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Engineering of Biomimetic Bone Tissue Aerogel for Sustainable Phosphorus Cycle Remodeling

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ABSTRACT

Human activities have induced a twofold imbalance in the global phosphorus (P) cycle, manifesting as accelerated depletion of phosphate rock reserves and localized P overabundance in industrial wastewater, which fundamentally disrupts P resource sustainability. Recovery of P from wastewater for valorization as fertilizers is a sustainable strategy to alleviate the P resource limitations, however, current practical adsorbent-based approaches are constrained by low adsorption capacity, subpar fertilization efficacy, and elevated ecotoxicological risks. Here we designed an eco-friendly biomimetic bone tissue aerogel (BBTA) via self-assembly technique of waste biomass to remodel the P cycle. Its anisotropic winding structure supported development of highly active biomimetic interface, which significantly enhanced site utilization (adsorption capacity of 188.82 mg·g⁻¹) and overcame kinetic barriers to hydroxyapatite conversion (<48 h). Consequently, BBTA achieved continuous P recovery for over 540 min (effluent-to-influent concentration ratio < 0.1) during actual wastewater treatment under fixed-bed conditions. Compared to commercial P-fertilizer, the recovered nutrient-rich products induced a 1.84- to 3.44-fold enhancement in wheat growth. P-footprint and techno-economic analyses revealed that our strategy enabled ~22.1% of P resource regeneration and eliminated ~24.2% of phosphate rock extraction, with adsorbent cost as low as 19.95 USD·kg⁻¹ (calculated based on quality of recovered P), showing great potential for engineered P cycle remodeling within industry–resource–environment nexus.

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1. Introduction

Phosphorus (P), a cornerstone of life, establishes a closed-loop cycling system within the natural world encompassing phosphate rock (PR)–soil–plant–animal–water–soil–PR, fostering the flourishing of ecosystems (Fig. 1(a)) [1]. However, as shown in Fig. 1(b), high-input but low-output industrial processes result in substantial unutilized P resources (~34.2% of total PR-input, mainly phosphate) being lost through wastewater [2–4]. These P resources cannot enter the normal water–soil migration path due to inert deposition and explosive algal cycling growth, leading to serious aquatic ecological degradation [5]. Meanwhile, to guarantee global food security, ~29.5% of total PR-input is converted into fertilizer,

significantly exceeding other application scenarios (Fig. 1(c)) [6–9]. The huge demand, non-renewable nature, geographically uneven distribution, and hypercyclic price volatility (PR; from ~50 USD·t⁻¹ in 2020 to ~160 USD·t⁻¹ in 2024) have exacerbated concerns regarding P resource shortages [10,11]. Overall, the accelerated depletion of PR reserves and localized P overabundance in wastewater induces a twofold imbalance in global P cycle.

In theory, efficient phosphate recovery from high-concentration P-containing industrial wastewater for valorization as fertilizer is a sustainable strategy for P cycle remodeling and P challenge relieving [12]. Due to high recovery efficiency, low energy consumption, and minimal sludge generation, metal-based adsorption stands out as the most practical and commercially viable approach for recovering insoluble phosphate fertilizers, compared to electrochemical and chemical precipitation technologies [4,13–15]. Among them, Ca-based adsorbents hold great promise for converting waste P into nutrient-rich fertilizers, benefiting from relatively high

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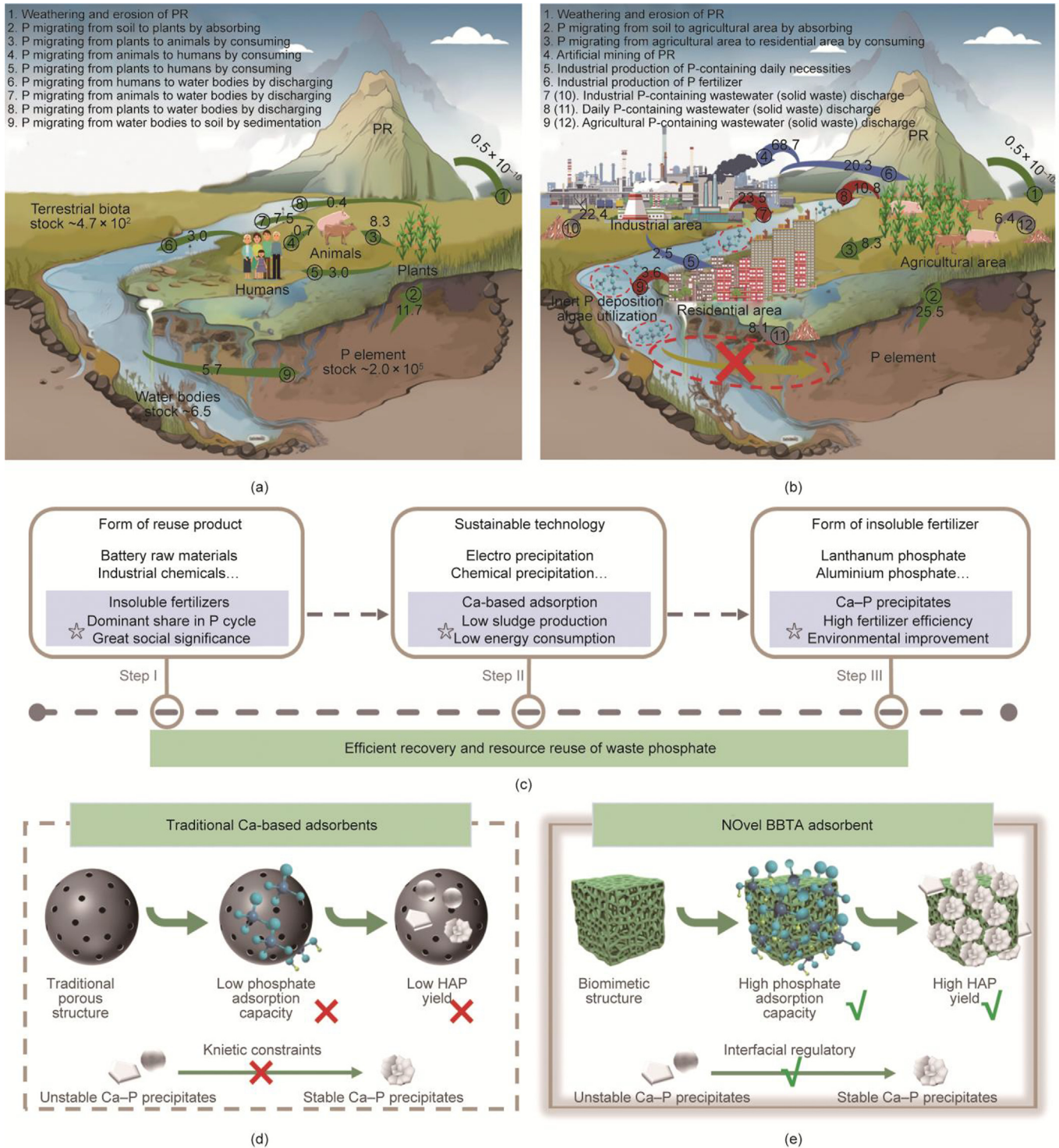


Fig. 1. (a, b) Schematic diagram of simplified P cycles ($10^6 \text{ t} \cdot \text{a}^{-1}$) (a) without and (b) with industrial intervention. Green arrow represents normal P migration pathway, blue arrow represents P migration pathway with industrial interference, red arrow represents discharge pathway of P-containing wastewater, gray arrow represents discharge pathway of P-containing solid waste, brown arrow represents return pathway of waste P to cycle. (c) Selection basis for reuse product forms and recovery technologies in P cycle remodeling. (d, e) Comparison between (d) traditional Ca-based adsorbents and (e) novel BBTA adsorbent in terms of adsorption capacity and precipitates evolution.

solubility of Ca-P precipitates and additional benefits of Ca in plant growth and soil improvement. Currently, Ca-based adsorbents primarily include two categories: integrating Ca compounds into high-surface-area substrates and directly modifying Ca-rich matrices [16]. During adsorption, Ca sites would adsorb phosphate to initially form amorphous calcium phosphate (ACP) through surface precipitation, which then gradually evolves into stable crystals. As

the final product of Ca-P multi-step crystallization, the bioavailable hydroxyapatite (HAP) with superior P immobilization performance can minimize resource re-loss, allowing gradual uptake by plants [17]. However, two critical challenges constrain the HAP yield by Ca-based adsorbents: ① unsatisfactory adsorption capacity (theoretical maximum adsorption capacity ($Q_{\max}$) $< 50 \text{ mg} \cdot \text{g}^{-1}$) due to limited and under-utilized active sites; ② slow Ca-P

precipitate evolution (>60 h) driven by kinetic barriers (Fig. 1(d)) [13,14]. Specifically, inertness of carrier and absence of interfacial features in existing adsorbents impair the utilization of insufficient sites and weaken the efficiency of waste P recovery [18,19]. In addition, although conventional Ca-P precipitate evolution is a thermodynamically favorable process (Gibbs free energy (ΔG) < 0), it is hindered by multiple energy barriers (activation energy (E_a) > 30 kJ·mol⁻¹) such as lattice reorganization [20,21]. Without additional energy input, Ca-P precipitates may remain in ACP state for extended periods, weakening efficiency of fertilizer reuse.

