Supporting Information for

Ethylenediamine modified ZnAlCu-LDO with high adsorption for phosphate

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Text S1

1.Calculation of adsorption capacity and removal rate. Adsorption capacity Q (mg P/g) and removal rate η were calculated using the following equations:

$$Q = (C_0 - C_e)\frac{v}{m} \quad (1)$$

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Where, C_0 and C_e (mg P/L) is the phosphate concentration in solution before adsorption and after adsorption, respectively; Q (mg P/g) is adsorption capacity of the adsorbent; v (mL) is the volume of solution; m (mg) is the mass of adsorbent; η (%) is removal rate.

2.Calculation of adsorption isotherms. Freundlich and Langmuir isotherm models were used to fit the experimental data.

Langmuir isotherm adsorption model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{(k_L q_{max})} \quad (3)$$

Freundlich isotherm adsorption model:

$$lnq_e = (\frac{1}{n})lnC_e + lnk_F \quad (4)$$

Where C_e (mg P/L) and q_e (mg P/g) represent the solution concentration and adsorption amount at adsorption equilibrium state; q_{max} (mg P/g) represents adsorption capacity of the adsorbent; k_L (L/mg) represents Langmuir adsorption constant; k_F (mg/[g·(mg/L)$^{1/n}$]) and **1/n** represent Freundlich adsorption constants, respectively.

3.Calculation of adsorption kinetics. Pseudo-first-order and pseudo-second-order kinetic models were used to characterize adsorption behaviors.

Pseudo-first-order dynamic model equation:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (5)$$

Pseudo-second-order dynamic model equations:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e (mg P/g) is the adsorption amount at equilibrium; q_t (mg P/g) is the adsorption amount at time t; k_1 (1/min) is the rate constant of pseudo-first-order kinetic model; k_2 (g/(mg·min)) is the rate constant of pseudo-second-order kinetic model.

4.Calculation of adsorption thermodynamics. Thermodynamic properties were determined using three thermodynamic data of entropy change (ΔS), enthalpy change (ΔH) and Gibbs free energy (ΔG). The calculation formula is as follows:

$$ln(\frac{q_e}{C_e}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

$$\Delta G = \Delta H - T\,\Delta S \quad (8)$$

Where R (8.314 J/mol·K) represents the ideal gas constant, T (K) represents the absolute temperature; C_e (mg P/L) and q_e (mg P/g) represent the phosphate concentration and adsorption amount at the adsorption equilibrium state.

5.Calculation of regeneration rate. Regeneration rate is calculated as follows:

$$R_n = \frac{q_n}{q} \quad (9)$$

Where R_n (%) represents regeneration rate of the nth use, q_n (mg P/g) represents phosphate adsorption capacity of the adsorbent after the nth use, q (mg P/g) represents phosphate adsorption capacity of the adsorbent at the first use.

Text S2

1 Experimental section

1.1 Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$), copper nitrate trihydrate ($Cu(NO_3)_2·3H_2O$), ethylenediamine (EDA), urea (CH_4N_2O), potassium dihydrogen phosphate (K_2HPO_4), etc. were of analytical grade and purchased from Xilong Chemical Co., Ltd.. All the experiments were carried out using deionized water (DI water).

1.2 Relevant instruments and characterization

Oscillatory adsorption using a frozen thermostatic oscillator (HZQ-2). Centrifugal operation was performed using a desktop high-speed centrifuge (TG16-WS). The morphology of the adsorbent was observed by scanning electron microscope (JSM-6010LA) and transmission electron microscope (FEI Tecnai G2 F20). The crystal structure and surface chemical state were determined by powder X-ray diffractometer (Ultima IV) and X-ray photoelectron spectroscopy (K-Alpha), respectively. The chemical structure of the adsorbent was recorded on Fourier transform infrared spectroscopy (NICOLET IS10) by KBr tableting method. The nanoparticle size and Zeta potential analyzer (Nano ZS90) were used to evaluate Zeta potential. The automatic surface area and porosity analyzer (ASAP2460) was used to measure the adsorption-desorption isotherms of N_2.

