@LO-Pal revealed that the La content was 5.9 mol%, and thus the exchanged amount of $CO_3^{2^-}$ in LO was 2.95 mol%. Meanwhile, the CO_3^{2-} in LO was exchanged and replaced by two equivalents of the $H_2PO_4^-$ ion. Hence, 2.95 mol% of CO_3^{2-} could completely replace 5.9 mol% of H₂PO₄⁻. XPS and FTIR analysis of the P@LO-Pal sample indicated the occurrence of two phosphate adsorption processes by the LO nanoparticles, namely, the exchange of $H_2PO_4^-$ with CO_3^{2-} between the LO interlayers and surface complexation of phosphate *via* the La sites of the LO surface. Therefore, the surface-complexed P on LO was 1.336 mol%, as determined by subtracting the amount of exchanged P (5.9 mol%). In conclusion, the $CO_3^{2-}-H_2PO_4^{-}$ exchanged P, surface-complexed P with La, and the other metal (Al, Mg, and Fe) sites in LO-Pal accounted for 5.9, 1.336, and 2.814 mol%, respectively. The percentages of P adsorbed by CO_3^{2-} exchange and surface complexation with LO and the metal oxides (Fe₂O₃, Al₂O₃, and MgO) were thus 58.7%, 13.3%, and 28%, respectively.

Discussion of the efficiency and energy-saving of the LO-Pal regeneration

Alkali activation is the main method reported by decoupling the interaction between phosphate and metal oxide adsorbents. To recover phosphorus, 6 mol·L⁻¹ NaOH solution was used to desorb phosphate from the adsorbent surfaces. It usually takes time to break the strong chemical binding of phosphate and the adsorbent. La-based particles could react with phosphate to form LaPO₄^{5,6}. As shown in Table S4, the solubility product value (pK_{sp}) of lanthanum phosphate is lower than most of the metal phosphates^{7–10}, suggesting a high affinity of La-based adsorbent for phosphate.

The regenerated adsorbent was obtained by centrifugation for 5 minutes in the laboratory. But in engineering implementation, we could separate the regenerated adsorbent from the solution by way of natural sedimentation to save energy. As particles larger than 2 μ m in diameter settle in 3 h¹¹, most of the R-LO-Pal can be settled, thus avoiding much energy consumption. Because the volume fraction of LO-Pal particles larger than 2 μ m in diameter was 96.3% (Fig. S3), determined using the Mastersizer. The parameters of recovery time and energy efficiency will be further optimized in the pilot and scale-up system.

A solution of sodium hydroxide containing a high concentration of phosphate is obtained after adsorbent regeneration. This solution can be used as an industrial raw material for the preparation of sodium-phosphates (NaH₂PO₄, Na₂HPO₄, Na₃PO₄) by mixing with H₃PO₄ solution^{12,13}. It could be also used to prepare sodium trimetaphosphate (Na₃P₃O₉) and pyrophosphate (Na₄P₂O₇) for industrial applications^{14,15}. Therefore, the phosphate contained regenerated solutions can be should for producing fertilizers of sodium-phosphates and phosphorus contained chemicals, *i.e.*, Na₃P₃O₉ and Na₄P₂O₇.

Supplementary Fig.s



Fig. S1 EDS elemental mapping images of LO-Pal for La, Mg, Si, Fe, Al, and O.



Fig. S2 SEM image of LO-Pal without dispersion



Fig. S3 Particle size distribution of the LO-Pal sample



Fig. S4 TG and DTG curves of LO-Pal at a heating rate of 10°C/min, (b) Emissions of gases evolved from LO-Pal heating based on TG-MS experiments.



Fig. S5 TEM image of P@R-LO-Pal; the inset shows the selected-area electron diffraction pattern, revealing the amorphous nature of the regenerated Pal nanostructure following alkaline treatment.



Fig. S6 Nitrogen adsorption/desorption isotherms for the R-LO-Pal; the inset shows the corresponding PSD curves.

