

Supplementary Material (SM)

Sustainable Approach for The Removal of Cu(II) from Aqueous Solutions Using Lotus Seedpod-alginate Composite Biosorbents

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Supplementary Text S1 Chemicals and reagents

Sodium alginate ((C₆H₇NaO₆)_n, 86%), calcium chloride dihydrate (CaCl₂·2H₂O, 96%), ethanol (C₂H₅OH, 96%), sulfuric acid (H₂SO₄, 98%), copper (II) sulfate pentahydrate (CuSO₄·5H₂O, 99%), ethylenediaminetetraacetic acid disodium (Na₂EDTA, 99%), sodium chloride (NaCl, 99.5%), potassium chloride (KCl, 99.5%), magnesium sulfate (MgSO₄·7H₂O, 99%) were prepared from Xilong (China). Besides, river water was collected from Hau River (Can Tho City, Vietnam) and was filtered to remove solids before use.

Supplementary Text S2 Synthesis of LSA bio-composite

Raw LS, collected at the local market, Can Tho City, Vietnam, was thoroughly washed to eliminate impurities, and subsequently oven-dried overnight. Then, raw LS was cut into about 1.0 cm in length and soaked in water at 100 °C for 2 h with a solid to liquid ratio of 1:20 (g mL⁻¹) (Li et al., 2025). This step was repeated several times to effectively remove sugars and other water-soluble organic compounds to obtain the water-soaked LS. Prior to the chemical or thermal treatment, the LS was dried and employed either with deionized water or sulfuric acid (Chen et al., 2018; Yankov., 2022). After reaction, the treated samples were rinsed to achieve a neutral pH and dried at 60 °C until a constant weight. Detailed treatment conditions were described in Supplementary Table S1.

The synthesis of LSA was conducted as follows: First, the treated LS was gradually introduced into the AG solution under a stirring speed of 400 rpm for 30 min. In the subsequent cross-linking step, the obtained suspension was dropwise into a CaCl₂ solution and kept for a specified duration. After filtering, washing and drying under freeze-drying conditions (-40 °C and 0.5 mbar) for 24 h, the bio-composites were obtained. Besides, the solution after the cross-linking stage was collected and analyzed the remained Ca²⁺ concentration (C_a, mg L⁻¹). The Ca²⁺ content attached to the bio-composite was determined as the Eq. S1):

$$\text{Content of Ca}^{2+} \text{ (mg g}^{-1}\text{)} = \frac{(C_i - C_a) \times V}{m} \quad (\text{Eq. S1})$$

whereas C_i (mg L⁻¹) was denoted as the initial concentration of Ca²⁺ solution. V (L) and m (g) were the volume of CaCl₂ solution used and the weight of LSA, respectively.

The LSA synthesis parameters including AG concentration (1.0-5.0%), CaCl₂ concentration (0.1-2.0%), cross-linking time (15-360 min), and a mass ratio of raw LS to AG (0.2:1.0 - 5.0:1.0, g g⁻¹), were investigated in this work (Supplementary Table S2). All the LSA synthesis experiments were conducted at room temperature.

Supplementary Text S3 Characterization

FTIR spectra were used for the identification of the characteristic functional groups associated with cellulose in both LS and AG by a Jasco instrument (Japan) in the range of 4,000–400 cm^{-1} . The surface morphology of LSA were imaged using a SEM (JCM 7000, Jeol, Japan), while the compositional mass percentage of LSA and LS was analyzed with TGA (Mettler Toledo, Switzerland). The concentrations of Ca^{2+} and Cu^{2+} ions were quantified using AAS (AA7000, Shimadzu, Japan). Specific surface area, pore diameter and pore volume of bio-composites were also assessed using BET method (TriStar II Plus, Micromeritics, US). Zeta potential was evaluated using dynamic light scattering (DLS, SZ100, Horiba, Japan).

Supplementary Text S4 Mechanical stability of LSA12

In this work, the stability of LSA12 materials was evaluated through two factors: the swelling in different pH solutions and the stability during agitation at the room temperature, based on published studies and adjusted accordingly (Li et al., 2016; Liu et al., 2021; Teow et al., 2018). First, the swelling test was conducted by immersing 0.2 g L^{-1} LSA12 in H_2O at the different pH values between 3 and 10. After 24 h absorption, the swollen LSA12 was collected, gently wiped to remove water at the material surface, and determined the actual weight. Subsequently, the mechanical stability under agitation was evaluated by adding LSA12 to H_2O at the conditions: dose of 2 g L^{-1} , stirring speed of 200 rpm at room temperature for different time (15–1440 min). The samples were then collected by filtration, freeze-dried at -40°C and 0.5 mbar for 24 h until constant weight, and weighed to calculate the weight loss. The swelling ratio (%) and the weight loss (%) were calculated using Eqs. S2 and S3:

$$\text{Swelling ratio (\%)} = \frac{W_s - W_i}{W_i} \times 100 \quad (\text{Eq. S2})$$

$$\text{Weight loss} = \frac{W_0 - W_t}{W_0} \times 100 \quad (\text{Eq. S3})$$

whereas W_i and W_s represented the mass of initial LSA12 and the mass of swollen LSA12. For the determination of weight loss, W_0 and W_t indicated the mass of the initial LSA12 and the mass of LSA12 at t time, respectively.