1.3 Synthesis of CuZnAl-1%-LDO adsorbents

The chemicals and instruments used in this work are detailed in the supporting information. The method of urea hydrolysis was used to create ZnAlCu-1%-LDHs, which were subsequently converted into ZnAlCu-1%-LDO by calcination. 13.84 mL of 0.5 mol/L zinc nitrate hexahydrate, 2.00 mL of 0.5 mol/L aluminum nitrate nonahydrate and 0.80 mL of 0.1 mol/L copper nitrate trihydrate were transferred into a glass bottle, and the solution was mixed with deionized water until it reached 40 mL (the total molar amount of Zn + Al + Cu was 8 mmol, and the Cu content was 1%). 1585.6 mg urea was added and mixed by ultrasonic for 10 min. After being agitated at

90 ℃ for 12 h, the mixture was cooled to room temperature. Then, after three washes in deionized water. Centrifugation was used to separate the precipitate at 6000 rpm. The resulting solid was dried at 60 ℃ to produce the light blue powder. Finally, to create ZnAlCu-1%-LDO, the light blue powder was calcined at 350 ℃ for 2 h (5 ℃/min programmed heating rate).

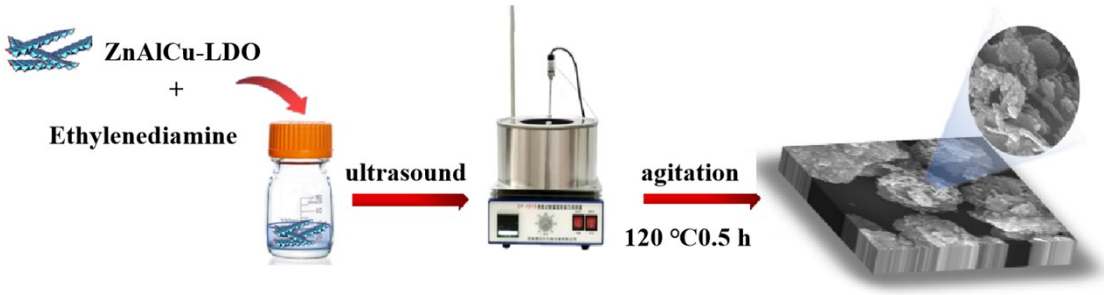

Figure S1. Preparation flow chart of ethylenediamine modified zinc aluminum copper hydrotalcite

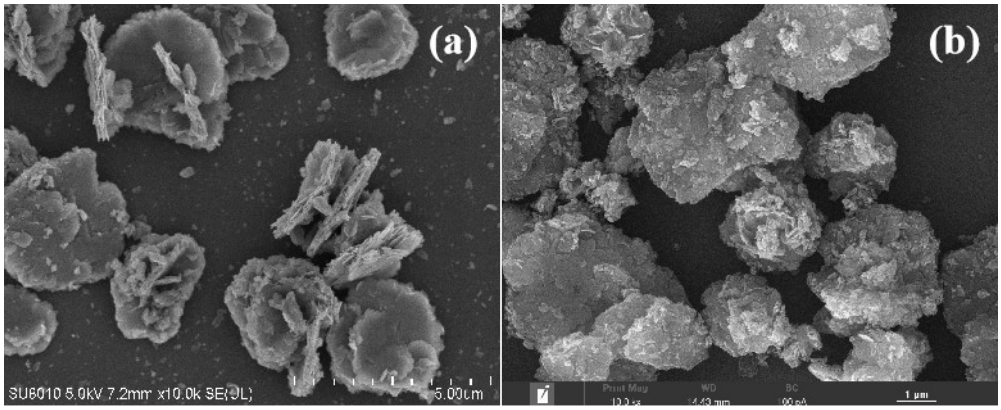

Figure S2. SEM image at 10.0 kx magnifications: (a) ZnAlCu-1%-LDO;