Therefore, developing an adsorbent with high adsorption capacity and rapid Ca-P precipitate evolution is crucial for enhancing the valorization of waste P into nutrient-rich fertilizers. The unique structure and high HAP content (~70%) of bone tissue provide a prototypical model for adsorbent design. Specifically, its highly cooperative peptide folding (e.g., triple-helix) achieves conformational minimization through free energy minimization, thereby substantially enhancing the structural stability [22,23]. The ordered conformation, which stems from anisotropic winding and internal dipole force of amino acids, promotes the binding of Ca and phosphate. Meanwhile, the increased local surface energy of Ca-P precipitates, induced by active proteins during crystallization, facilitates the reduction or bypass of energy barriers to accelerate phase transformations [24,25]. Importantly, template effects such as hydrophilic-hydrophobic coordination enable vectorial control over the growth of precipitates via supramolecular recognition mechanisms. This characteristic prevents occlusion of active sites by unordered or excessive crystallization. Overall, a novel biomimetic bone tissue adsorbent demonstrates the potential for rapidly producing large quantities of high-purity HAP during wastewater treatment, eliminating demand for additional energy input. Given the structural similarity to biological systems, three-dimensional (3D) aerogels are widely used to simulate physiological tissues in biomedical studies [26]. Meanwhile, the porous structure and large active site capacity confer them significant adsorption potential. Therefore, the 3D aerogel is a promising form for implementing the biomimetic bone tissue adsorbent design (Fig. 1(e)). The resultant P cycle remodeling strategy would simultaneously alleviate the current P pollution and P shortage.

Herein, a biomimetic bone tissue aerogel (BBTA-2:1) was prepared via coordination-driven self-assembly using bone tissue-like active cellulose (CE) and silk fibroin (SF) to sustainably remodel the P cycle. The ordered stable conformation and interface regulation capacity markedly enhanced utilization of active sites and overcame kinetic barriers of Ca-P precipitate evolution during phosphate adsorption. BBTA-2:1 exhibited unparalleled performance in the full-cycle application of P cycle remodeling (recovery from high-concentration P-containing industrial wastewater and reuse as agricultural fertilizers), surpassing typical commercial and reported adsorbents. Utilizing waste biomass as feedstock further renders the application process eco-friendly and economically feasible, while alleviating pressure of agricultural waste disposal. Overall, this strategy for enhancing valorization of waste P into nutrient-rich fertilizer based on BBTA-2:1 led to ~22.1% of P resource regeneration and ~24.2% of PR extraction reduction. This study provided new opportunities for engineered P resource reconstruction and P cycle remodeling to address unprecedented P challenges.

2. Materials and methods

2.1. Chemicals

Absorbent cotton was obtained from Hualu Sanitary Materials Co., Ltd., China. Silkworm cocoon was sourced from Northwest

Sericulture Base, China. The CE and SF solutions were prepared from absorbent cotton and silkworm cocoons, respectively, as described in Method S1 in Appendix A. NaCl (analytical reagent grade (AR)), CaCl₂·2H₂O (AR), KCl (AR), MgCl₂ (≥98%), HCl (AR), NaOH (AR), NaNO₃ (AR), Na₂CO₃ (AR), Na₂SO₄ (AR), KH₂PO₄ (AR), urea (AR), and humic acid (HA, 85%) were purchased from Sino-pharm Chemical Reagent Co., Ltd., China. Epichlorohydrin (ECH) and citric acid (CA, 1 mol) were purchased from Aladdin Biochemical Co., Ltd., USA. Tissue inorganic P content assay kit was obtained from Beijing Boxbio Science and Technology Co., Ltd., China. Milli-Q ultrapure water system (Merck Millipore, USA) was used to provide deionized water.

2.2. Preparation of BBTAs

First, 10 mL of CE solution with a mass fraction of 0.02 (2 wt%) was thoroughly mixed with 10 mL of SF solution (0.5, 1, and 2 wt%) under magnetic stirring for 40 min. Subsequently, 2 mL of ECH was introduced into the CE/SF mixed solution under vigorous stirring until all bubbles disappeared. The above solution was poured into a mold and crosslinked at 60 °C for 2 h. Afterwards, the obtained hydrogels were immersed in deionized water for thorough washing to remove unreacted components. Finally, the cleaned hydrogels were immersed in a 2 wt% CaCl₂·2H₂O solution to introduce sufficient active sites. After freeze-drying at -50 °C for 36 h, the BBTAs were obtained and labeled separately as BBTA-1:1, BBTA-2:1, and BBTA-4:1 according to the mass ratios of CE and SF. The aerogels without Ca²⁺ were labeled A-1:1, A-2:1, and A-4:1, respectively. Besides, the pure CE and SF aerogels with (without) Ca²⁺ were prepared and labeled BBTA-CE (A-CE) and BBTA-SF (A-SF), respectively. Detailed characterizations of the BBTAs were provided in Method S2 in Appendix A.

2.3. Phosphate adsorption experiments

Typically, adsorption experiments were performed by utilizing 1 g·L⁻¹ BBTA in a synthetic high-concentration P-containing wastewater, with stirring (200 r·min⁻¹) for 5 h at 25 °C. The concentration was set at 100 milligram P per liter water (mgP·L⁻¹) based on the commonly used value in literature for comparison. Kinetic evaluation was conducted by measuring the specific adsorption capacities (q_t) at intervals of 1, 5, 10, 20, 40, 60, 90, 120, 180, 240, and 300 min, with the data fitted to Pseudo-first-order and Pseudo-second-order models. Isotherm evaluation was performed across concentration gradients (50, 100, 150, 200, 250, and 300 mgP·L⁻¹). Langmuir, Freundlich, and Langmuir-Langmuir models (Eq. (1)) were adopted to fit the equilibrium adsorption capacity (q_e) after sufficient adsorption (24 h). Meanwhile, kinetic and isotherm experiments were conducted at both 25 and 50 °C to calculate the E_a (Arrhenius equation), ΔG , enthalpy change (ΔH), and entropy change (ΔS) of BBTA adsorption.

$$q_a + q_p = \frac{k_a Q_a C_e}{1 + k_a C_e} + \frac{k_p Q_p C_e}{1 + k_p C_e} \quad (1)$$

where q_a (mg·g⁻¹) denotes adsorption capacity at adsorption equilibrium; q_p (mg·g⁻¹) denotes adsorption capacity at precipitation equilibrium; Q_a (mg·g⁻¹) denotes maximum adsorption capacity; Q_p (mg·g⁻¹) denotes maximum precipitation capacity; C_e (mgP·L⁻¹) denotes equilibrium phosphate concentration; k_a (L·mg⁻¹) and k_p (L·mg⁻¹) denote binding constants associated with adsorption and precipitation energies, respectively. Other related formulas can be found in Method S3 in Appendix A.

Impacts of pH, temperature, and coexisting species on BBTA's adsorption capacity were evaluated following the typical experimental processes and parameters. The solution pH was adjusted

to 2, 4, 6, 8, 10, and 12 by adding HCl or NaOH solution (1 mol·L⁻¹). The solution temperatures were set at 5, 15, 25, and 35 °C. Typical coexisting species included anions (NO₃⁻, SO₄²⁻, CO₃²⁻, and Cl⁻; sodium salt; each at 100 mg·L⁻¹), cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺; chloride; each at 100 mg·L⁻¹), and HA (20, 50, and 100 mg·L⁻¹). Desorption and slow-release experiments were carried out using 100 mL CA solution (0.5%) and deionized water at 25 °C, respectively.