Supplementary Text S5 Adsorption experiments

A stock solution of Cu^{2+} ions at a determined concentration was prepared by dissolving an appropriate amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized water. The lower concentrations of Cu^{2+} solution were subsequently obtained by a serial dilution of the stock solution. For each adsorption experiment, a mixture of 0.05 g of LSA and 50 mL of Cu^{2+} solution was agitated at 200 rpm for a determined time. Following the adsorption process and subsequent filtration, the concentrations of Cu^{2+} in the initial and post-adsorbed solutions were detected using AAS. The experimental parameters, including adsorbent dosage (0.5–5.0 g L^{-1}), initial Cu^{2+} concentration (10–120 mg L^{-1}), and contact time (15–1,440 min), were investigated in this work. The AE (%) and AC (mg g^{-1}) were calculated using Eqs. S4–S5, respectively:

$$\text{AE} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (\text{Eq. S3})$$

$$\text{AC} = \frac{(C_0 - C_t) \times V}{m} \quad (\text{Eq. S4})$$

where V was denoted as the volume of Cu^{2+} solution (L) and m was the mass of LSA (g). C_0 and C_t were Cu^{2+} concentrations in the initial and post-adsorbed solutions (mg L^{-1}), respectively.

Furthermore, the competitive adsorption behavior of Cu^{2+} ions in the presence of coexisting ions (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) was assessed. To evaluate the thermodynamic properties of the composites, a procedure of these experiments was conducted as follows: A mixture of 0.05 g of adsorbent and 50 mL of Cu^{2+} solution (10–100 mg L^{-1}) was stirred at 200 rpm and different temperatures (30°C – 50°C) within 30 min. After filtration, the obtained liquid was determined the Cu^{2+} concentration by AAS. The thermodynamic parameters for the adsorption of Cu^{2+} onto LSA, calculated in Eqs. S6–S8, were used to clarify the thermodynamic nature of process:

$$\Delta G = -RT \ln K_L \quad (\text{Eq. S6})$$

$$\Delta H = -R \frac{T_1 T_2}{T_1 - T_2} \ln \left(\frac{K_{L1}}{K_{L2}} \right) \quad (\text{Eq. S7})$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{Eq. S8})$$

where R and T were denoted as the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$) and the absolute temperature (K), respectively. K_{L1} and K_{L2} were the respective Langmuir parameters at these two temperatures.

The Cu^{2+} leaching experimental series were conducted as follows: The LSA12- Cu^{2+} material after adsorption at the optimal condition was freeze-dried (-40°C and 0.5 mbar) for 24 h. The dried materials were then placed in deionized water for the Cu^{2+} leaching test at the conditions: dose of 2 g L^{-1} , stirring speed of 200 rpm, at room temperature and the agitation time range of 15-1440 min. The leached solution was collected after centrifuge and analyzed by AAS to determine the Cu^{2+} concentration (Yusop et al., 2026). The Cu leaching percentage (%) was determined as the Eq. S9:

$$\text{Cu leaching percentage (\%)} = \frac{C_{\text{leaching}}}{C_0 - C_t} \times 100 \quad (\text{Eq. S9})$$