The nitrogen adsorption/desorption isotherms for R-LO-Pal showed that the Brunauer–Emmett–Teller specific surface area and total pore volume of R-LO-Pal (38.39 m²·g⁻¹ and 0.22 cm³·g⁻¹, respectively) were higher than those of LO-Pal (33.59 m²·g⁻¹ and 0.09 cm³·g⁻¹, respectively).



Fig. S7 (a) High-resolution Mg 1s XPS spectra of Pal, Pal calcined at 450°C, LO-Pal, P@LO-Pal, R-LO-Pal, and P@R-LO-Pal. (b) High-resolution Fe 2p XPS spectra of Pal, Pal calcined at 450°C, LO-Pal, P@LO-Pal, R-LO-Pal, and P@R-LO-Pal. (c) High-resolution Al 2p XPS spectra of Pal, Pal calcined at 450°C, LO-Pal, P@LO-Pal, R-LO-Pal, and P@R-LO-Pal. (d) High-resolution La 3d5/2 XPS spectra of LO, LO-Pal, P@LO-Pal, R-LO-Pal, R-LO-Pal, R-LO-Pal, and P@R-LO-Pal. In the panels, the solid lines represent the measured and fitted XPS spectra, respectively, and the values indicate the binding energies.

The phosphate adsorption performance of LO-Pal was further evaluated using a combination of spectroscopic methods to examine the underlying mechanism and possible synergistic interactions between the components of LO-Pal. XPS analysis of the LO-Pal and P@LO-Pal samples elucidated the phosphate adsorption mechanism via surface complexation. The XPS results for the LO-Pal sample (Figs. S3a and 3c) revealed two peaks in both the Mg 1s (1305 and 1303 eV) and Al 2p (75.9 and 73.8 eV) spectra. Among them, the peaks at 1303 eV and 73.8 eV indicated the presence of MgO¹⁶ and Al₂O₃,¹⁷ respectively. The Fe 2p satellite peaks at 726 and 712 eV shifted to lower binding energies (Fig. S7b), indicating structural transformation of the Fe in Pal. Thus, the XPS results for the LO-Pal sample indicated that heating of the mixed powder of Pal and the LO precursors at 450°C transformed the Pal structure and afforded Al₂O₃, MgO, and possibly Fe₂O₃. The Mg 1s spectrum of P@LO-Pal revealed shifts in the binding energies to 1304 and 1306 eV after phosphate adsorption (Fig. S7a), suggesting the occurrence of surface complexation between the MgO nanoparticles and P with the generation of Mg–O–P bonds. In addition, the Al 2p spectrum revealed shifts in the binding energies to 74.1 and 75.2 eV after phosphate adsorption (Fig. S7c), suggesting that surface complexation also occurred between the Al₂O₃ nanoparticles and P with the generation of Al-O-P bonds. Furthermore, the Fe 2p binding energies shifted to 725.5 and 711.5 eV in P@LO-Pal (Fig. S7b), indicating interactions between Fe₂O₃ nanoparticles and P with the formation of Fe–O–P bonds, which likely occurred at the Fe-containing surface of Pal. Finally, compared with the as-synthesized LO-Pal,

the peak La 3d^{5/2} binding energies of P@LO-Pal decreased to 839 and 836.3 eV (Fig. S7d), which indicates the formation of La–O–P bonds at the LO surface of LO-Pal upon phosphate adsorption.



Fig. S8 Zeta potential of the LO-Pal nanohybrid.



Fig. S9 FTIR spectra of Pal, LO-Pal, P@LO-Pal, LO, and P@LO. The values indicate the wavenumbers of the corresponding peaks.