Fixed-bed adsorption was performed in a customized acrylic column (diameter = 2 cm, height = 10 cm). The synthetic wastewater and actual wastewater from a phosphating enterprise in Guizhou, China, were continuously flowed through the column using a peristaltic pump (5 mL·min⁻¹). Effluent samples were collected at predetermined intervals to monitor phosphate concentration.

2.4. Resource reuse experiments

The wheat cultivation experiment was designed to demonstrate the resource reuse effects of BBTA recovered products. First, adsorption was conducted by immersing BBTA (1 g·L⁻¹) in a phosphate solution (100 mgP·L⁻¹) for 5 h, followed by filtration and separation for subsequent testing. Then, the wheat seeds were soaked, disinfected, and germinated. Finally, 100 mg of BBTA recovered product was dispersed in culture dishes containing 15 mL of deionized water and 20 seeds per dish to serve as P fertilizer for wheat cultivation. The tested wheats were cultivated under an alternating light and dark environment (25 °C, 70% relative humidity). Dry-weight, fresh-weight, shoot-length, and root-length were measured after 3 and 7 d. In addition, the BBTA, after phosphate adsorption from actual wastewater under fixed-bed conditions, were also employed for wheat cultivation under the same conditions. Four commercial adsorbents (Fe-based adsorbent (Fe-B), organic-based adsorbent (TJDQ-C1), Al-based adsorbent (Al-B), and La-modified bentonite (LMB)), a commercial calcium phosphate fertilizer (available P (P₂O₅) ≥ 12%, S ≥ 8%, Ca ≥ 12%), and blank were used for comparison. Relevant data were analyzed through one-way analysis of variance (ANOVA; IBM SPSS Statistics 22, USA) to evaluate the differences between wheat cultured with BBTA recovered products and controls. In statistical analyses, ns indicated no significance, while **p* ≤ 0.05 and ***p* ≤ 0.01 indicated statistically significant differences.

2.5. Global P cycle evaluation

The global P-footprint was set by referencing forecasts from academic studies, official documents, and expert consultations. Specifically, the simplified global P cycles without and with industrial intervention were established based on previous studies, encompassing sources, applications, and emissions [4,7,9]. In the remodeling process, the yield of BBTA-2:1 was initially evaluated based on the reported output of waste biomass. Subsequently, the amount of P resource recovered for reuse as fertilizer was calculated according to the adsorption capacity of BBTA-2:1. Finally, the new P-footprint was determined by proportionally adjusting the existing P-footprint to evaluate the P cycle remodeling effects, including the reduction in PR extraction and waste discharge.

2.6. Environmental toxicological evaluation

The toxicological properties of BBTA and four commercial adsorbents were evaluated through *Escherichia coli* (*E. coli*) growth inhibition assays, using both plate and supernatant culture methods. The utilized *E. coli* (MG1655 K12) was a non-pathogenic, wild-type strain, which was commonly employed in standardized toxicity assays because of its simple cultivation, experimental ease, and quantifiable endpoints. The experiments were conducted at

the same (consistent with adsorption experiment: 1 mg·mL⁻¹) and different (conversion of adsorption capacity: BBTA of 1 mg·mL⁻¹, Fe-B of 1.14 mg·mL⁻¹, TJDQ-C1 of 2.54 mg·mL⁻¹, Al-B of 6.63 mg·mL⁻¹, LMB of 6.73 mg·mL⁻¹) dosages, respectively. Detailed experimental steps were described in [Method S4](#) in Appendix A. The inhibition (%) of *E. coli* growth was represented by OD₆₀₀ (optical density at 600 nm) and CFU (colony-forming units), as calculated by Eqs. (2) and (3), respectively.

$$\text{Inhibition} = \frac{\text{OD}_{600,0} - \text{OD}_{600}}{\text{OD}_{600,0}} \times 100\% \quad (2)$$

$$\text{Inhibition} = \frac{(\text{CFU}_c - \text{CFU}_t)}{\text{CFU}_c} \times 100\% \quad (3)$$

where OD_{600,0} denotes mean OD₆₀₀ values under control conditions; OD₆₀₀ denotes mean OD₆₀₀ values under treatment conditions; CFU_c (CFU·mL⁻¹) and CFU_t (CFU·mL⁻¹) denote average CFU values for the controls and treatments, respectively.

2.7. Overall sustainability evaluation

The overall sustainability evaluation (OSE) of BBTA and four commercial adsorbents was conducted according to a simplified set of eight indicators: environmental friendliness, preparation simplicity, waste utilization, treatment efficiency, cost, degradability, scalability, and public acceptability. Each indicator was scored using a three-level scale: low (L, evaluation level is 1 (*p* = 1)), Medium (M, *p* = 2), and high (H, *p* = 3), and comprehensive OSE scores were then calculated through Eq. (4):

$$\text{OSE} = 100\% \times \sum_{z=1}^8 \left(\frac{p_z}{3} \right) \times \frac{1}{8} \quad (4)$$

where *z* denotes evaluation indicator.

3. Results

3.1. Preparation and characterization of BBTAs

Given their unique and superior eco-economic benefits, high tunability, and bio-like activity, natural polymers CE and SF were employed to prepare BBTA. The regenerated composite polymer chains were first cross-linked by epichlorohydrin, and subsequently underwent directional alignment and pore modulation via Ca²⁺ coordination, thus completing the customized engineering of anisotropic BBTA with a highly compact and ordered structure ([Fig. 2\(a\)](#)). The entire synthesis process relied on self-assembly through intermolecular interactions, as illustrated by the mechanisms shown in [Fig. S1](#) in Appendix A. The controls lacking part of feedstocks were also prepared to demonstrate the feasibility of the proposed scheme. Importantly, the integration of Ca²⁺-bridged rigid CE and flexible SF held promise for achieving anisotropic alignment reminiscent of bone tissue, thereby enhancing the crosslinking stability and pore structure openness of BBTA [26]. Meanwhile, benefiting from the self-twining and phase separation of regenerated CE and SF chains during gelation process, the resulting nanoscale polymer network could expose abundant Ca²⁺ and mimic the microenvironment of bone tissue to promote biomimetic mineralization [27,28]. As shown in Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) results, attenuation of O-containing functional group peaks associated with crosslinking and coordination confirmed successful synthesis of BBTA ([Note S1](#) and [Fig. S2](#) in Appendix A). Notably, the absence of CE, SF, or Ca²⁺ led to irregular stacking or smooth structures rather than the characteristic bone tissue structure for