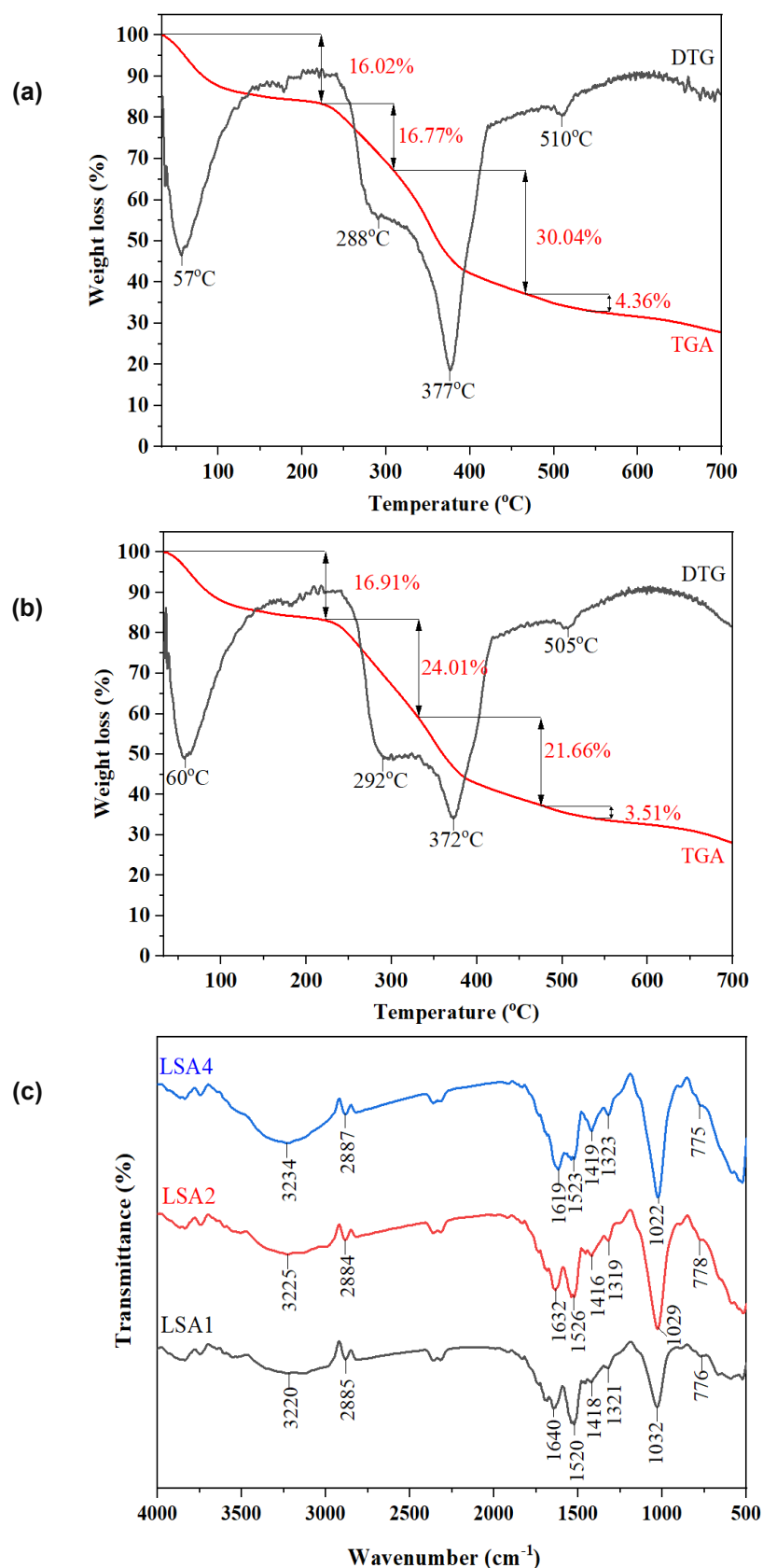
where C_{leaching} , C_0 and C_t were denoted as the Cu^{2+} concentration leached into deionized water (mg L^{-1}), the initial Cu^{2+} concentration (mg L^{-1}) in the fresh Cu^{2+} solution, and the Cu^{2+} concentration (mg L^{-1}) in the solution after the removal, respectively.

Supplementary Text S6 Regeneration of LSA

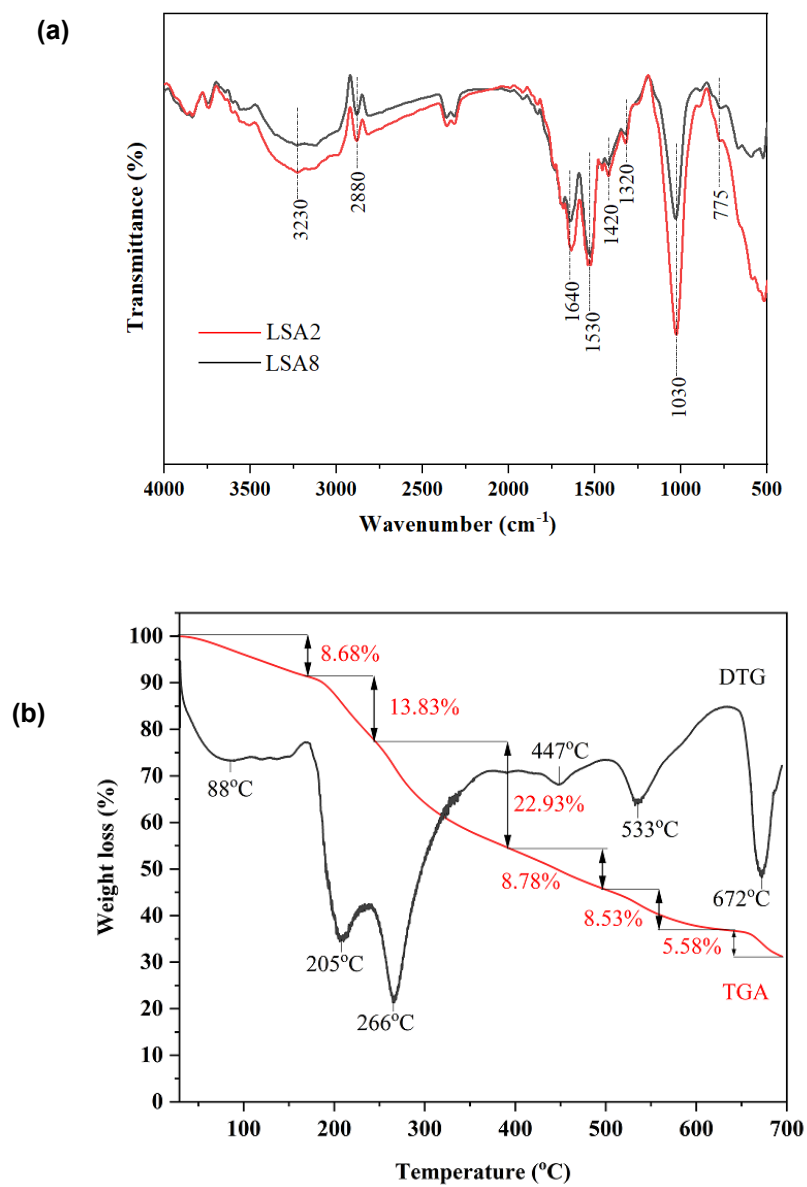
The reusability of LSA was evaluated using desorption conditions: 0.01 M desorption agent, a ratio of solid and solvent = $2:1 \text{ (g L}^{-1}\text{)}$ at a stirring speed of 200 rpm for 30 min [8, 9]. The effect of different desorbing agents was tested for the regeneration of the LSA12 composite, including H_2O , KCl , NaCl , HNO_3 , HCl , and EDTA . After regeneration process, the desorbed LSA was rinsed with deionized water and freeze-dried (-40°C and 0.5 mbar) for 24 h prior to use in the subsequent adsorption cycle. The AE after desorption and desorption efficiency (DE) of LSA were determined using Eqs. S4 and S10, respectively.

