Supplementary Information

Lanthanum Modified Biochar Particles Derived from Municipal Sludge: Preparation and mechanisms for phosphate recovery

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Contents

Text S1

Characterization of SBP and SBP-La

The physicochemical properties of SBP and SBP-La were analyzed before and after phosphate adsorption. BET surface area was detected by a Micromeritics ASAP 2046 surface area analyzer (Micromeritics Co., U.S.). The gas adsorption isotherm (N_2, 77.30 K) was used. Scanning electron microscope (SEM) (ZEISS Ultra 55, German) with Energy Dispersive Spectroscopy (EDS) line scanning was applied to determine biochar surface morphology and element compounds. The powder X-ray diffraction (XRD) (Ultima IV, Japan) was used to identify the material crystalline phases. Fourier transform infrared spectrometer (SepctrumTwo, Germany) was employed to identify surface functional groups of materials with a wave number range of 400-4000 cm^{-1}. Zeta potentials at a series of pH values were measured to determine the zero charge point (pH_{PZC}) of biochar sample (Zetasizer Nano ZS90, Malvern Instruments, United Kingdom). The coordination environment of La was investigated by an X-ray photoelectron spectrometer (ThermoFisher 3600, U.K.) with CuKa irradiation (40 kV, 30 mA).

Text S2

Preparation of anaerobic digestion liquid

After collecting from anaerobic tank from a WWTP in Guangzhou, the sludge was settled down overnight and anaerobically digested in a shaking incubator (180 rpm) at 37 ºC for 15 days. The liquid phase (supernatant) was collected from the fermented sludge solution by centrifugation (6000 rpm) for 20 min.

Text S3

Batch adsorption experiments procedures and modelling

Batch experiments were conducted by adding 20.0 mg of SBP or SBP-La into 25.0 mL of phosphate (50.0 mg P/L) solution (pH 5.0) in 50 mL centrifuge tubes, The effects of material dosage and solution pH on phosphate adsorption were tested by varying the biochar dosages from 0.4 g/L to 6.0 g/L and varying pH from 3 to 11 (adjusting by 0.1 mol/L NaOH and 0.1 mol/L HCl), respectively. Meanwhile, a set of experiments were carried out to study the influence of coexisting anions (50.0 and 100.0 mg/L), including nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-), on phosphate adsorption by biochar. Additionally, adsorption kinetics were investigated by collecting samples in suspensions at different predetermined time intervals (1-24 h). Phosphate adsorption isotherms were studied by changing initial phosphate concentrations (5−250 mg/L), in which samples were collected after reaching equilibrium (24 h). Phosphate adsorption was also conducted at 25, 35 and 45 ºC (298.15, 308.15 and 318.15 K) to investigate adsorption thermodynamics.

Kinetics, isotherm, and thermodynamic models For adsorption kinetics, pseudo first-order model, pseudo second-order model and intra-particle diffusion model were commonly used to describe kinetics process. The pseudo first-order model and pseudo second-order model equations are given as:[3]

$$\lg(q_e - q_t) = \lg q_e - k_1 t \tag{S1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{S2}$$

where q_t (mg/g) is the phosphate adsorption capacity at time t. k_1 (h) and k_2 (g·mg^{-1}·h^{-1}) are the rate constants of pseudo first-order and pseudo second-order adsorption, respectively.

The equation (S3) is the intra-particle diffusion equation:

$$q_t = k_s t^{1/2} + C \tag{S3}$$

where k_s (mg·g^{-1}·h$^{1/2}$) and C are the adsorption rate constant and intercept of the model, respectively. Additionally, the kinetics data were also fitted to Weber-Morris model to study the possible effect of intra-particle diffusion on anion adsorption process. Weber-Morris model (linear form) is given in Equation (S4):[4]

$$q_t = k_i t^{\frac{1}{2}} + C \tag{S4}$$

Where q_t was capacity of adsorbed contaminant at time t (h), k_i and C were the intra-diffusion rate constant ($mg \cdot g^{-1} \cdot h^{-0.5}$) and the intercept of the boundary layer thickness, respectively.