The structural transformation of Pal upon LO coating was examined *via* FTIR spectroscopy. The FTIR spectrum of LO-Pal (Fig. S9) contained absorption bands at 1505 and 1380 cm⁻¹, which were attributed to vibrations of $CO_3^{2^-,1}$ indicating the successful loading of LO. Upon co-calcination, the intensities of the *v*(Al₂OH) bands (3614 and 912 cm⁻¹), *v*(AlFe³⁺OH) bands (3580 and 864 cm⁻¹), and *v*(Mg₃OH) band (646 cm⁻¹) of Pal decreased substantially owing to partial dihydroxylation.¹⁹ The intensities of the bands corresponding to Si–O–Si vibrations (1095 cm⁻¹) and mixed Al–O–Si and Si–O–Si vibrations (550–400 cm⁻¹) also decreased considerably. This suggested disconnection of the unit layer, including the Si–O tetrahedral and Mg–Al–Fe-rich octahedral layers, and the formation of a new amorphous phase.²⁰

FTIR spectroscopy was also applied to probe the functional group changes in LO-Pal after phosphate adsorption to saturation. As shown in Fig. S9, P@LO-Pal exhibited absorption bands at 614 and 540 cm⁻¹, corresponding to an O-P-O bending vibration, in addition to an absorption band at 1053 cm⁻¹, corresponding to a P-O stretching vibration.^{21,22} Simultaneously, the bands corresponding to CO_3^{2-} vibrations^{23,24} at 1505 and 1380 cm⁻¹ disappeared, indicating the complete exchange of the CO_3^{2-} groups in the $(La_2O_2^{2+})_n$ layers of LO by $H_2PO_4^{-1}$ ions, which is the dominant form of phosphate at pH 4.5.²⁵ The species formed in water from the exchanged CO_3^{2-} groups was further identified as the HCO₃⁻ anion. The HCO₃⁻ concentration exhibited a linear relationship with the initial phosphate concentration, suggesting that the CO_3^{2-} groups in the LO interlayer was exchanged with phosphate (Fig. S10). The spectrum of P@LO revealed that the intensities of the CO_3^{2-} vibrations only slightly decreased compared with LO. These results suggest that the CO_3^{2-} groups of LO only partially underwent CO_3^{2-} H₂PO₄⁻ exchange owing to aggregation of the LO particles (Fig. S11), which hindered the exchange process. However, as shown in the FTIR spectrum of P@LO-Pal, the uniform coating of LO nanoparticles in the pores and at the outer surfaces of Pal afforded a high rate of CO_3^{2-} -H₂PO₄⁻ exchange.



Fig. S10 Solution HCO₃⁻ concentration after phosphate adsorption and amount of adsorbed phosphate for various initial phosphate concentrations.



Fig. S11 TEM image of LO nanoparticles.

Supplementary Tables

wt%
wt/0
5.06
1.83
2.63
1.45
2.71
0.98
5.34
-
-
-
-
-

Table S1 XRF results for Pal, LO-Pal, P@LO-Pal, and R-LO-Pal, showing the molar fraction (mol%) and mass ratio (wt%) of each component.

Mn	0.06	0.23	0.05	0.10	0.01	0.03	-	-

Table S2 Reported adsorption rate constants (k_2) and fitted maximum phosphate adsorption capacities (Q_m) of phosphate adsorbents obtained using the pseudo-second-order model and Langmuir model, respectively. The adsorbent doses used for phosphate removal from sewage are also listed where available.

Adsorbent material	k_2 (g·mg ⁻¹ ·min ⁻¹)	$q_m (\mathrm{mg} \ \mathrm{P} \cdot \mathrm{g}^{-1})$	Efficiency after recycling (%)	$Dose^{a} (g \cdot L^{-1})$	Ref.
MgO/magnetic biochar	0.016	149.25	-	-	26
Nitrogen doped char	-	63	-		27
La(OH) ₃ nanospheres	8.50×10^{-4}	54.2	98	-	10
Fe ₂ O ₃ /g-C ₃ N ₄	0.26	52.5	83	0.1	28
Humic acid/magnetite	0.20	28.9	-	-	29
Fe ₃ O ₄ /ZnO	0.007	100.3		0.1	30
La/MOF/500	-	173.8	85.9	-	31
MPVC/EDA/Ce	0.39	18.2	-	-	32
Mg/Al/Cl/LDH	0.003	76.1	-	-	33
La/KIT-6	0.004	22.76	-	-	34
Fe/zeolite A	-	3.90	90	-	35
Biochar/LDO	0.27	132.8	6.7	-	36
MgAl-LDH	0.01	98	-	-	37
La@Fe/C	0.06	32.36	58.33		38
APANF/Fe ₂ O ₃	0.005	6.339	-	-	39
La vesuvianite	-	6.703	-	-	40
Zr chitosan/bentonite	0.19	65.35	-	-	41
Mg-Al LDH	-	100.7	-	-	42
Fe ₃ O ₄ /SiO ₂ /mCeO ₂	0.03	64.07	-	-	43
La(OH) ₃ palygorskite	0.19	99.01	90	-	44
Fe ₃ O ₄ /ZrO ₂	-	69.44	71	1	45