$$\text{DE (\%)} = \frac{C_d}{(C_0 - C_t)} \times 100 \quad (\text{Eq. S10})$$

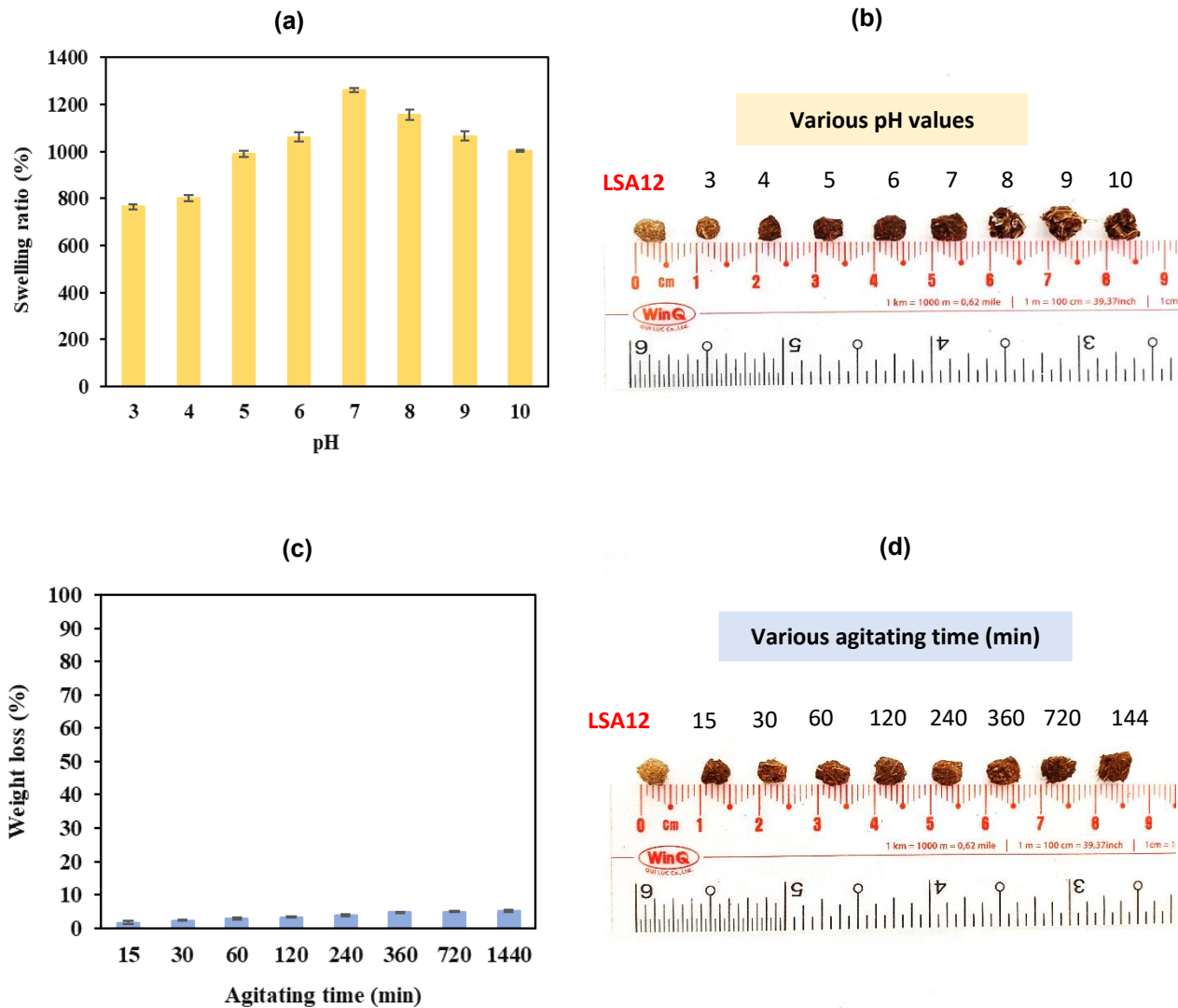
where C_d , C_0 and C_t were denoted as the Cu^{2+} concentration remained in solution after desorption, the initial Cu^{2+} concentration and the Cu^{2+} concentration at 30 min, respectively.



