

Phosphate Removal from Polluted Water via Lanthanum Modified Sludge Biochar

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The batch adsorption

For the batch adsorption experiments, 20 mg of adsorbents were placed into a polyethylene centrifuge tube containing, 15 mL of phosphate solution (pH=3.0) with an initial phosphorus concentration of 30 mg·L⁻¹ was added and then oscillated for a certain time at 25 °C and 200 r·min⁻¹. A 0.22 μm water filtration membrane was used to filter the supernatant. The phosphorus content in the supernatant was determined by ultraviolet-visible spectrophotometer (UV; UV-6100A, China).

Adsorption kinetics and isotherm models were used to investigate the overall interaction between phosphate and adsorbents. Specifically, the phosphate and adsorbents were adsorbed at a temperature of 298.15 K for different contact times (5-720 min). The adsorption isotherms were determined by oscillation at different temperatures (288.15, 298.15, 308.15, 318.15, and 338.15 K) for 24 h and taking into account the initial phosphate concentrations of 5-400 mg·L⁻¹.

The effects of environmental factors (pH and the dosage of adsorbents) on the adsorption of phosphate on LaSBC was explored. In detail, different initial pH (3, 5, 7, 9, and 11) and the dosage of adsorbents (4, 8, 10, 15, 20, 25, 30, 40, 50, and 60 mg), respectively, on the adsorption efficiency. pH values of this experiment were adjusted by dropping in 0.1 mol·L⁻¹ HCl or NaOH.

Formula and calculation

The adsorption capacity (q_e) was calculated using equation (S1) [1]. The kinetic curves were fitted using the first-order kinetic equation (equation (S2)) and second-order kinetic equation (equation (S3)) [2]. Isothermal adsorption curves in phosphate solutions were fitted to the Langmuir and Freundlich models according to equations (S4) and (S5) [3,4], respectively. The adsorption thermodynamic properties were calculated by equations (S6), (S7) and (S8) [5]. The apparent standard equilibrium constant for adsorption can be expressed as equation (S6). The standard molar adsorption Gibbs energies can be calculated as equation (S7). The standard molar entropies and the standard molar enthalpies can be obtained by applying equation (S8) from the linearly fitted intercept and slope.

$$q_e = \frac{(C_0 - C_t)V \times 10^{-3}}{m} \quad (S1)$$

In equation (S1), C_0 and C_t ($\text{mg} \cdot \text{L}^{-1}$) represent the P concentration at initial and contact time t , respectively, V (mL) is the volume of P solution, and m (g) is the adsorbent dosage.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (S2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (S3)$$

In equations (S2) and (S3), q_e and q_t ($\text{mg} \cdot \text{g}^{-1}$) represent the adsorption capacity of adsorbent at the final equilibrium time and at the reaction time t (min) and k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are rate constants.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (S4)$$

$$q_e = K_F C_e^{1/n} \quad (S5)$$

In equations (S4) and (S5), q_e and q_{\max} ($\text{mg} \cdot \text{g}^{-1}$) represent the equilibrium adsorption capacity and the theoretical maximum adsorption capacity of the adsorbent, respectively, K_L ($\text{L} \cdot \text{mg}^{-1}$) and K_F ($\text{L} \cdot \text{mg}^{-1}$) are constants for the Langmuir and Freundlich isotherms, respectively, C_e ($\text{mg} \cdot \text{L}^{-1}$) represents adsorbate concentration in the solution at equilibrium, and n indicates the adsorption intensity.

$$K_D = \frac{C_0 - C_e}{C_e} \quad (S6)$$

In equation (S6), C_0 and C_e ($\text{mg} \cdot \text{L}^{-1}$) represent adsorbate concentration in the solution before and during the adsorption equilibrium, respectively.

$$\Delta G = -RT \ln K_D \quad (S7)$$

In equation (S7), R is the gas constant (8.314 J/mol K) and T is absolute temperature (K).

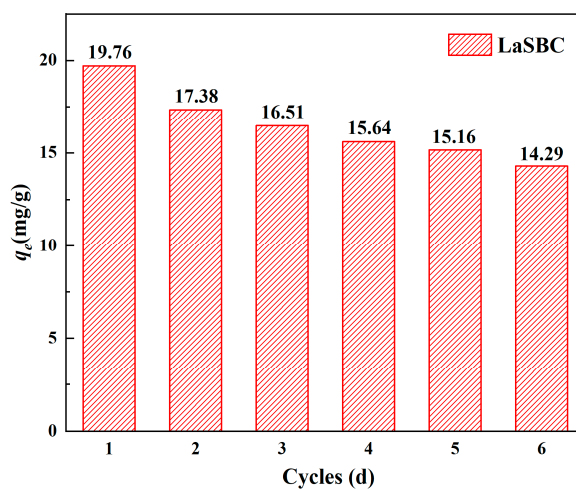
$$\Delta G = \Delta H - T \Delta S \quad (S8)$$

Table S1. Kinetic parameters for the phosphate adsorption of the LaSBC

Samples	Pseudo-first-order			Pseudo-second-order		
	Q_e (mg/g)	K_1 (h^{-1})	R^2	Q_e (mg/g)	K_2 (h^{-1})	R^2
LaSBC 15 °C	19.370	22.221	0.951	19.146	2.410	0.978
LaSBC 25 °C	19.599	20.285	0.946	19.319	2.060	0.979
LaSBC 45 °C	21.168	29.039	0.958	21.059	5.342	0.961

Table S2. Thermodynamic parameters for the phosphate adsorption of the LaSBC

Samples	ΔG (kJ/mol)	ΔS (J/mol·K)	ΔH (kJ/mol)
LaSBC 15 °C	-385.704		
LaSBC 25 °C	-42.14		
LaSBC 35 °C	-17.934	3.745	954.963
LaSBC 45 °C	-21.161		
LaSBC 65 °C	-581.955		

**Figure S1.** Adsorption capacity after desorption of LaSBC

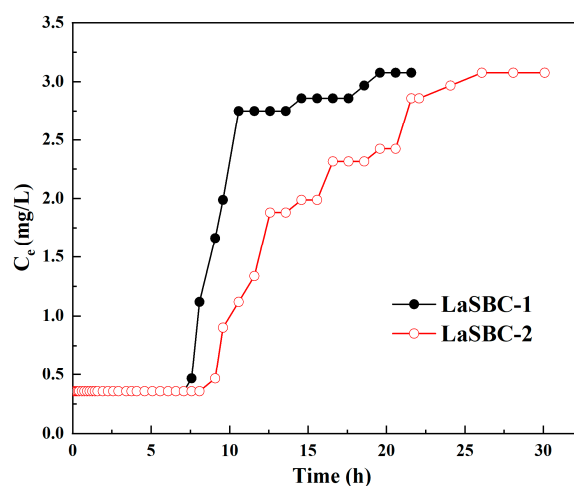


Figure S2. Effects of dosages on breakthrough point of LaSBC

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