(b) ZACen-0.5

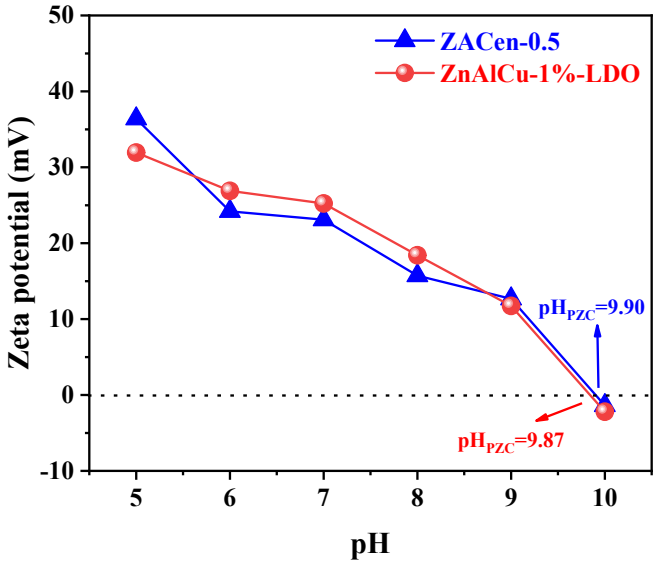

Figure S3. Zeta potential diagram of ZACen-0.5

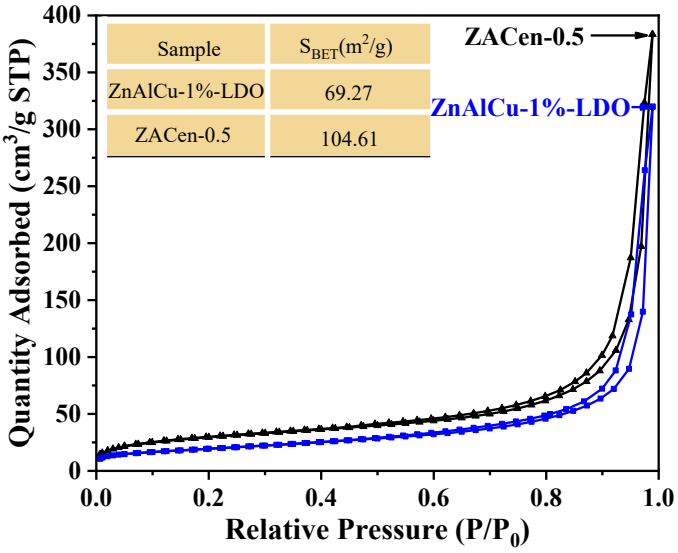

Figure S4. N_2 adsorption-desorption isotherms of ZACen-0.5 and ZnAlCu-1%-LDO

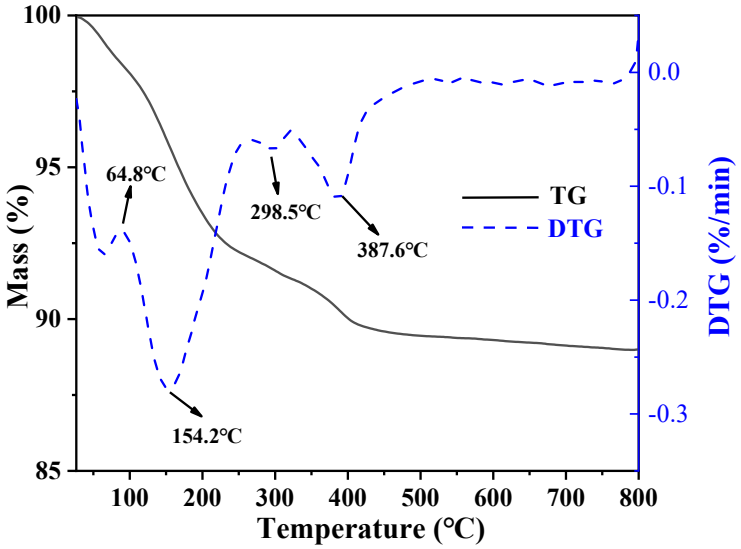

Figure S5. TG-DTG curve of ZACen-0.5