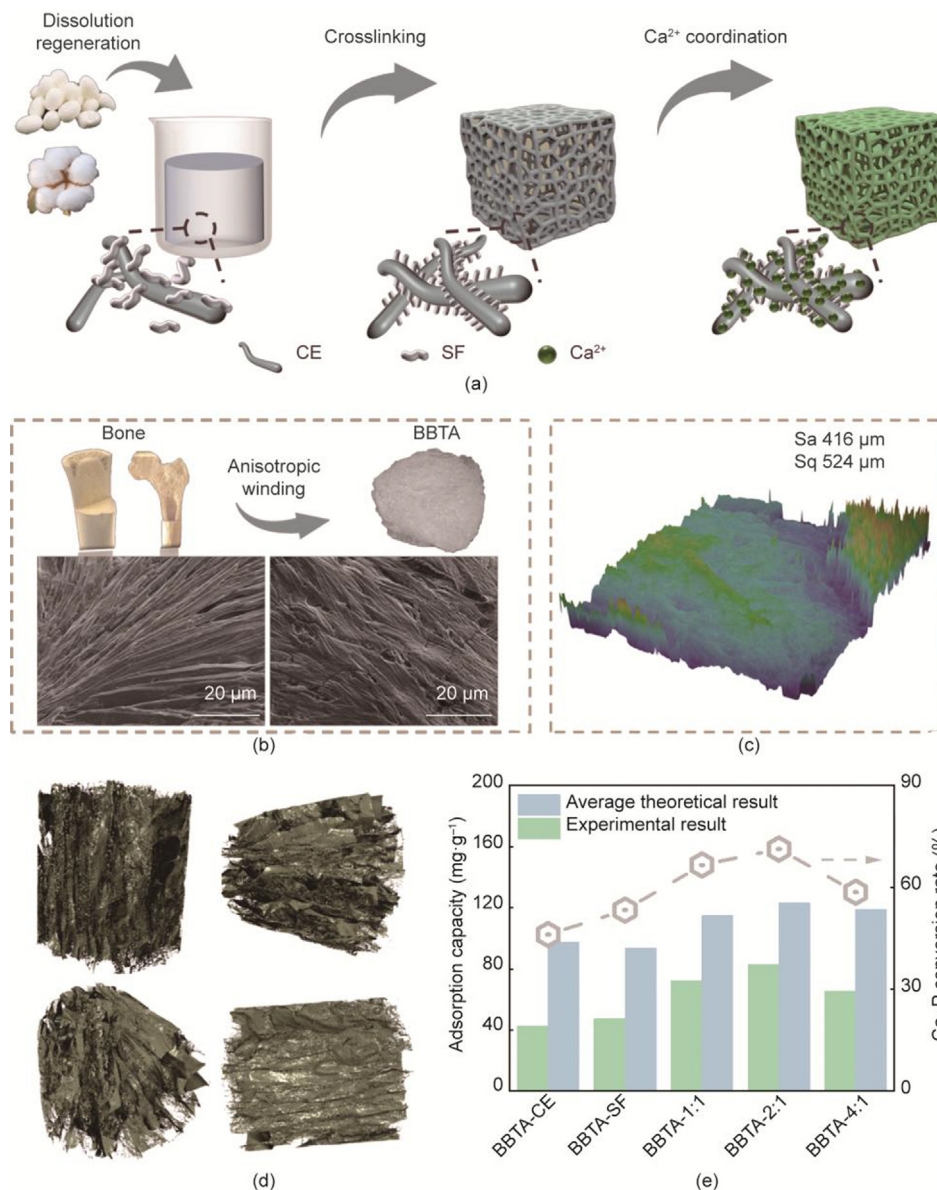


Fig. 2. (a) Fabrication schematic of BBTA via self-assembly approach; (b) optical pictures and SEM images of BBTA-2:1; (c) ultra-depth of field microscope (regional area: 162 mm²) and X-ray microscope (regional volume: 5 mm × 5 mm × 5 mm); (d) slice number: 1010 (X axis) × 992 (Y axis) × 988 (Z axis)) images of BBTA-2:1; (e) adsorption capacity and theoretical Ca-P conversion rate of BBTAs.

aerogels, which proved that all feedstocks were indispensable for BBTA preparation (Figs. S3 and S4(a)–(e) in Appendix A).

Variations in the ratio of CE to SF significantly affected the biomimetic effect of BBTAs. Among them, BBTA-2:1, with abundant and uniformly distributed C, O, and Ca elements, exhibited the most similar structure to that of bone tissue (Figs. 2(b), S4(f) and (g), and S5 in Appendix A) [29]. The highest specific surface area (69.66 m²·g⁻¹) and porosity (99.45%) further confirmed the optimal biomimetic effect of BBTA-2:1 (Table S1 in Appendix A). Large-area surface stitching and overall 3D reconstruction based on ultra-depth field microscopy and X-ray microscopy visually demonstrated its folded surface and 3D perforated micro–nano structures, which provided a satisfactory platform for efficient phosphate adsorption and biomineralization (Figs. 2(c)–(d)). The highest Ca content (19.88%), as confirmed by both inductively coupled plasma–optical emission spectrometry (ICP–OES) and X-ray fluo-

rescence spectroscopy (XRF) analyses, undoubtedly originated from the optimal BBTA-2:1 (Table S2 in Appendix A). Moreover, despite having 3.7% lower Ca content, BBTA-SF showed 11.3% higher adsorption capacity and 15.6% higher theoretical Ca–P conversion rate compared to BBTA-CE (Fig. 2(e) and Table S3 in Appendix A). This result indicated that the ordered β -folding structure of active SF imparted interface regulation for Ca–P precipitates, closely resembling biomineralization in bone tissue [30]. Therefore, BBTA-2:1 achieved the maximum phosphate adsorption capacity (82.8 mg·g⁻¹) and the highest theoretical Ca–P conversion rate (71.24%) among all BBTAs, and it was selected as the candidate for subsequent P cycle remodeling application. Notably, due to high scalability of the dissolution-regeneration technology, this self-assembly-induced anisotropic BBTA-2:1 was expected to achieve industrial production, making engineered P cycle remodeling feasible.

3.2. Adsorption performance and mechanism of BBTA's

Phosphate adsorption performance and mechanism of the specially structured BBTA-2:1 were initially assessed through isotherm, kinetic, and thermodynamic analyses, as well as through relevant characterizations. The better fitting with the Langmuir model revealed that phosphate adsorption onto BBTA-2:1 was mainly related to homogeneous monolayer coverage, which was conducive to nucleation, crystallization, and growth of Ca-P precipitates for biomimetic mineralization (Fig. 3(a) and Table S4 in Appendix A) [31]. Meanwhile, the $Q_{\max}$ of BBTA-2:1, calculated as $180.41 \text{ mg} \cdot \text{g}^{-1}$ at 25°C , was 1.53–6.89 times higher than those of typical commercial adsorbents such as Fe-B, TJDQ-C1, Al-B, and LMB. Besides, this $Q_{\max}$ remained highly competitive even in comparison with a large number of adsorbents reported in the literature, including both Ca-based and other widely studied adsorbents (Table S5 in Appendix A). Supported by biomimetic bone tissue structure, the utilization rate of Ca sites in BBTA-2:1 (90.79%) was also higher than other Ca-based adsorbents (<65%), maximizing its performance (Table S6 in Appendix A). Moreover, the Langmuir–Langmuir model enabled a more precise differentiation of adsorption mechanisms, while offering a similarly high fit-

ting correlation for BBTA-2:1's adsorption as the single Langmuir model (Fig. S6 and Table S7 in Appendix A). Specifically, a higher Q_p ($170.70 \text{ mg} \cdot \text{g}^{-1}$) than Q_a ($19.05 \text{ mg} \cdot \text{g}^{-1}$) indicated that Ca-based surface precipitation (chemical adsorption, 89.96%) was the dominant mechanism for phosphate adsorption [32,33]. In addition, BBTA-2:1 showcased rapid adsorption kinetics (equilibrium time < 100 min) across a range of concentrations (2, 20, 50, and $100 \text{ mgP} \cdot \text{L}^{-1}$), achieving P removal efficiencies of 83.8%–98.4% (Figs. 3(b) and S7(a) and Table S8 in Appendix A). Meanwhile, the lower initial concentration (< $20 \text{ mgP} \cdot \text{L}^{-1}$) mitigated the limitation of adsorption rate by intraparticle diffusion, due to the presence of sufficient active sites (Fig. S7(b) and Table S9 in Appendix A) [13]. Furthermore, the adsorption capacity of BBTA-2:1 still remained stable after several cycles, proving the satisfactory reusability (Fig. S8 in Appendix A).

For the recovered products, new peaks in FT-IR (563, 601, and 1025 cm^{-1}) and P 2p XPS (132.8 eV and 133.7 eV) spectra revealed BBTA-2:1's successful phosphate adsorption (Fig. S9 in Appendix A) [14,34]. Abundant peaks related to Ca-P precipitates in X-ray diffraction (XRD) patterns, containing dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), and HAP, further verified the predominant role of chemical adsorption (Ca-based