Mg alginate biochar	0.01	27.63	-	-	46
CFC800	0.37	70.9	-	-	47
Mag/Fh-La	-	44.8	95	0.2	48
La(OH) ₃ /Fe ₃ O ₄	0.22	83.5	70	0.1	22
Fe/EDA/SAMMS	-	43.3	-	-	49
La/MOSF	0.007	70.525	-	-	50
Zr mesostructure	0.00874	114	-	-	51
Zr loaded apple peels	0.0018	20.35	-	-	52
Magnetite/lanthanum hydroxide	0.28	52.7	-	-	53
ZrO ₂ /Fe ₃ O ₄	1.75	15.98	82.8	-	54
La Aerosil microspheres	1.21	71.83	-	-	55
Iron/MnO ₂	0.36	112.36	96	0.5	56
La coated graphene	0.18	82.6	-	-	57
Iron oxide	0.02	18.6	-	-	58
La ₂ O ₃	-	46.95	-	-	59
CuFe ₂ O ₄	0.004	32.59	-	-	60
La coatedzeolites	-	58.2	-	-	61
MCH/La(OH) ₃ /EW	0.1	90.2	74		25
La fibers	0.13	7.2	-	-	62
UiO-66	0.21	415	Almost 100	0.1	63
NH ₂ -MIL-101 MOFs	0.74×10^{-3}	94.33	80	-	64
La(OH) ₃ /zeolite	-	71.94	95	-	65
La/SiO ₂	-	23.1	75	-	66
La/carbon fiber	-	15.3	89	-	67

La/porous carbon	0.0009	30.87	-	-	68
Attapulgite	0.10	5.99	-	-	69
Phoslock	0.014	10.19	-	-	70
NT25-La	1.05	14.0	-	-	71
HZO-201	0.07	46.07	-	-	72
Fe/diatomite	-	37.3	-	-	73
Porous Pr(OH) ₃	-	128.96	-	-	74
La/tourmaline	0.05	108.7		-	75
La/silica	0.60	47.9	97.3	-	76
Lanthanum silica spheres	-	44.72	-	-	77
La(OH) ₃ nanofibers	0.002	154.40	-	-	78
Hydrated aluminium oxide/zeolite	0.6	7.0	-	-	79
HZO-201	7.96	18.0	-	-	80
La(III)-loaded silica/chitosan	0.008	84.2	92.6		81
Hydrous zirconium oxide coated wheat straw	-	31.9	89.4	-	82
Goethite/graphene	0.50	588	-	-	83
g-Fe ₂ O ₃ /g-FeOOH	-	143.4	-	-	84
Fe ₃ O ₄ @SiO ₂	-	27.8	82.4	0.2	85
La-201	0.02	113.64	95	-	86
Fe–La magnetic silica	0.002	71.99	90	-	87
Magnetic diatomite	0.25	11.89	96.8	-	88
LO-Pal	2.88	126.5	112 ^b		Present study

^aAdsorbent dose for almost complete removal of phosphate from actual wastewater.

^b The phosphate removal capacity of R-LO-Pal after six cycles was 1.12 times that of pristine LO-Pal.