Meanwhile, Langmuir and Freundlich patterns are used to describe phosphate adsorption isotherms. The equations are expressed as equation (S5) and (S6), respectively.[5, 6]

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \tag{S5}$$

$$\lg q_e = \lg K_F + \frac{\lg C_e}{n} \tag{S6}$$

where Q_0 (mg/g) is the maximum phosphate adsorption capacity estimated by Langmuir model, in which K_L (mg/L) represents Langmuir equilibrium constant relating to the adsorption energy. In equation (S6), K_F ($(mg/g)(mg/L)^{1/n}$) represents the adsorption affinity, and n is the indicator for adsorbent surface heterogeneity.

For thermodynamic study, Gibbs Free Energy was applied to determine the properties of adsorption process, in which the equations are given as:

$$\Delta G_0 = - RT\ln K \tag{S7}$$

$$\ln K = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \tag{S8}$$

Where ΔG_0 (KJ/mol) represents the change of Gibbs free energy. R (8.314 J/(mol·K)) and K (Q_e / C_e) are the thermodynamic constants at absolute temperature T (K). The ΔS_0 (J/(mol·K)) and ΔH_0 (KJ/mol) are reaction entropy and enthalpy, respectively.

Table S1

Classification of ecological risk level based on *Ei* and RI [1]

E_i	RI	Risk level
≤40	≤150	low risk
41-80	151-300	moderate risk
81-160	301-600	considerable risk
161-320	601-1200	high risk
＞320	＞1200	very high risk

Table S2

Water quality of municipal wastewater and anaerobic digestion liquid of sludge

Parameters of water quality (unit)	Municipal wastewater	anaerobic digestion liquid of sludge
pH (/)	6.56	7.02
ORP (mV)	-35.0	-239
SCOD (mg/L)	34.4	274
PO_4^{3-} (mg/L)	4.97	55.1
NH_4^+ (mg/L)	8.61	274
SO_4^{2-} (mg/L)	26.3	7.75
Cl^- (mg/L)	30.7	12.5
NO_3^- (mg/L)	5.74	1.19
HCO_3^- (mg/L)	224	1205

Table S3

Major elements of SBP and SBP-La measured by SEM-EDS

Element	Contents/%	
	SBP	SBP-La
C	32.74	36.28
O	44.22	30.74
Si	8.42	4.65
Ca	4.56	0.80
Al	2.60	1.64
Fe	1.51	0.84
S	1.31	0.37
Mg	0.61	0.38
P	1.17	--
La	-[a]	13.52

[a] Not detected

Table S4

Physical properties of SBP and SBP-La

sample	Surface area（m^2/g）	Pore volume（cm^3/g）	Average pore size（nm）
SBP	19.2	0.0462	9.64
SBP-P[a]	23.2	0.0540	9.37
SBP-La	6.49	0.0141	8.67
SBP-La-P[a]	39.9	0.0617	6.19

[a] SBP or SBP-La samples after phosphate adsorption.

Table S5

Leachable heavy metals from SBP and SBP-La in batch experiments (μg/L)

pH		As	Cd	Cu	Ni	Pb	Zn
3.0	SBP	72.71	15.08	18.89	11.87	19.15	51.79
	SBP-La	79.59	15.08	18.89	11.86	19.13	51.83
5.0	SBP	72.69	15.08	18.89	11.87	19.15	51.83
	SBP-La	76.99	15.08	18.89	11.86	19.14	51.83
7.0	SBP	72.69	15.08	18.89	11.87	19.16	51.79
	SBP-La	76.53	15.08	18.89	11.86	19.17	51.83
9.0	SBP	72.69	15.08	18.89	11.87	19.15	51.82
	SBP-La	76.46	15.08	18.89	11.86	19.14	51.83
11.0	SBP	72.69	15.08	18.89	11.87	19.15	51.80
	SBP-La	76.90	15.08	18.89	11.86	19.14	51.83