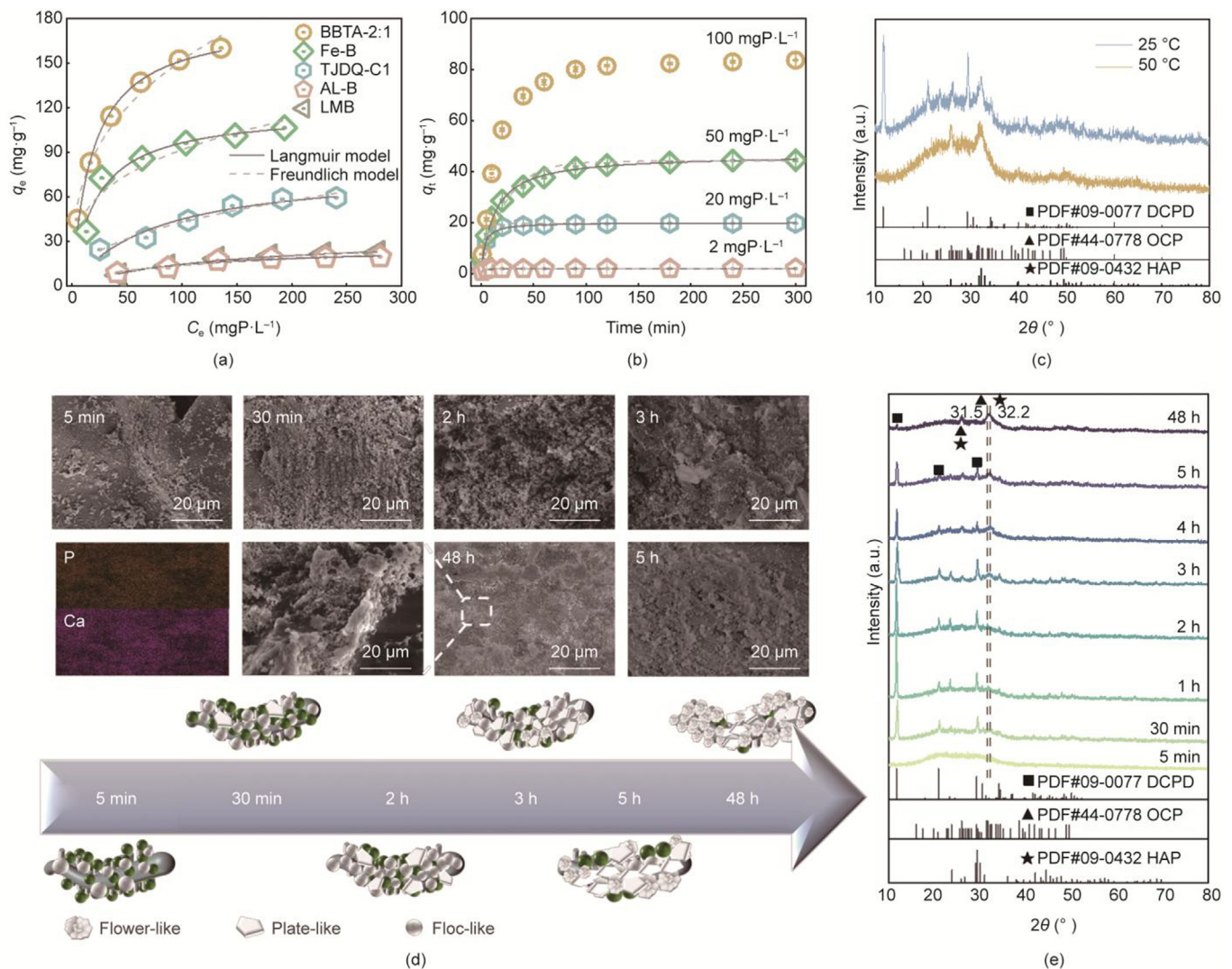
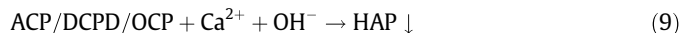
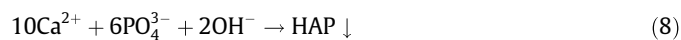
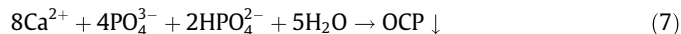
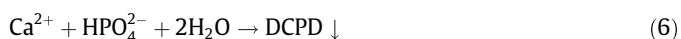


Fig. 3. (a) Adsorption isotherm of phosphate onto Fe-B, TJDQ-C1, Al-B, LMB, and BBTA-2:1 accompanied by models fitting; (b) adsorption kinetics of phosphate onto BBTA-2:1 at different phosphate concentrations accompanied by models fitting; (c) XRD patterns of BBTA-2:1 recovered products at 25 and 50°C ; (d, e) SEM images with (d) EDS mapping and (e) XRD patterns of BBTA-2:1 recovered products over time; (f) schematic diagram of Ca-P precipitates evolution.

surface precipitation; Fig. 3(c) [31]. Moreover, the improved adsorption capacity (4.66%) and rate (13.13%) induced by higher temperature (50 °C compared to 25 °C) represented the acceleration of biomimetic mineralization and HAP crystallization conversion (Fig. S10 and Tables S10 and S11 in Appendix A) [35]. Based on this, the calculated thermodynamic parameters according to Arrhenius and Van't Hoff equations quantified that the phosphate adsorption (biomimetic mineralization) of BBTA-2:1 was a low-energy barrier, spontaneous, and endothermic process, evidenced by the low E_a requirement (2.43 kJ·mol⁻¹), negative ΔG , and positive ΔH (20.59 kJ·mol⁻¹) (Fig. S11 and Table S12 in Appendix A) [36,37]. The positive ΔS (82.72 J·mol⁻¹·K⁻¹) suggested the heightened degree of P freedom at adsorption interface, which confirmed that the microenvironment was conducive to biomimetic evolution of Ca-P precipitates [38]. It was supported by the enhanced intensity of HAP characteristic peaks in recovered products obtained at 50 °C. These results underscored the amplification effect of biomimetic structure on adsorption performance of BBTA-2:1, highlighting its promising potential for efficient P resource recovery in practical applications.

3.3. Biomimetic evolution of Ca-P precipitates

Owing to the existence of multi-step crystallization, Ca-P precipitates may exist in diverse forms depending on the conditions during their nucleation-crystallization-growth processes [39]. Therefore, unveiling the formation times and biomimetic evolution pathways of various Ca-P precipitates during adsorption process was crucial for obtaining high-purity HAP, enabling efficient P resource recovery and reuse. As shown in Fig. 3(d), gradual morphological changes in the products from floc-like to plate-like and flower-like structures, as observed in SEM images, indicated the transformation into crystalline states [20]. Specifically, no crystalline XRD peaks were observed for the product obtained at 5 min (P-5 min), proving that ACP was produced as a precursor (Fig. 3(e)) [40]. In comparison, sharp diffraction peaks (11.8°, 21.1°, and 29.5°) observed in P-30 min suggested that DCPD crystals began to form in large quantities. The similar but more intense characteristic peaks of P-1 h indicated a more mature crystallinity. Subsequently, OCP was generated in P-2 h, as evidenced by diffraction peaks at 25.9° and 31.5° [41]. The well-matched peak at 32.2° observed between P-3 h and standard HAP pattern confirmed the formation of HAP. Notably, the peak at 25.9° may reflect both OCP and HAP [41]. Although characteristic peaks of ACP, DCPD, and OCP persisted, HAP peaks became more pronounced in the recovered products with extended adsorption times (4 and 5 h), indicating a gradual precursor transformation to thermodynamically stable HAP. The purer HAP signals and weaker signals from other Ca-P phases in P-48 h further substantiated this observation. The peak intensities corresponding to phosphates in the FT-IR spectra also increased with prolonged adsorption time, in accordance with Ostwald's rule (Fig. S12 in Appendix A) [20,40]. Overall, the biomimetic evolution of Ca-P precipitates mainly followed the ACP-DCPD-OCP-HAP sequence, and the final predominant product was HAP, as summarized in Fig. 3(f). Importantly, the biomimetic evolution of Ca-P precipitates from amorphous to crystalline structures required less time and produced HAP under milder conditions, in comparison with other studies summarized in Table S13 in Appendix A. This demonstrated enhanced P recovery from wastewater and a high potential for resource reuse, highlighting the benefits of biomimetic biomineralization. The involved reactions are summarized as Eqs. (5)–(9):



3.4. P recovery performance of BBTA

Considering the complexity of actual wastewater, the impacts of hydrochemical conditions (temperature, coexisting species, and pH) on P resource recovery performance of BBTA-2:1 were first evaluated. As shown in Fig. S13(a) in Appendix A, its adsorption capacity increased monotonically from 78.07 mg·g⁻¹ at 5 °C to 87.1 mg·g⁻¹ at 35 °C, due to the spontaneous endothermic nature of biomimetic mineralization process. Benefiting from low E_a demand, BBTA-2:1 exhibited minimal performance fluctuations at low temperatures, showing its impressive temperature adaptability. Meanwhile, the weaker coordination affinities of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, and K⁺ (100 mg·L⁻¹) with Ca²⁺ or phosphate had minor impacts (<12.5%) on phosphate adsorption of BBTA-2:1 (Figs. S13(b) and (c)). Presence of CO₃²⁻ resulted in a 27% reduction in adsorption capacity, given the competitive formation of CaCO₃. Notably, despite this competition, solubility product constants (K_{sp} , 25 °C) of the related products followed the order of CaCO₃ (3.4×10^{-9}) > OCP (5.7×10^{-49}) > HAP (6.3×10^{-59}), proving higher priority of Ca-P precipitates. Although DCPD (1.0×10^{-7}) had a higher K_{sp} than CaCO₃, it would gradually evolve into HAP due to the dissolution-recrystallization during biomimetic evolution process [40]. In comparison, coexistence of Ca²⁺ (4.1%) and Mg²⁺ (0.9%) led to enhanced adsorption capacity by providing additional binding sites. Even under co-interference of all anions (or cations), BBTA-2:1 still adsorbed 55.03 mg·g⁻¹ (81.53 mg·g⁻¹) of P, exhibiting remarkable anti-interference performance. Moreover, BBTA-2:1 retained 78.65%–97.27% of its initial adsorption capacity, even when interfered with 20–100 mg·L⁻¹ of HA (Fig. S13(d)). This effect was attributed to the protection of Ca sites through the electrostatic interactions between organic carrier and HA.