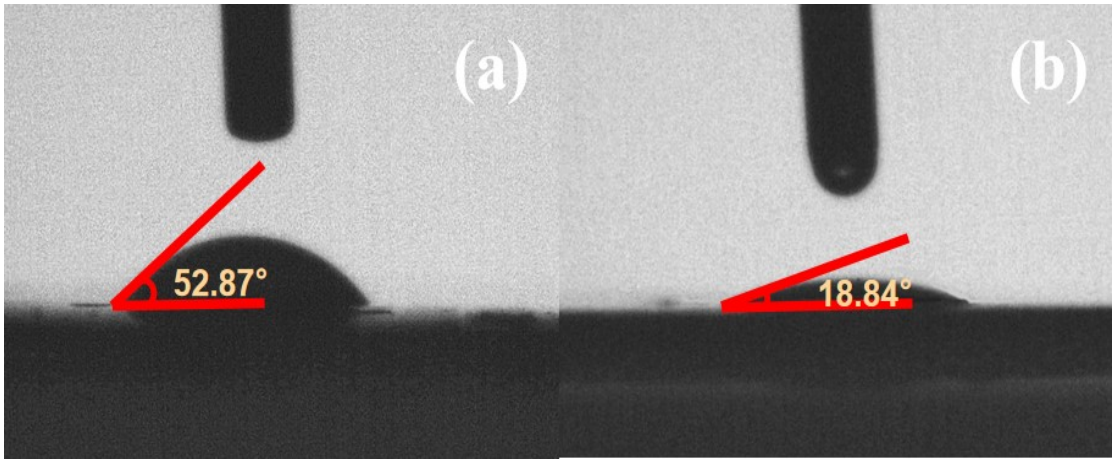

Figure S6. Contact angle test diagram: (a) ZnAlCu-1%-LDO; (b) ZACen-0.5

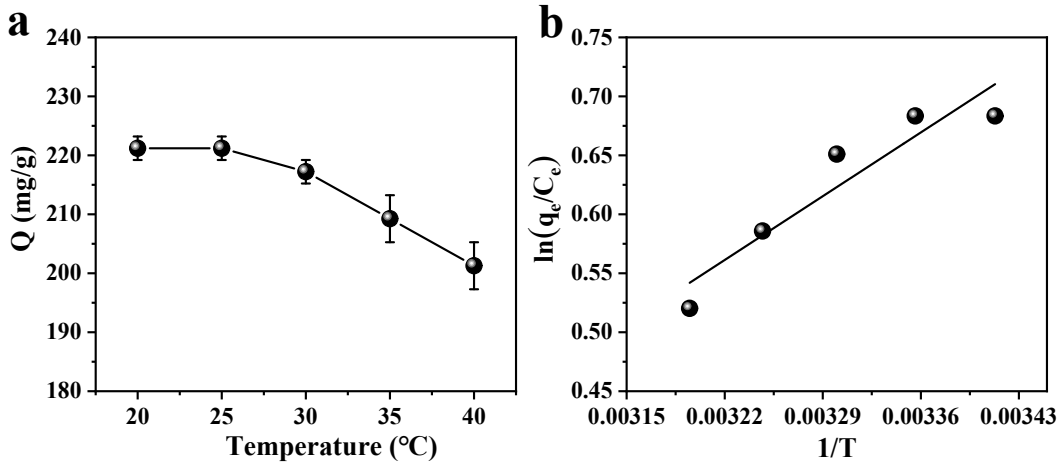

Figure S7. (a) The effect of adsorption temperature on the phosphate adsorption performance of ZACen-0.5; (b) Van 't Hoff graph