Table S6

Kinetic curve fitting parameters for phosphate adsorption on SBP and SBP-La

Biochar	Pesudo first-order model			Pesudo second-order model		
	Q_{e1} （mg/g）	K_1 (/h)	R^2	Q_{e1} (mg/g)	K_2 ((g/mg)/h)	R^2
SBP	7.42±0.30	0.247±0.027	0.913	7.62±0.30	0.317±0.004	0.977
SBP-La	39.1±1.1	0.310±0.042	0.897	45.6±0.9	0.942±0.103	0.978

Table S7

Isotherm curve fitting parameters for phosphate adsorption on SBP and SBP-La

	Langmuir			Freundlich		
Biochar	Q_0 (mg/g)	K_L (L/mg)	R^2	K_F ((mg/g)·(L/mg)$^{1/n}$)	n	R^2
SBP	7.67±0.37	2.85±0.18	0.981	6.27±0.26	0.045±0.010	0.680
SBP-La	46.5±0.31	0.413±0.065	0.923	32.3±2.5	0.004±0.015	0.774

Table S8

Thermodynamic curve fitting parameters for phosphate adsorption on SBP and SBP-La

	Temperature (K)	ΔG_0 (KJ/mol)	ΔH_0 (KJ/mol)	ΔS_0 (KJ/mol·K)
SBP	298.0	4191	1330	1.031
	308.0	3349		
	318.0	2727		
SBP-La	298.0	-2162	8790924	1.494
	308.0	-3380		
	318.0	-4238		

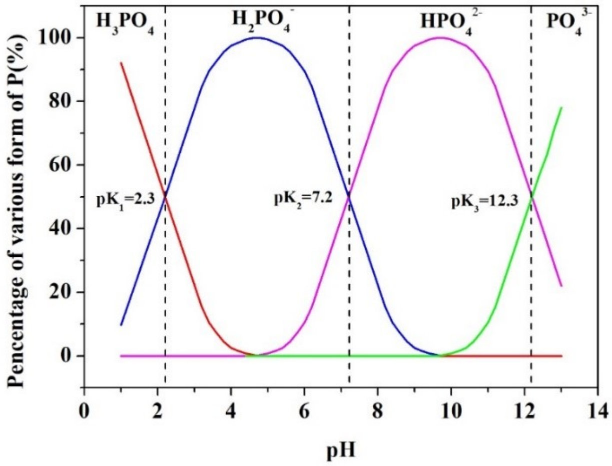

Fig. S1 Fractions of phosphate species at different pH[2]

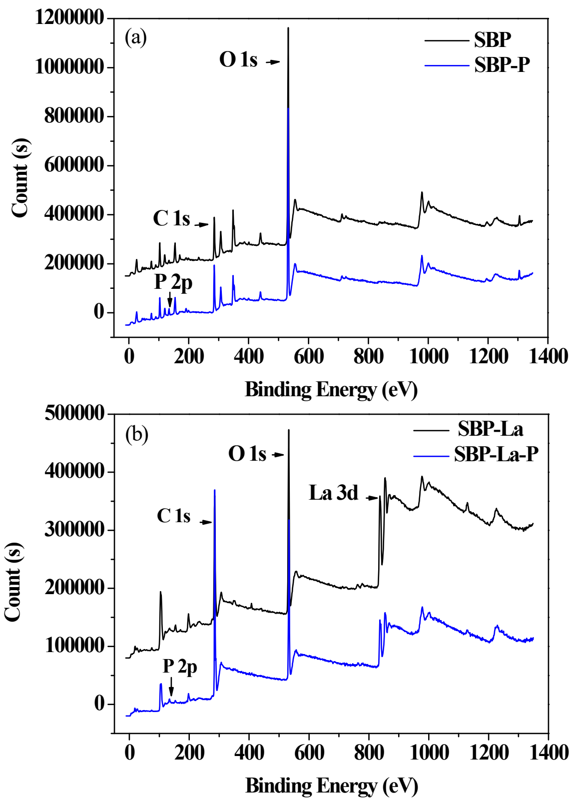

Fig. S2 XPS full spectrum of SBP (a) and SBP-La (b) before and after phosphate adsorption.

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