Sample	Pseudo-second-order kinetic model			Laı	ngmuir mod	lel
	k_2 (g·mg ⁻¹ ·min ⁻¹)	$q_{ m m} \ ({ m mg} \ { m P} \cdot { m g}^{-1})$	R^{2} (%)	$\frac{K_{\rm L}}{(\rm L} \cdot \rm mg^{-1})$	$q_m (\mathrm{mg} \ \mathrm{P} \cdot \mathrm{g}^{-1})$	R^{2} (%)
LO-Pal	2.88	108.6	99.99	0.025	126.5	99.95

Table S3 Fitting parameters for phosphate adsorption by the LO-Pal nanohybrid.

Table S4 pK_{sp} values of metal phosphates.

Metal	LaPO ₄	$Mg_3(PO_4)_2$	MgHPO ₄	CaHPO ₄	$Ca_3(PO_4)_2$	AlPO ₄ ·2H ₂ O	Ag ₃ PO ₄	FePO ₄ ·2H ₂ O
phosphates								
pK _{sp}	26.15	25.20	5.82	6.90	28.68	21.00	16.05	15.00

Supplementary references

- 1 Y. Wei, P. Yuan, D. Liu, D. Losic, D. Tan, F. Chen, H. Liu, J. Zhou, P. Du and Y. Song, *Chem. Commun.*, 2019, **55**, 2110–2113.
- 2 A. El-Ghamry, A. Mosa and E. El-Naggar, Acta Agronomica Hungarica, 2009, 57, 363–370.
- 3 B. Ravel and M. Newville, J Synchrotron Rad, J Synchrotron Radiat, 2005, 12, 537–541.
- 4 M. Newville, Journal of Synchrotron Radiation, 2001, 8, 322–4.
- 5 L. Dithmer, A. S. Lipton, K. Reitzel, T. E. Warner, D. Lundberg and U. G. Nielsen, *Environmental Science & Technology*, 2015, **49**, 4559–4566.
- 6 Y. Zhang, M. Wang, X. Gao, J. Qian and B. Pan, Environ. Sci. Technol., , DOI:10.1021/acs.est.0c05577.
- 7 Y.-J. Shih, H.-C. Chang and Y.-H. Huang, *Journal of the Taiwan Institute of Chemical Engineers*, 2016, **62**, 177–186.
- 8 Y. Bashan, A. A. Kamnev and L. E. de-Bashan, Biol Fertil Soils, 2013, 49, 465–479.
- 9 B. Wu, J. Wan, Y. Zhang, B.-C. Pan and I. M. C. Lo, Environ. Sci. Technol., , DOI:10.1021/acs.est.9b05569.
- 10 L. Chen, Y. Li, Y. Sun, Y. Chen and J. Qian, Chemical Engineering Journal, 2019, 360, 342-348.
- 11 P. Yang, X. Hu, F. Zi, B. Yang, Q. Wang, Y. Chen and S. Chen, *Minerals Engineering*, 2020, 155, 106444.
- 12 K. V. Yatish, H. S. Lalithamba, R. Suresh and G. N. Dayananda, Sustainable Energy & Fuels, 2018, 2, 1299– 1304.
- 13 L. V. Soboleva and A. É. Voloshin, Crystallogr. Rep., 2002, 47, 871-878.
- 14 F. Vasconcelos, S. Cristol, J.-F. Paul, G. Tricot, J.-P. Amoureux, L. Montagne, F. Mauri and L. Delevoye, *Inorg. Chem.*, 2008, **47**, 7327–7337.
- 15 Li Longyan, Zhong Benhe, Xu Haiquan, Fang Weimao, and Ou Qingzhu, Inorganic Chemicals Industry.
- 16 S. A. Khromova, A. A. Smirnov, S. A. Selishcheva, R. G. Kukushkin, V. O. Dundich, L. I. Trusov and V. A. Yakovlev, *Catal. Ind.*, 2013, 5, 260–268.
- 17 L. Li, W. Kang, Y. Zhao, Y. Li, J. Shi and B. Cheng, Ceramics International, 2015, 41, 409–415.
- 18 S. Li, T. Lei, F. Jiang, M. Liu, Y. Wang, S. Wang and X. Yang, *Journal of Colloid and Interface Science*, 2020, 560, 321–329.
- 19 J. Madejová, W. P. Gates and S. Petit, in *Developments in Clay Science*, eds. W. P. Gates, J. T. Kloprogge, J. Madejová and F. Bergaya, Elsevier, 2017, vol. 8, pp. 107–149.
- 20 J. L. Valentín, M. A. López-Manchado, A. Rodríguez, P. Posadas and L. Ibarra, *Applied Clay Science*, 2007, **36**, 245–255.