Moreover, adsorption capacity of BBTA-2:1 gradually increased with pH, which exhibited a significant rise between pH 4 and 6, and reached a maximum of 88.37 mg·g⁻¹ at pH 10 (Fig. 4(a)). The pH of post-adsorption solutions displayed increase (pH ≤ 4) and decrease (pH ≥ 6) changes (ΔpH), respectively, and the degrees were positively correlated with adsorption capacity, such as maximum value of $\Delta\text{pH}_{10} = -3.49$ (Fig. S14(a) in Appendix A). Given the diverse pH conditions in actual wastewater, and their critical influence on phosphate species and material electronegativity, the adsorption performance and mechanism of BBTA-2:1 were analyzed under typical acidic (pH 4) and alkaline (pH 10) conditions to reveal the pH adaptability of biomimetic mineralization (Fig. S14(b)) [42]. Specifically, the appearance of new peaks related to phosphates in the XPS and FT-IR spectra initially demonstrated successful adsorption at pH 4 and 10 (Fig. S15 in Appendix A) [34]. At pH 4, preferable Pseudo-first-order kinetic model fitting and absence of crystal formation in the recovered products revealed that the physical adsorption dominated process did not involve surface precipitation and mineralization (Figs. 4(b) and (c) and Table S14 in Appendix A). The increased solution pH ($\Delta\text{pH} > 0$) and weakened -OH peak ($\sim 3400 \text{ cm}^{-1}$) reflected the phosphate adsorption via ligand exchange [43]. Electrostatic attraction also played an important role, as proven by the opposite potentials of BBTA-2:1 (>0 mV) and H₂PO₄⁻ (main species of phosphates, <0 mV; Fig. S16 in Appendix A) [13]. In comparison, preferable Pseudo-second-order kinetic model fitting and no-interference of electrostatic repulsion on adsorption performance suggested the existence of chemical adsorption at pH 10 [44]. The decreased

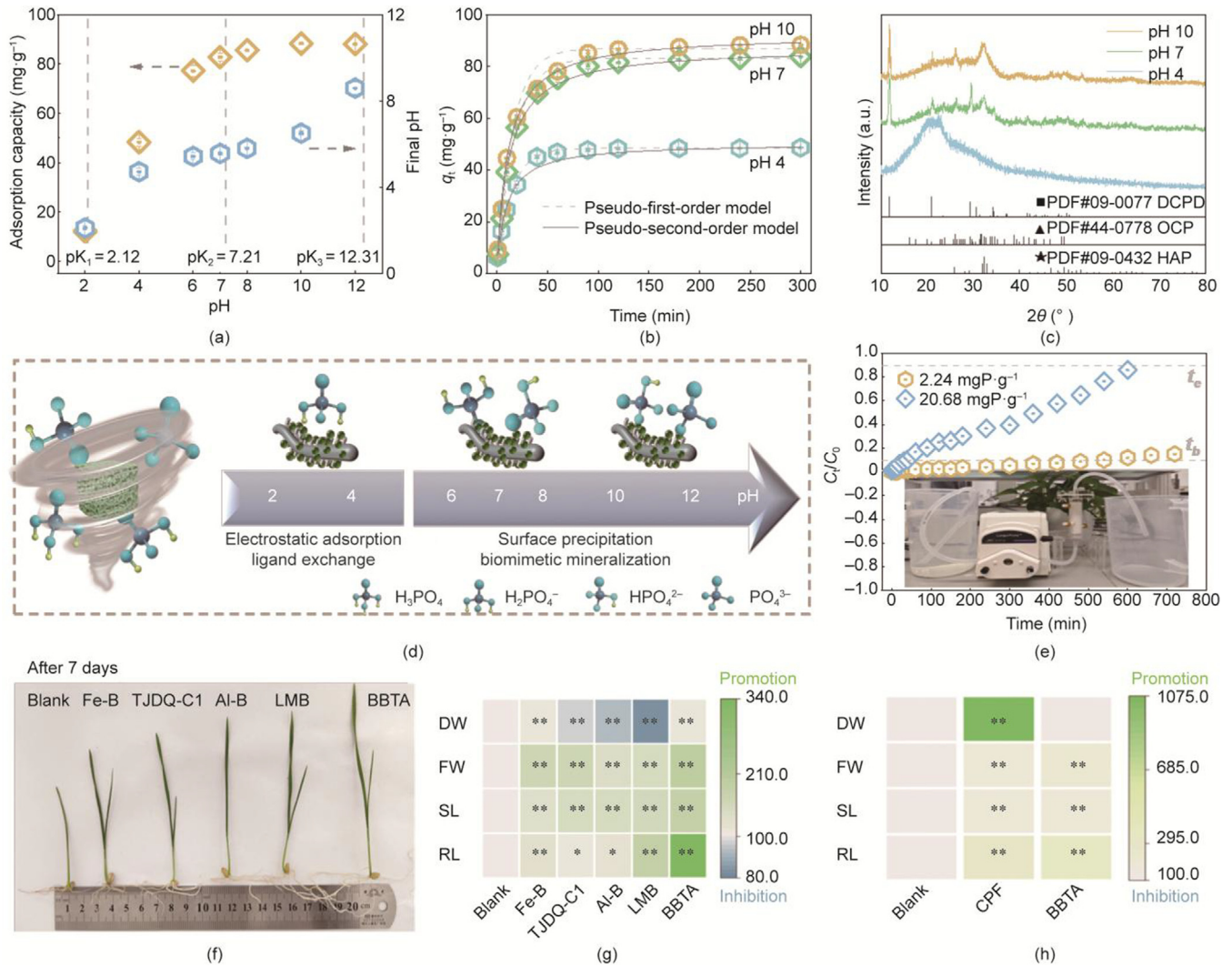


Fig. 4. (a) Impact of initial pH conditions on adsorption capacity of BBTA-2:1 and final pH value; (b) adsorption kinetics of phosphate onto BBTA-2:1 at different pH; (c) XRD patterns of BBTA-2:1 recovered products at different pH; (d) schematic diagram of recovered mechanisms of BBTA-2:1 at different pH; (e) residual phosphate concentrations in effluent during actual wastewater treatment under fixed-bed conditions using BBTA-2:1; (f) picture of wheats fed by BBTA-2:1 recovered products and controls (blank, Fe-B recovered products, TJDQ-C1 recovered products, Al-B recovered products, and LMB recovered products) after 7 d, respectively; (g) significant differences in weights and lengths of wheats cultured by BBTA-2:1 recovered products and controls after 7 d, respectively; (h) significant differences in weights and lengths of wheats cultured by BBTA-2:1 recovered products from actual wastewater treatment, blank, and commercial P-fertilizer (CPF) after 7 d, respectively. DW, FW, SL, and RL are dry-weight, fresh-weight, shoot-length, and root-length, respectively.

solution pH ($\Delta\text{pH} < 0$) from OH^- consumption, and abundant Ca-P precipitates (DCPD, OCP, and HAP) in recovered products highlighted the dominant role of surface precipitation and biomimetic mineralization. Meanwhile, the higher intensities of characteristic peaks in XRD and FT-IR spectra, compared to those at pH 7, emphasized the facilitative effect of an appropriate increase in alkalinity on biomimetic mineralization. Notably, excessively high alkalinity (pH 12) would present slightly adverse results owing to the competitive precipitation of excessive OH^- and the shielding-effect of active sites by locally induced large particles. In summary, it was inferred that BBTA-2:1 primarily adsorbed phosphate through electrostatic interactions and ligand exchange when $\text{pH} < \text{pH}_{\text{pzc}}$, whereas surface precipitation and biomimetic mineralization were mainly responsible for this process across the more commonly encountered pH range (from weakly acidic to strongly alkaline), as shown in Fig. 4(d) [45]. The moderately high temperature (50°C) and alkalinity (pH 10) conditions were critical for enhancing crystallization kinetics.