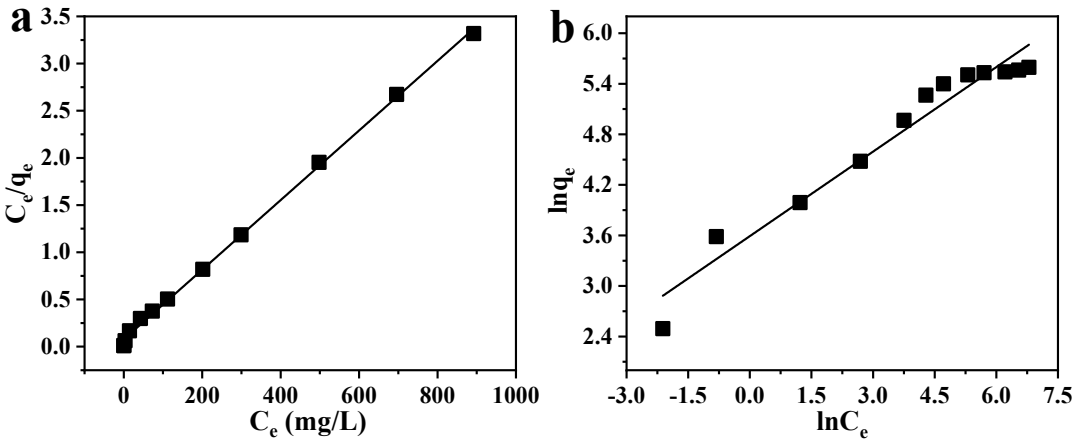

Figure S8.. Adsorption isotherm model: (a) Langmuir model; (b) Freundlich model

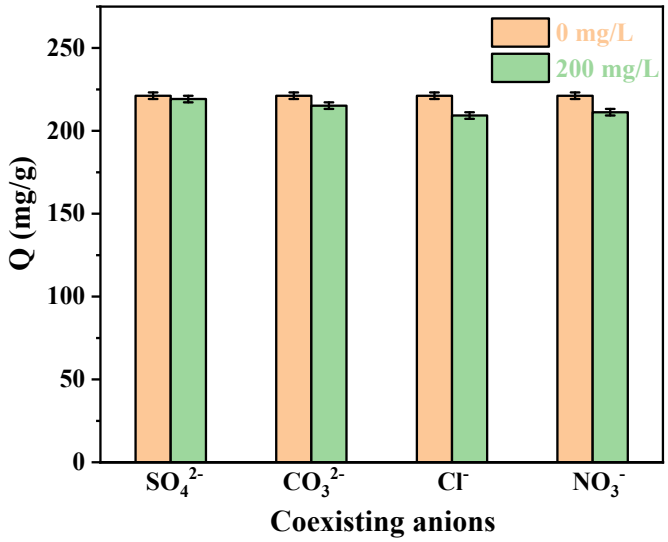

Figure S9. Effect of coexisting anions on phosphate adsorption by ZACen-0.5

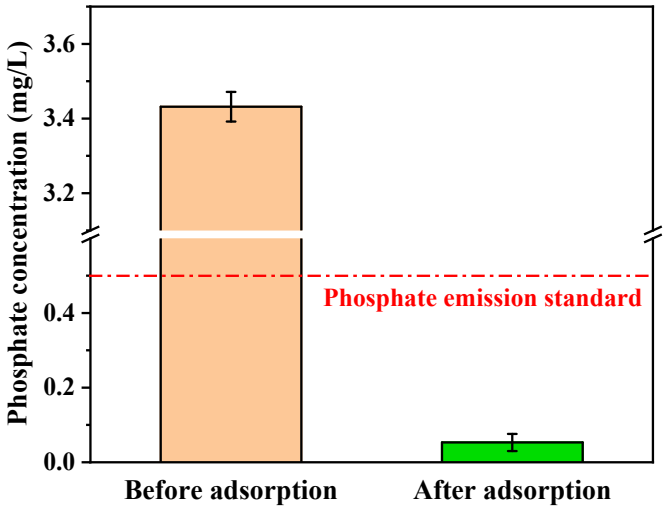

Figure S10. Comparison of phosphate concentration in wastewater before and after adsorption