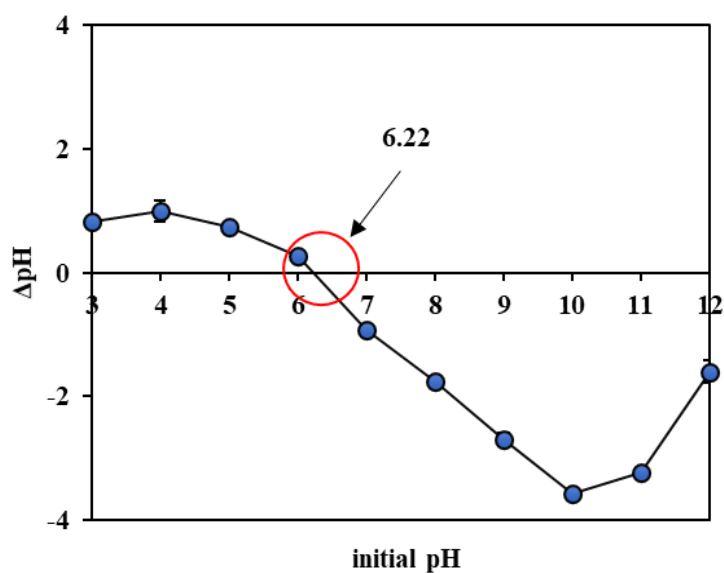
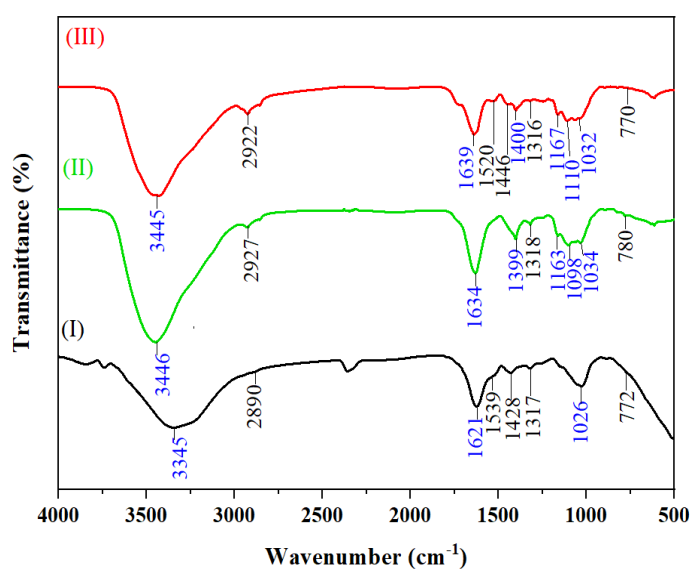
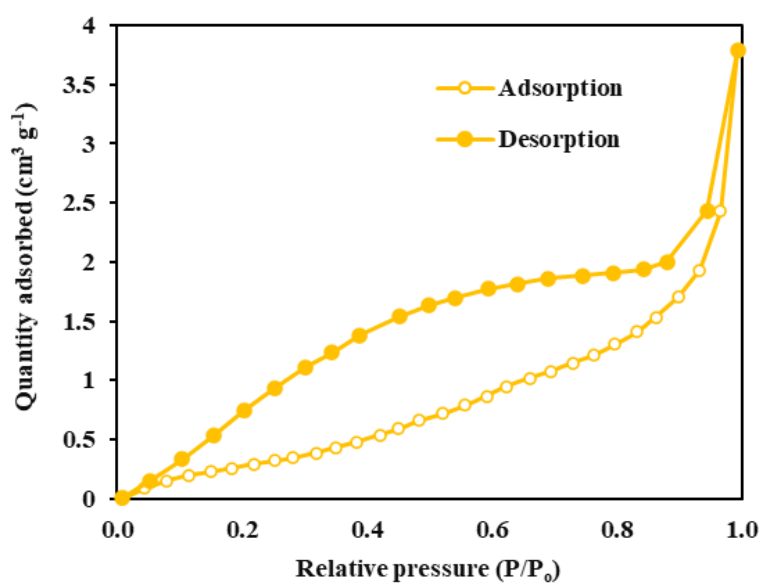
Supplementary Figure S1 TGA analysis of LSA1 (a) and LSA4 (b); FTIR spectra of LSA1, LSA2 and LSA4.