- 21 Z. Wang, D. Shen, F. Shen and T. Li, Chemosphere, 2016, 150, 1-7.
- 22 B. Wu, L. Fang, J. D. Fortner, X. Guan and I. M. C. Lo, Water Research, 2017, 126, 179–188.
- 23 L. M. Cornaglia, J. Múnera, S. Irusta and E. A. Lombardo, Applied Catalysis A: General, 2004, 263, 91–101.
- 24 P. Fleming, R. A. Farrell, J. D. Holmes and M. A. Morris, *Journal of the American Ceramic Society*, 2010, **93**, 1187–1194.
- 25 S. Dong, Y. Wang, Y. Zhao, X. Zhou and H. Zheng, Water Research, 2017, 126, 433–441.
- 26 J. Liu, J. Jiang, A. Aihemaiti, Y. Meng, M. Yang, Y. Xu, Y. Gao, Q. Zou and X. Chen, *Journal of Environmental Management*, 2019, **250**, 109438.
- 27 S. H. Mood, M. Ayiania, Y. Jefferson-Milan and M. Garcia-Perez, Chemosphere, 2020, 240, 124889.
- 28 E. Gamshadzehi, M. Nassiri and H. Ershadifar, *Colloids and Surfaces A: Physicochemical and Engineering* Aspects, 2019, **567**, 7–15.
- 29 M. Rashid, N. T. Price, M. Á. Gracia Pinilla and K. E. O'Shea, Water Research, 2017, 123, 353-360.
- 30 N. Li, Y. Tian, J. Zhao, W. Zhan, J. Du, L. Kong, J. Zhang and W. Zuo, *Chemical Engineering Journal*, 2018, 341, 289–297.
- 31 X. Zhang, F. Sun, J. He, H. Xu, F. Cui and W. Wang, Chemical Engineering Journal, 2017, 326, 1086–1094.
- 32 T. Li, P. Huang, T. Liao, J. Guo, X. Yu, B. Han, L. Peng, Y. Zhu and Y. Zhang, *Environ Sci Pollut Res*, , DOI:10.1007/s11356-019-06351-z.
- 33 Q. Zhang, F. Ji, T. Zhao, Q. Shen, D. Fang, L. Kuang, L. Jiang and S. Ding, *Applied Clay Science*, 2019, 174, 159–169.
- 34 M. Gholami, M. H. Amin and J. Tardio, Microporous and Mesoporous Materials, 2019, 286, 77-83.
- 35 M. Saifuddin, J. Bae and K. S. Kim, Water Research, 2019, 158, 246-256.
- 36 Z. Zhang, L. Yan, H. Yu, T. Yan and X. Li, *Bioresource Technology*, 2019, 284, 65–71.
- 37 C. Liu, M. Zhang, G. Pan, L. Lundehøj, U. G. Nielsen, Y. Shi and H. C. B. Hansen, *Applied Clay Science*, 2019, 177, 82–90.
- 38 P. Wang, A. Armutlulu, W. Jiang, B. Lai and R. Xie, RSC Adv., 2019, 9, 28312–28322.
- 39 Y. Jung, Y. G. Ko, T. Do, Y. Chun, U. S. Choi and C. H. Kim, *Journal of Hazardous Materials*, 2019, **378**, 120726.
- 40 H. Li, J. Ru, W. Yin, X. Liu, J. Wang and W. Zhang, Journal of Hazardous Materials, 2009, 168, 326–330.