Fix-bed operation experiments were further conducted to illustrate the applicability of BBTA-2:1 for actual P resource recovery. Results showed that BBTA-2:1 could ensure that the effluent quality from fix-bed unit met the water framework directive standard (0.1 mgP L^{-1}) within 90 min, and continue to function about 720 min for synthetic wastewater (20 mgP L^{-1}) without reaching exhaustion time (t_e , when effluent-to-influent concentration ratio (C_t/C_0) > 0.9) (Fig. S17 in Appendix A). More importantly, BBTA-2:1 also maintained efficient phosphate adsorption toward the actual effluent (pH 8.37) from a phosphating enterprise in Guizhou, China, which contained multiple interfering substances (Table S15 in Appendix A). As the influent concentration decreased from 20.68 to 2.24 mgP L^{-1} , the breakthrough curve became gentler with a longer breakthrough time (t_b , ~ 540 min when $C_t/C_0 < 0.1$) (Fig. 4 (e)). The effluent P level remained stable at 0.336 mgP L^{-1} until 720 min, far from reaching performance depletion, highlighting the satisfactory applicability of BBTA-2:1 for P resource recovery from actual wastewater.

3.5. Resource reuse of recovered products

To highlight its advantages in resource reuse, P-sensitive wheat was cultivated using BBTA-2:1 recovered products and compared with typical commercial adsorbents (Fe-B, TJDQ-C1, Al-B, and LMB) and a blank (Fig. S18 in Appendix A). Owing to moisture evaporation and shrinkage of cellular structures, the dry-weights (<0.036 g) of all wheat varieties were uniformly consistent. After 3 d, the wheat cultivated with BBTA-2:1 recovered products exhibited more vigorous growth compared to the controls, with a 1.18 to 1.87 times increase in fresh-weight, 1.30 to 1.79 times increase in root-length, and 1.12 to 1.73 times increase in shoot-length (Fig. S19 in Appendix A). The gap increased with the extension of the cultivation time (7 d), exhibiting impressive fertilizer efficiency (Figs. 4(f) and (g)). Notably, their root length (11.9 cm, 7 d) conspicuously surpassed that of other controls, owing to the enhanced root differentiation facilitated by additional Ca supply.

Slow-release experiments were conducted to determine the reasons for the satisfactory fertilizer efficiency of BBTA-2:1 recovered products. The P release rate in deionized water within 24 h was only 1.64%, far below the $<15\%$ standard for slow-release fertilizers (Fig. S20(a) in Appendix A) [14,46]. Fine-scale monitoring within 12 h exhibited certain fluctuations in the P release rate, which indicated that the re-adsorption of Ca sites contributed to the nutrient fixation (Fig. S20(b)). Low P (2.03%) and Ca (0.3%) release capacities even after 7 d further indicated its outstanding nutrient fixation ability. Notably, the wheat cultivated with BBTA-2:1 recovered products achieved a P absorption rate of $\sim 61.2\%$ after 7 d, significantly surpassing the value in slow-release experiment. These results strongly demonstrated BBTA's capacity to prevent resource re-loss while promoting targeted absorption by plants through rhizosphere microorganisms. Moreover, the accumulation of excess environmentally unfriendly metals during fertilizer reuse would bury safety hazards for wheat growth and subsequent P cycle remodeling. ICP-OES analysis exhibited that 0.194 wt% Fe and 0.131 wt% Al were present in wheat (7 d) cultivated by Fe-B and Al-B recovered products, respectively, highlighting obvious security implications (Table S16 in Appendix A) [47]. Overall, compared to the commonly used commercial adsorbents, BBTA-2:1 showed an unparalleled advantage in P resource reuse capacity.

Importantly, the products recovered from actual wastewater treatment using BBTA-2:1 under fixed-bed conditions (540 min) also remarkably promoted wheat growth within 7 d. Compared to the blank, the cultivated wheats exhibited 1.99, 3.44, and 1.84 times increase in fresh-weight, root-length, and shoot-length, respectively (Fig. 4(h) and Fig. S21 in Appendix A). Even in relation to the commercial P-fertilizer, it exhibited superior effectiveness in promoting wheat growth. The high-purity HAP in the recovered products, resulting from satisfactory adsorption capacity of BBTA-2:1 and rapid biomimetic evolution of Ca-P precipitates, was responsible for these improvements. These results further demonstrated the outstanding capacity of BBTA-2:1 for P resource integration, facilitating the reutilization of waste phosphate in a high-value form. In summary, only BBTA-2:1 achieved satisfactory P cycle remodeling, whereas commercial adsorbents were limited by their P resource recovery and/or reuse capabilities.

3.6. Evaluation of P cycle remodeling

Constrained by global economic and material limitations, BBTA-2:1 yield was estimated based on the annual availability of cost-free waste biomass. Global annual production of abandoned plants and silkworm cocoons amounts to ~ 140 Gt (1 Gt = 10^9 t) and ~ 10 Mt (1 Mt = 10^6 t), with CE and SF contents comprising $\sim 10\%$ and $\sim 75\%$, respectively [48,49]. The availability of these highly

active waste resources, combined with the novel biomimetic engineering of BBTA-2:1, enabled engineered production of this adsorbent. Consequently, BBTA-2:1 could achieve an annual output of ~ 29.9 Mt, while simultaneously mitigating the agricultural waste burden. P-footprint analysis indicated that, in the face of ~ 23.5 Mt of global P loss from industrial wastewater, application of BBTA-2:1 could achieve ~ 5.4 Mt of fertilizer recovery, thereby promoting $\sim 22.1\%$ of P resource regeneration. Due to the fulfillment of plant growth requirements, a significant reduction ($\sim 26.6\%$) in fertilizer production could be achieved by substituting traditional chemical-based fertilizers with BBTA-2:1 recovered products. Considering that fertilizer production accounted for $\sim 90.8\%$ of global total PR-input, the widespread application of BBTA-2:1 could lead to a ~ 10.2 Mt decrease in waste output, including ~ 5.2 Mt ($\sim 22.1\%$) of wastewater and ~ 5.5 Mt (24.6%) of solid waste [4]. These reductions not only alleviated existing pollution but also mitigated the likelihood of future environmental contamination. More importantly, the annual PR mining output was anticipated to decrease by $\sim 24.2\%$, in an effort to conserve non-renewable P resources and promote a more sustainable resource utilization (Fig. 1(b) and Fig. 5(a)) [4]. This strategy, which enhanced the valorization of waste P into nutrient-rich fertilizer, was seamlessly integrated with circular economic principles. Overall, the application of BBTA-2:1 derived from plants and returned to plants was expected to establish a green closed-loop system for pollution mitigation and resource recovery within the ecological environment, highlighting its considerable feasibility for P cycle remodeling (Fig. 5(b)).

3.7. Sustainability of P cycle remodeling

Given that environmental friendliness was a prerequisite for sustainable applications, the toxicological effects of BBTA-2:1 were evaluated in combination with the typical commercial adsorbents (Fe-B, TJDQ-C1, Al-B, and LMB) by monitoring OD_{600} and CFU indicators of *E. coli* growth (Fig. 5(c)). At the same dosage, OD_{600} results showed that BBTA-2:1 had an 11.22% promotion effect on *E. coli* growth, second only to LMB, whereas other commercial adsorbents exhibited inhibitory effects. According to CFU analysis, BBTA-2:1 still demonstrated negligible toxicity. Notably, all four commercial adsorbents showed severe toxicity after adjusting the dosage based on phosphate adsorption capacity, with *E. coli* inhibition rates (OD_{600}) of 51.30% (Fe-B), 23.52% (TJDQ-C1), 56.94% (Al-B), and 52.95% (LMB), respectively. CFU analysis also provided evidence for this, showing inhibitory effects (7.30%–18.09%) of commercial adsorbents (except LMB) on *E. coli* growth. These data indicated that BBTA-2:1 exhibited minimal toxicity, and could be safely applied to engineered P cycle remodeling.