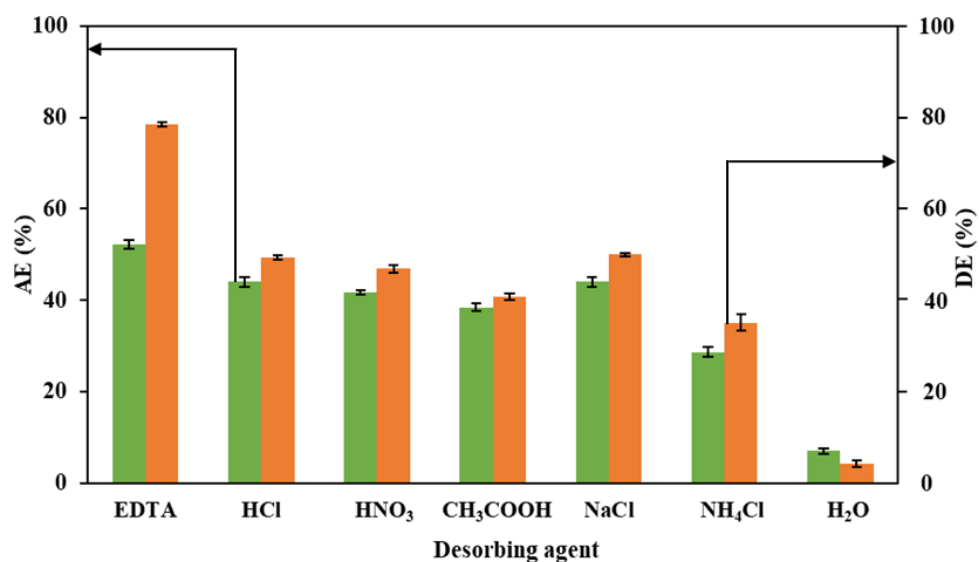


Supplementary Figure S2 FTIR spectra of LSA2 and LSA8 (a); TGA analysis of LSA16 (b).

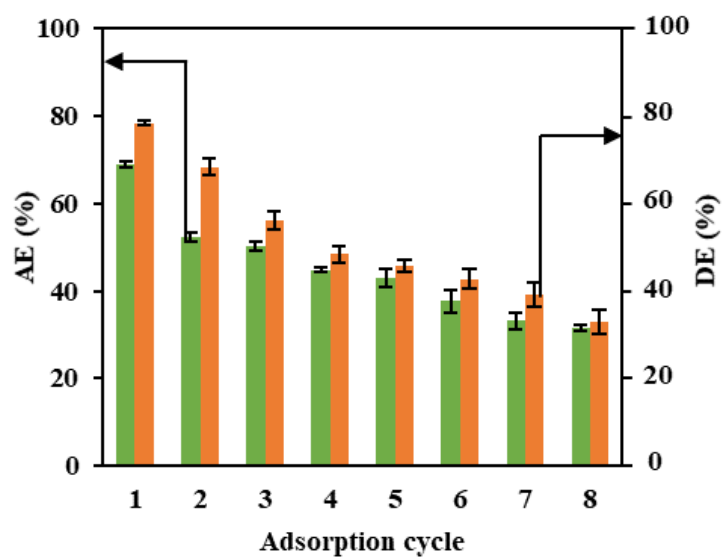


Supplementary Figure S3 Mechanical stability of LSA12: swelling ratio at various pH values (a); images of LSA12 after swelling at pH 3-10 (b); effect of the agitating time (c); and images of LSA12 after agitation from 15 min to 1440 min (d).