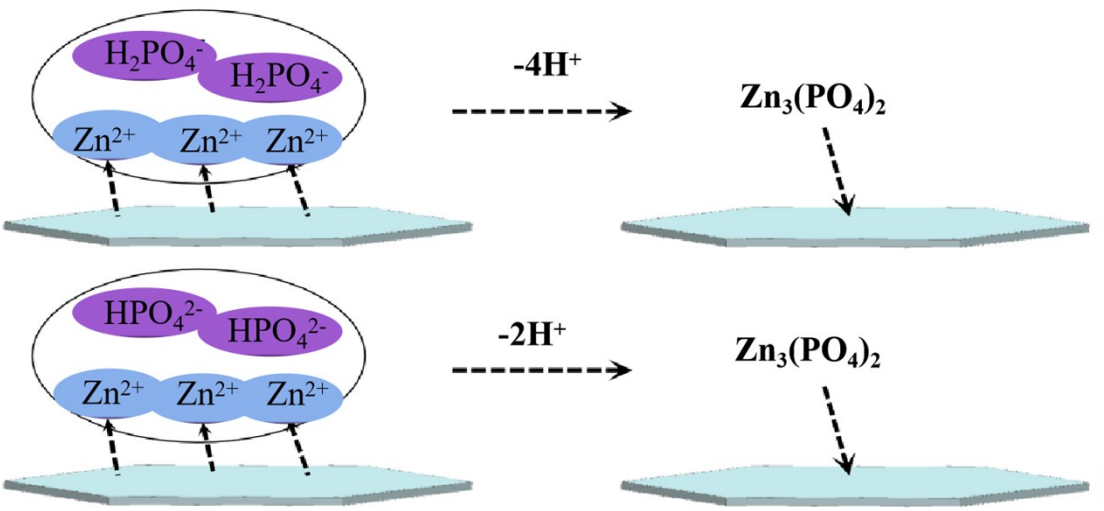

Figure11. Surface precipitation mechanism of ZACen-0.5

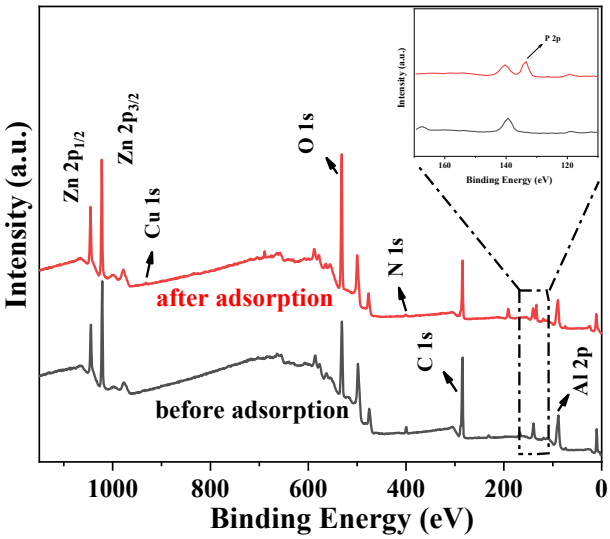

Figure S12. XPS full spectrum of ZACen-0.5 before and after phosphorus adsorption

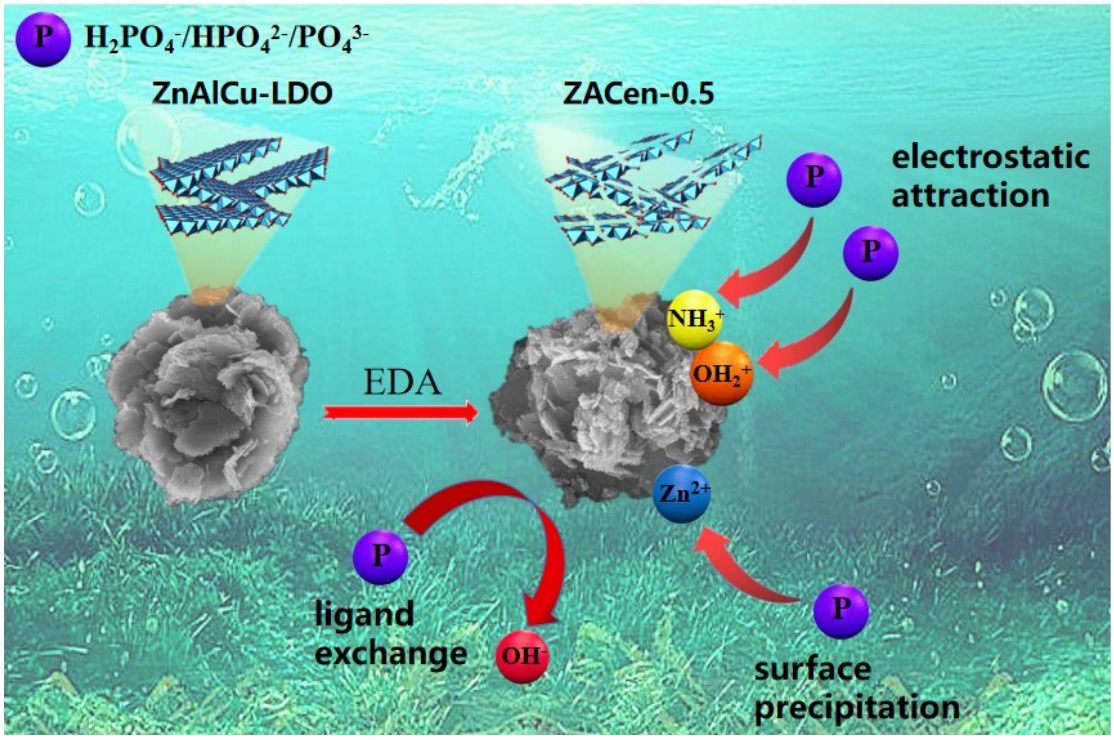

Figure S13. Adsorption mechanism of phosphate on ZACen-0.5

Table S1. Physical parameters of ZACen-0.5 and ZnAlCu-1%-LDO

Adsorbent	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
ZnAlCu-1%-LDO	69.27	0.1392	28.71
ZACen-0.5	104.61	0.2102	25.91