- 41 J. Wang, Y. Liu, P. Hu and R. Huang, Environ. Prog. Sustain. Energy, 2018, 37, 267–275.
- 42 H. Yan, Q. Chen, J. Liu, Y. Feng and K. Shih, Water Research, 2018, 145, 721-730.
- 43 D. Hong, Z. Yanling, D. Qianlin, W. Junwen, Z. Kan, D. Guangyue, X. Xianmei and D. Chuanmin, *J. Rare Earths*, 2017, **35**, 984–994.
- 44 L. Kong, Y. Tian, N. Li, Y. Liu, J. Zhang, J. Zhang and W. Zuo, Applied Clay Science, 2018, 162, 507–517.
- 45 Z. Wang, M. Xing, W. Fang and D. Wu, Appl. Surf. Sci., 2016, 366, 67–77.
- 46 X. Cui, X. Dai, K. Y. Khan, T. Li, X. Yang and Z. He, Bioresour. Technol., 2016, 218, 1123–1132.
- 47 J.-H. Park, J. J. Wang, R. Xiao, B. Zhou, R. D. Delaune and D.-C. Seo, *Journal of Colloid and Interface Science*, 2018, **525**, 143–151.
- 48 H. Fu, Y. Yang, R. Zhu, J. Liu, M. Usman, Q. Chen and H. He, *Journal of Colloid and Interface Science*, 2018, **530**, 704–713.
- 49 W. Chouyyok, R. J. Wiacek, K. Pattamakomsan, T. Sangvanich, R. M. Grudzien, G. E. Fryxell and W. Yantasee, *Environmental Science & Technology*, 2010, **44**, 3073–3078.
- 50 J. Yang, P. Yuan, H.-Y. Chen, J. Zou, Z. Yuan and C. Yu, *Journal of Materials Chemistry*, 2012, **22**, 9983–9990.
- 51 N. Pitakteeratham, A. Hafuka, H. Satoh and Y. Watanabe, Water Research, 2013, 47, 3583–3590.
- 52 R. Mallampati and S. Valiyaveettil, Acs Applied Materials & Interfaces, 2013, 5, 4443–4449.
- 53 L. Fang, R. Liu, J. Li, C. Xu, L.-Z. Huang and D. Wang, Water Research, 2018, 130, 243–254.
- 54 L. Fang, B. Wu and I. M. C. Lo, Chemical Engineering Journal, 2017, 319, 258–267.
- 55 I. Emmanuelawati, J. Yang, J. Zhang, H. Zhang, L. Zhou and C. Yu, Nanoscale, 2013, 5, 6173–6180.
- 56 X. Ge, X. Y. Song, Y. Ma, H. J. Zhou, G. Z. Wang, H. M. Zhang, Y. X. Zhang, H. J. Zhao and P. K. Wong, *Journal of Materials Chemistry A*, 2016, 4, 14814–14826.
- 57 M. Chen, C. Huo, Y. Li and J. Wang, ACS Sustainable Chemistry & Engineering, 2016, 4, 1296–1302.
- 58 D. Cao, X. Jin, L. Gan, T. Wang and Z. Chen, *Chemosphere*, 2016, **159**, 23–31.
- 59 J. Xie, Y. Lin, C. Li, D. Wu and H. Kong, Powder Technology, 2015, 269, 351-357.
- 60 W. Gu, X. Li, M. Xing, W. Fang and D. Wu, Science of The Total Environment, 2018, 619–620, 42–48.