As discussed in Note S2 in Appendix A, the adsorbent cost was calculated by determining the ratio of production cost (chemicals, water, and electricity) to Q_{max} to assess its economic feasibility. The adsorbent cost of 19.95 USD·kgP⁻¹ for BBTA-2:1 was highly competitive compared to Fe-B (12.05 USD·kgP⁻¹), TJDQ-C1 (21.09 USD·kgP⁻¹), Al-B (177.99 USD·kgP⁻¹), and LMB (114.17 USD·kgP⁻¹) (Fig. 5(d)). Importantly, BBTA-2:1 could additionally achieve high-quality fertilizer (~ 0.03 USD·kg⁻¹) recovery while reducing waste adsorbent disposal cost by ~ 0.37 USD·kg⁻¹ and agricultural waste disposal cost by ~ 0.11 USD·kg⁻¹, further enhancing its economic benefits [50–52].

The OSE was further implemented to assess the sustainability of five adsorbents across environmental, economic, and social dimensions [53]. Based on eight indicators involved in P cycle remodeling (environmental friendliness, preparation simplicity, waste utilization, treatment efficiency, cost, degradability, scalability, and public acceptability), OSE values of BBTA-2:1, Fe-B, TJDQ-C1, LMB, and Al-B were 87.5%, 75.0%, 70.8%, 66.7%, and 62.5%, respectively

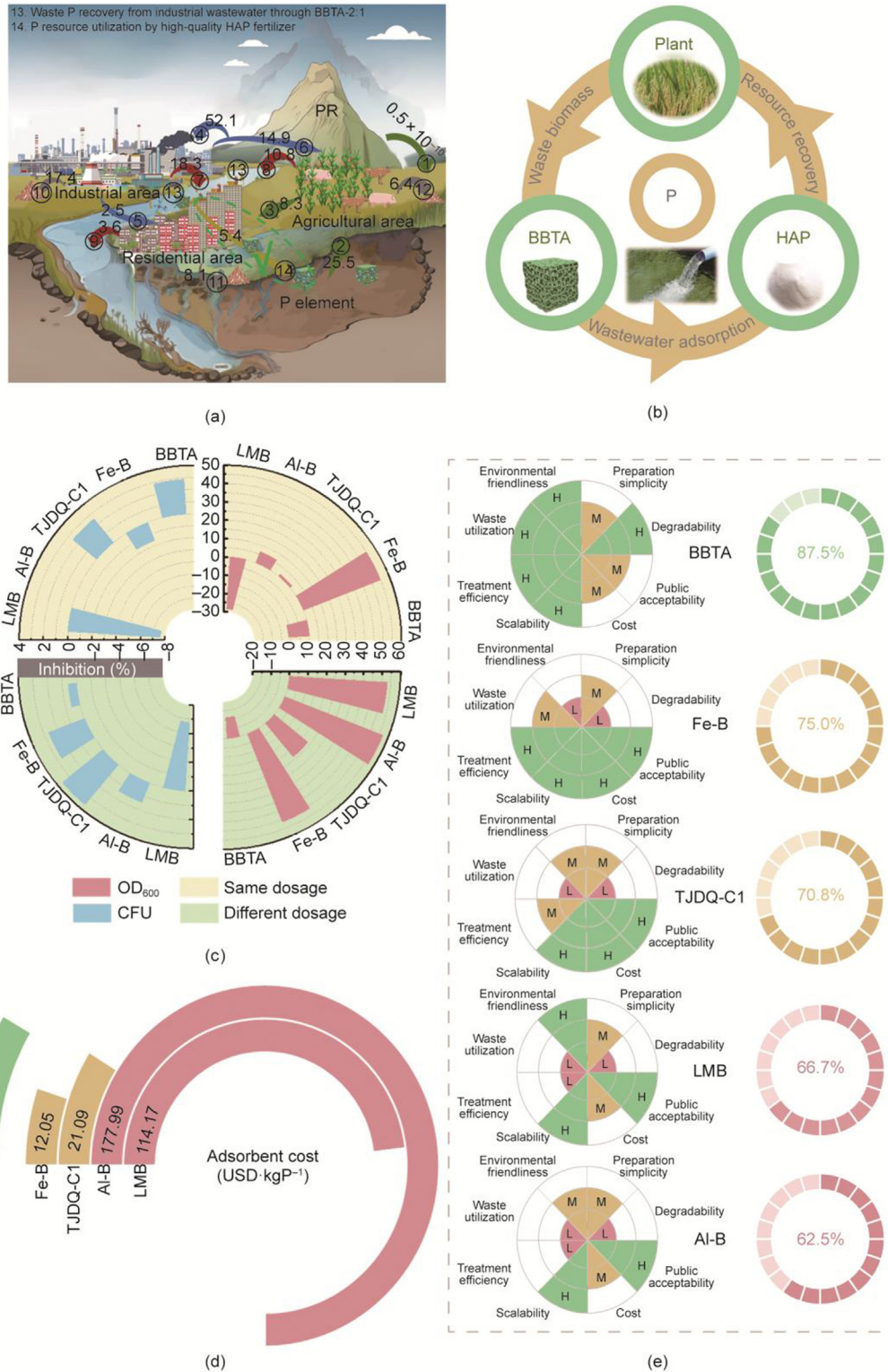


Fig. 5. (a) Schematic diagram of simplified P cycles (10^6 t a^{-1}) with BBTAs-2:1 assisted remodeling; (b) green closed-loop system for P pollution alleviation and P resource recovery constructed by BBTAs-2:1; (c) *E. coli* inhibition rates of BBTAs-2:1, Fe-B, TJDQ-C1, AI-B, and LMB at same and different dosages; (d) adsorbent costs of BBTAs-2:1, Fe-B, TJDQ-C1, AI-B, and LMB in P recovery process; (e) OSE analyses and their comprehensive scores of BBTAs-2:1, Fe-B, TJDQ-C1, AI-B, and LMB using eight indicators involved in P cycle remodeling.

(Fig. 5(e) and Note S3 in Appendix A). Experimental data highlighted the advantages of BBTAs-2:1 in terms of environmental friendliness ($p = 3$) and treatment efficiency ($p = 3$). Besides, biomass feedstocks were widely available, and BBTAs-2:1 could also re-enter the Earth's carbon cycle while assisting in P cycling (costs

($p = 2$), degradability ($p = 3$), and waste utilization ($p = 3$)). Moreover, successful fixed-bed experiments with BBTAs-2:1 laid the foundation for scaled-up operations, thereby facilitating the valorization of waste P for public recycling (public acceptability, $p = 2$). Overall, BBTAs-2:1 exhibited robust multifunctional

properties without critical limitations (e.g., degradability in controls), underscoring its sustainability for P cycle remodeling.

4. Conclusions

In summary, our proposed P cycle remodeling strategy based on the novel BBTA-2:1 offered a practical scenario for sustainable development of P resources. Biomimetic engineering of BBTA-2:1 using natural CE and SF polymers was simple and easily scalable. The developed BBTA-2:1 exhibited an ordered stable conformation and high interfacial activity for maximizing site utilization efficiency and reinforcing biomimetic evolution. The P cycle remodeling strategy simultaneously demonstrated significant advantages for waste P recovery from industrial wastewater, fertilizer reuse in agriculture, resistance to environmental interference, and environmental friendliness. P-footprint analysis revealed that this strategy led to ~22.1% of P resource regeneration and ~24.2% of PR extraction reduction, exhibiting a leading P cycle remodeling effect. Moreover, utilizing waste biomass as feedstock for BBTA-2:1 preparation enabled this strategy to achieve resource recovery and waste reduction from multiple perspectives, accompanied by significant cost reduction. This work laid the foundation for further exploration and optimization of valorization of waste P into high-quality nutrient-rich fertilizer, with immense potential for addressing the global challenge of P cycle in a sustainable manner.

CRediT authorship contribution statement

Lidong Feng: Writing – original draft, Investigation, Data curation. **Jiamin Dai:** Software, Formal analysis. **Long-Fei Ren:** Writing – review & editing, Funding acquisition. **Haoyu Sun:** Writing – review & editing, Formal analysis. **Liang Tang:** Software, Conceptualization. **Jiahui Shao:** Writing – review & editing, Supervision, Funding acquisition. **Minghong Wu:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eng.2025.12.033>.

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