Table S2. Thermodynamic parameters of phosphate adsorption by ZACen-0.5

Temperature(K)	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS(J/(mol·K)
293	-1.73		
298	-1.65		
303	-1.57	-6.422	-16.014
308	-1.49		
313	-1.41		

Table S3. Kinetic model parameters of phosphate adsorption by ZACen-0.5

Experimental		Pseudo-first-order			Pseudo-second-order		
C_0 (mg/L)	q_e (mg/g)	k_1	R^2	q_e (mg/g)	k_2	R^2	q_e (mg/g)
50	88.18	0.00358	0.8217	36.04	4.019×10^{-4}	0.9987	88.73
100	143.48	0.00416	0.9478	87.43	1.399×10^{-4}	0.9972	146.63
200	221.2	0.00406	0.9391	131.94	9.177×10^{-5}	0.9982	226.24

Table S4. Adsorption isotherm model parameters

Langmuir			Freundlich		
q_{max} (mg/g)	k_L (L/mg)	R^2	k_F(mg/[g·(mg/L)$^{1/n}$])	1/n	R^2
271.00	0.04777	0.9985	36.29	0.3345	0.9538

Table S5. The comparison of adsorption properties of adsorbents for phosphate

Adsorbent	pH	T(℃)	Q(mg P/g)	Reference
Zr-CaM1	4	25	22.37	[1]
Ce-MOF-500(S)	6	25	189.4	[2]
Ce-BC	3	20	77.7	[3]
Mg/Al-LDO	6	30	103.6	[4]
Fe_3O_4/Zn-Al-Fe-La-LDH	4	30	165.9	[5]
ZnAl-LDO-BC	6	45	111.11	[6]
ZnAlCu-1%-LDO	3.5	25	231.48	[7]
ZACen-0.5	3.5	25	271.00	This work

References

[1] Y. Zou, R. Zhang, L. Wang, K. Xue, J. Chen, Strong adsorption of phosphate from aqueous solution by zirconium-loaded Ca-montmorillonite, Appl. Clay Sci. 192 (2020) 105638. https://doi.org/10.1016/j.clay.2020.105638.

[2] J. He, Y. Xu, W. Wang, B. Hu, Z. Wang, X. Yang, Y. Wang, L. Yang, Ce (III) nanocomposites by partial thermal decomposition of Ce-MOF for effective phosphate adsorption in a wide pH range, Chem. Eng. J. 379 (2020) 122431. https://doi.org/10.1016/j.cej.2019.122431.

[3] Y. Wang, X. Xie, X. Chen, C. Huang, S. Yang, Biochar-loaded Ce^{3+}-enriched ultra-fine ceria nanoparticles for phosphate adsorption, J. Hazard. Mater. 396 (2020) 122626. https://doi.org/10.1016/j.jhazmat.2020.122626.

[4] X. Zhang, J. Shen, Y. Ma, L. Liu, R. Meng, J. Yao, Highly efficient adsorption and recycle of phosphate from wastewater using flower-like layered double oxides and their potential as synergistic flame retardants, J. Colloid Interface Sci. 562 (2020) 578–588. https://doi.org/10.1016/j.jcis.2019.11.076.

[5] W. Qiao, H. Bai, T. Tang, J. Miao, Q. Yang, Recovery and utilization of phosphorus in wastewater by magnetic Fe_3O_4/Zn-Al-Fe-La layered double hydroxides (LDHs), Colloids Surf. A 577 (2019) 118–128. https://doi.org/10.1016/j.colsurfa.2019.05.046.

[6] A. Li, H. Deng, Y. Wu, C. Ye, Y. Jiang, Strong Adsorption of Phosphorus by ZnAl-LDO-Activated Banana Biochar: An Analysis of Adsorption Efficiency, Thermodynamics, and Internal Mechanisms, ACS Omega 6 (2021) 7402–7412. https://doi.org/10.1021/acsomega.0c05674.

[7] D.L. Gao, W.W. Lin, Q.J. Lin, F.F. Dai, Y.X. Xue, J.H. Chen, Y.X. Liu, Y. Huang, Q. Yang, Remarkable adsorption capacity of Cu^{2+}-doped ZnAl layered double hydroxides and the calcined materials toward phosphate, J. Environ. Chem. Eng. 11 (2023) 109472. https://doi.org/10.1016/j.jece.2023.109472.