- 61 J. Goscianska, M. Ptaszkowska-Koniarz, M. Frankowski, M. Franus, R. Panek and W. Franus, *Journal of Colloid and Interface Science*, 2018, **513**, 72–81.
- 62 E. W. Shin, K. G. Karthikeyan and M. A. Tshabalala, Environ. Sci. Technol., 2005, 39, 6273-6279.
- 63 Y. Gu, D. Xie, Y. Ma, W. Qin, H. Zhang, G. Wang, Y. Zhang and H. Zhao, ACS Appl. Mater. Interfaces, , DOI:10.1021/acsami.7b10024.
- 64 R. Liu, L. Chi, X. Wang, Y. Wang, Y. Sui, T. Xie and H. Arandiyan, *Chemical Engineering Journal*, 2019, **357**, 159–168.
- 65 J. Xie, Z. Wang, D. Fang, C. Li and D. Wu, Journal of Colloid and Interface Science, 2014, 423, 13–19.
- 66 E. Ou, J. Zhou, S. Mao, J. Wang, F. Xia and L. Min, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2007, **308**, 47–53.
- 67 L. Zhang, Q. Zhou, J. Liu, N. Chang, L. Wan and J. Chen, Chemical Engineering Journal, 2012, 185, 160–167.
- 68 P. Koilraj and K. Sasaki, Chemical Engineering Journal, 2017, 317, 1059–1068.
- 69 H. Yin, X. Yan and X. Gu, Water Research, 2017, 115, 329–338.
- 70 F. Haghseresht, S. Wang and D. D. Do, Applied Clay Science, 2009, 46, 369–375.
- 71 V. Kuroki, G. E. Bosco, P. S. Fadini, A. A. Mozeto, A. R. Cestari and W. A. Carvalho, *Journal of Hazardous Materials*, 2014, **274**, 124–131.
- 72 B. Lin, M. Hua, Y. Y. Zhang, W. M. Zhang, L. Lv and B. C. Pan, Chemosphere, 2017, 166, 422–430.
- 73 W. H. Xiong and J. Peng, *Water Research*, 2008, **42**, 4869–4877.
- 74 J. Tang, J. Chen, W. Huang, D. Li, Y. Zhu, Y. Tong and Y. Zhang, *Chemical Engineering Journal*, 2014, **252**, 202–209.
- 75 G. Li, D. Chen, W. Zhao and X. Zhang, Journal of Environmental Chemical Engineering, 2015, 3, 515–522.
- 76 W. Huang, Y. Zhu, J. Tang, X. Yu, X. Wang, D. Li and Y. Zhang, *Journal of Materials Chemistry A*, 2014, **2**, 8839–8848.
- 77 W. Y. Huang, X. Yu, J. P. Tang, Y. Zhu, Y. M. Zhang and D. Li, *Microporous And Mesoporous Materials*, 2015, **217**, 225–232.
- 78 J. He, W. Wang, F. Sun, W. Shi, D. Qi, K. Wang, R. Shi, F. Cui, C. Wang and X. Chen, *ACS Nano*, 2015, **9**, 9292–9302.
- 79 D. Guaya, C. Valderrama, A. Farran, C. Armijos and J. L. Cortina, *Chemical Engineering Journal*, 2015, **271**, 204–213.
- 80 L. Chen, X. Zhao, B. Pan, W. Zhang, M. Hua, L. Lv and W. Zhang, *Journal of Hazardous Materials*, 2015, **284**, 35–42.
- 81 A. Sowmya and S. Meenakshi, Environmental Progress & Sustainable Energy, 2015, 34, 146–154.
- 82 H. Qiu, C. Liang, X. Zhang, M. Chen, Y. Zhao, T. Tao, Z. Xu and G. Liu, Acs Applied Materials & Interfaces, 2015, 7, 20835–20844.
- 83 D. N. H. Tran, S. Kabiri, L. Wang and D. Losic, Journal of Materials Chemistry A, 2015, 3, 6844-6852.
- 84 R. P. Kralchevska, R. Prucek, J. Kolařík, J. Tuček, L. Machala, J. Filip, V. K. Sharma and R. Zbořil, *Water Research*, 2016, **103**, 83–91.
- 85 L. Lai, Q. Xie, L. N. Chi, W. Gu and D. Y. Wu, Journal of Colloid and Interface Science, 2016, 465, 76-82.
- 86 Y. Zhang, B. Pan, C. Shan and X. Gao, *Environmental Science & Technology*, 2016, **50**, 1447–1454.
- 87 C. Wang, X. Zheng, F. Zhang, Y. Huang and J. Pan, RSC Advances, 2016, 6, 87808–87819.
- 88 J. Chen, L. G. Yan, H. Q. Yu, S. Li, L. L. Qin, G. Q. Liu, Y. F. Li and B. Du, *Chemical Engineering Journal*, 2016, **287**, 162–172.