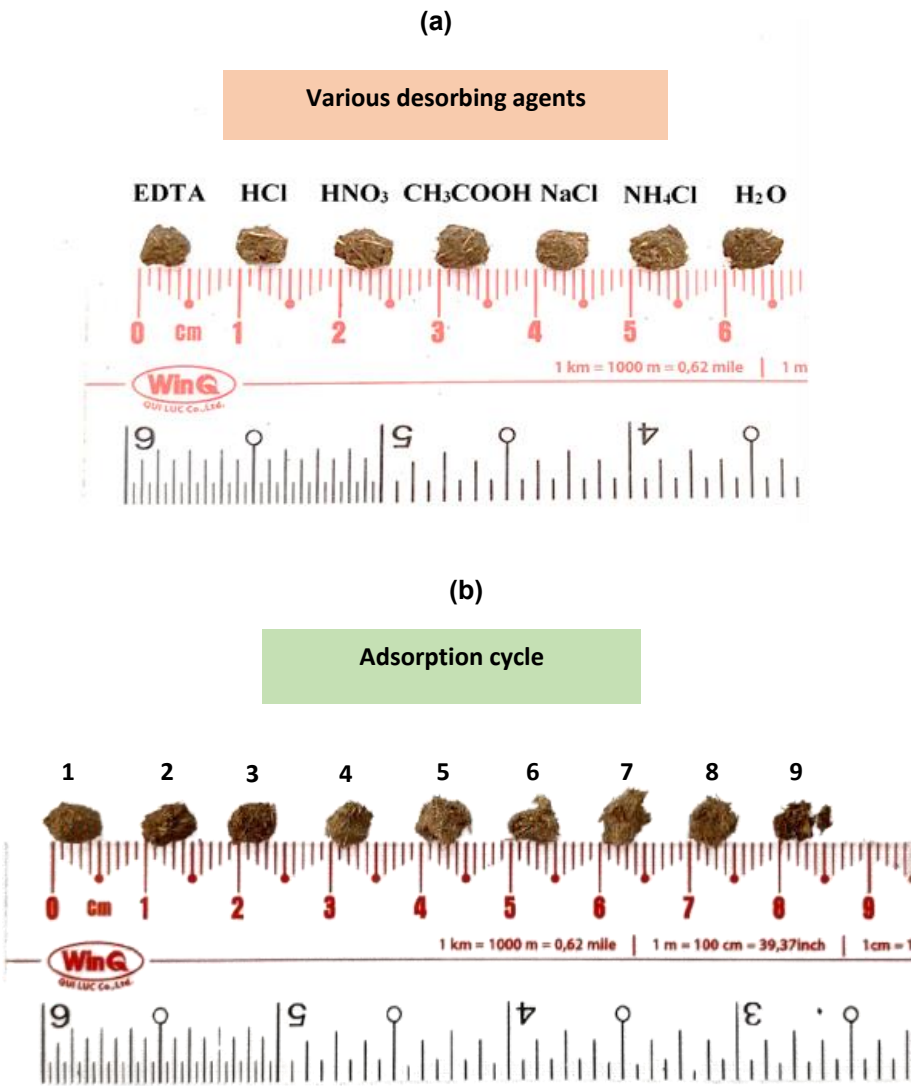
Supplementary Figure S4 pH_i value of LSA12.Supplementary Figure S5 FTIR spectra of fresh LSA12 (spectrum I), LSA12- Cu^{2+} (spectrum II), and regenerated LSA12 (spectrum III).Supplementary Figure S6 BET results of LSA12 after Cu^{2+} adsorption.



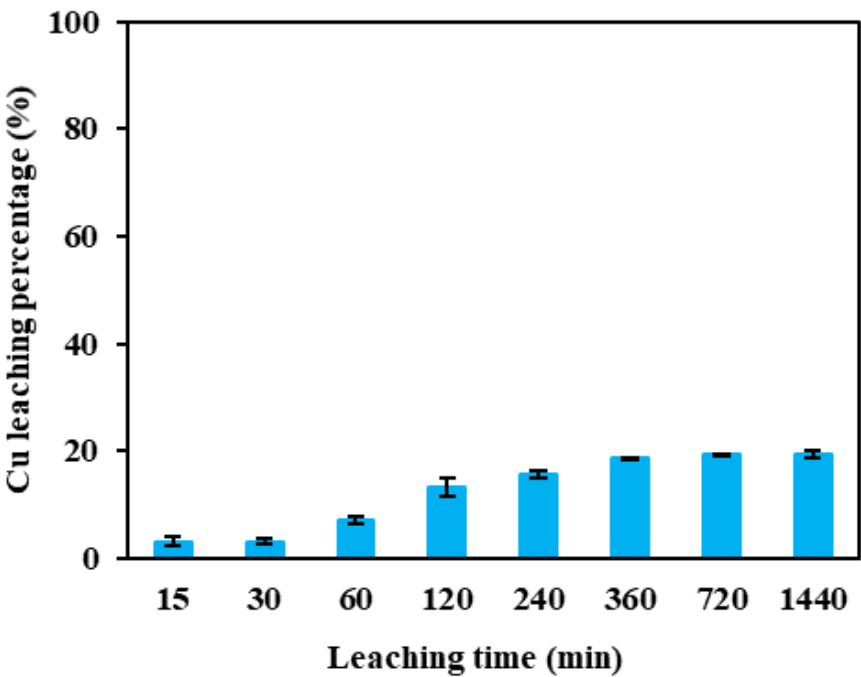
Supplementary Figure S7 The reusability of LSA12 at different desorbing agents



Supplementary Figure S8 The reusability of LSA12 through adsorption-desorption cycles.



Supplementary Figure S9 Images of LSA12 after regeneration at different desorption agents (a) and after adsorption-desorption cycles (b).



Supplementary Figure S10 Cu²⁺ leaching of LSA in deionized water after adsorption at 15-1,440 min, dose of 2 g L⁻¹, and stirring speed of 200 rpm (d).

Supplementary Table S1 Treatment conditions of LS using different solvents

Sample	Solvent	Condition	Solvent concentration (%)	LS : solvent (g mL ⁻¹)
LS1	Deionized H ₂ O	Conventional method at 90 °C and 30 min	-	1:5
LS2				1:10
LS3				1:15
LS4				1:20
LS5	Deionized H ₂ O	Subcritical treatment at 20 bar, 150 °C and 15 min	-	1:5
LS6				1:10
LS7				1:15
LS8				1:20
LS9	H ₂ SO ₄	Conventional method, 90 °C and 30 min	1.0	1:15
LS10			3.0	
LS11	H ₂ SO ₄	Subcritical treatment at 20 bar, 150 °C and 15 min	0.1	1:15
LS12			0.3	

Supplementary Table S2 The synthesis conditions of LSA bio-composite

Sample	AG (%)	CaCl ₂ (%)	Crosslinking time (min)	LS:AG (w/w)
LSA1	1.0	2.0	120	2.0 : 1.0
LSA2	1.5			
LSA3	2.0			
LSA4	3.0			
LSA5	4.0			
LSA6	5.0			
LSA7	1.5	0.1	120	2.0 : 1.0
LSA8		0.2		
LSA9		0.4		
LSA10		0.8		
LSA11		1.4		
LSA2		2.0		
LSA12	1.5	0.2	15	2.0 : 1.0
LSA13			30	
LSA14			60	
LSA8			120	
LSA15			360	
LSA16			15	0.2 : 1.0
LSA17				0.5 : 1.0
LSA18				1.0 : 1.0
LSA12				2.0 : 1.0
LSA19				5.0 : 1.0

Supplementary Table S3 The content of Ca^{2+} in the LSA composites at the different synthesis conditions

Sample	AG (%)	CaCl_2 (%)	Cross-linking time (min)	C_i (mg L^{-1})	C_a (mg L^{-1})	Ca^{2+} content (mg g^{-1})
LSA1	1.0	2.0	120	$19,456.59 \pm 350.67$	$17,158.65 \pm 472.44$	191.50 ± 39.37
LSA2	1.5				$15,913.51 \pm 429.49$	230.58 ± 23.86
LSA3	2.0				$15,609.82 \pm 607.39$	295.26 ± 35.79
LSA4	3.0				$15,407.35 \pm 350.67$	337.44 ± 29.22
LSA5	4.0				$15,366.86 \pm 515.38$	340.81 ± 42.95
LSA6	5.0				$15,215.01 \pm 558.33$	353.46 ± 46.53
LSA7	1.5	0.1	120	$1,046.80 \pm 29.32$	709.59 ± 20.73	18.73 ± 1.15
LSA8		0.2		$2,198.74 \pm 42.95$	$1,530.61 \pm 42.95$	35.43 ± 3.37
LSA9		0.4		$4,579.69 \pm 171.79$	$3,324.43 \pm 70.13$	65.24 ± 3.90
LSA10		0.8		$7,872.73 \pm 122.74$	$5,888.61 \pm 300.64$	110.23 ± 16.70
LSA11		1.4		$13,121.22 \pm 204.56$	$9,991.50 \pm 250.53$	173.87 ± 13.92
LSA2		2.0		$19,456.59 \pm 350.67$	$15,913.51 \pm 429.49$	230.58 ± 23.86
LSA12	1.5	0.2	15	$2,198.74 \pm 42.95$	$1,633.24 \pm 29.32$	30.60 ± 1.15
LSA13			30		$1,594.14 \pm 44.79$	33.59 ± 2.49
LSA14			60		$1,577.53 \pm 29.76$	34.67 ± 1.63
LSA8			120		$1,530.61 \pm 42.95$	35.43 ± 3.37
LSA15			360		$1,515.95 \pm 58.64$	37.93 ± 2.30

Supplementary Table S4 The change in Ca^{2+} concentration in the adsorption-desorption process

Cycle number	Initial Ca^{2+} concentration in LSA12 (mg g^{-1})	Ca^{2+} concentration in LSA12 (mg g^{-1})	
		LSA12 after adsorption	LSA12 after desorption
1	30.60 ± 1.15	28.67 ± 0.24	25.63 ± 0.35
2		24.12 ± 0.13	21.36 ± 0.15
3		20.38 ± 0.33	18.48 ± 0.27
4		17.80 ± 0.22	16.14 ± 0.37
5		15.84 ± 0.25	14.48 ± 0.13
6		14.14 ± 0.25	13.01 ± 0.15
7		12.73 ± 0.52	11.91 ± 0.27
8		11.61 ± 0.42	11.28 ± 0.13

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