

Supporting Information

Mechanism study on the removal of Cd²⁺ and acetamiprid from wastewater treatment plant effluent by PMS activated by tobacco stem biochar under humic acid induction

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S1. Adsorption isotherm

In this work, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were used to describe the experimental results in 3.2.6 to explore the adsorption mechanism. The linear equation of the Langmuir (1), Freundlich (2) Temkin (3) and Dubinin-Radushkevich (4) isotherm model

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$$

(1)

$$q_e = k_F C_e^{1/n} \tag{2}$$

$$q_e = \frac{RT}{b} \ln(a C_e)$$

(3)

$$\ln q_e = \ln q_{\max} - K \varepsilon^2 \tag{4}$$

where q_e and q_{\max} are the amounts and maximum amounts of Cd (II) adsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), respectively; C_e is the equilibrium concentration of adsorbate ($\text{mg}\cdot\text{L}^{-1}$); K_L and K_F are the Langmuir and Freundlich adsorption coefficient ($\text{L}\cdot\text{mg}^{-1}$), respectively; ε is adsorption potential; b is the Temkin constant ($\text{J}\cdot\text{mol}^{-1}$); and a is the Temkin equal temperature constant ($\text{L}\cdot\text{g}^{-1}$).

$$R_L = \frac{1}{1 + K_L C_o}$$

(5)

K_L is the Langmuir adsorption coefficient ($\text{L}\cdot\text{mg}^{-1}$), C_o is the initial concentration of adsorbate ($\text{mg}\cdot\text{L}^{-1}$)

S2. Adsorption kinetics

Pseudo-first-order kinetic model (6), pseudo-second-order kinetic model (7), and intra-particle diffusion (8) were used to perform nonlinear fitting to explore the adsorption kinetics characteristics.

$$q_t = q_e(1 - e^{-K_1 t}) \quad (6)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$$

(7)

$$q_t = k_3 t^{1/2} + C \quad (8)$$

where q_e and q_t are the amounts of Cd^{2+} (mg g^{-1}) adsorbed on the adsorbent at equilibrium and time t , respectively; while t denotes the adsorption time (min); K_1 represents the pseudo-first-order rate constant (min^{-1}); K_2 is the pseudo-second-order rate constant (g mg^{-1}

min⁻¹), K_3 is the intra-particle diffusion rate constant (mg g⁻¹ min^{-1/2}).

S3. Method for determining pH_{PZC}

By potentiometric titration of the catalyst surface, its surface potential can be measured at different pH values. By plotting the relationship curve between surface potential and pH value (zeta pH plot), the pH value corresponding to zero potential can be found, which is the zero point charge.

S4. Regeneration experiment of materials

Firstly, the used catalyst was subjected to ultrasonic cleaning using ultrapure water, H₂SO₄ (1mM), and NaOH (1mM) sequentially for 45 minutes to remove impurities and oxides on the surface; Secondly, heat treat the catalyst at 450 °C for 2 hours to remove residual organic compounds and reaction products on the catalyst.

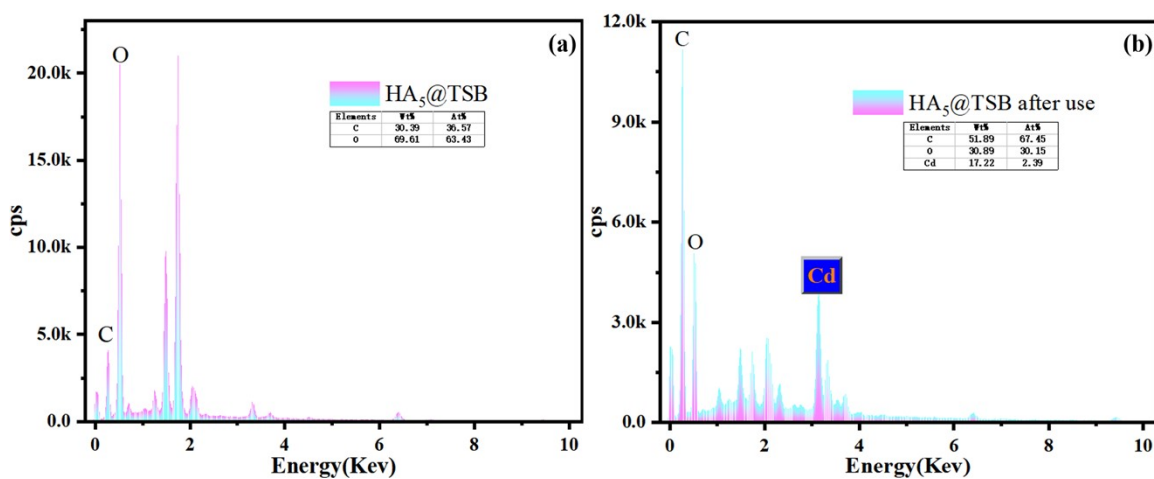


Fig. S1. The EDS images of different samples: (a) HA₅@TSB, (b) HA₅@TSB after use.

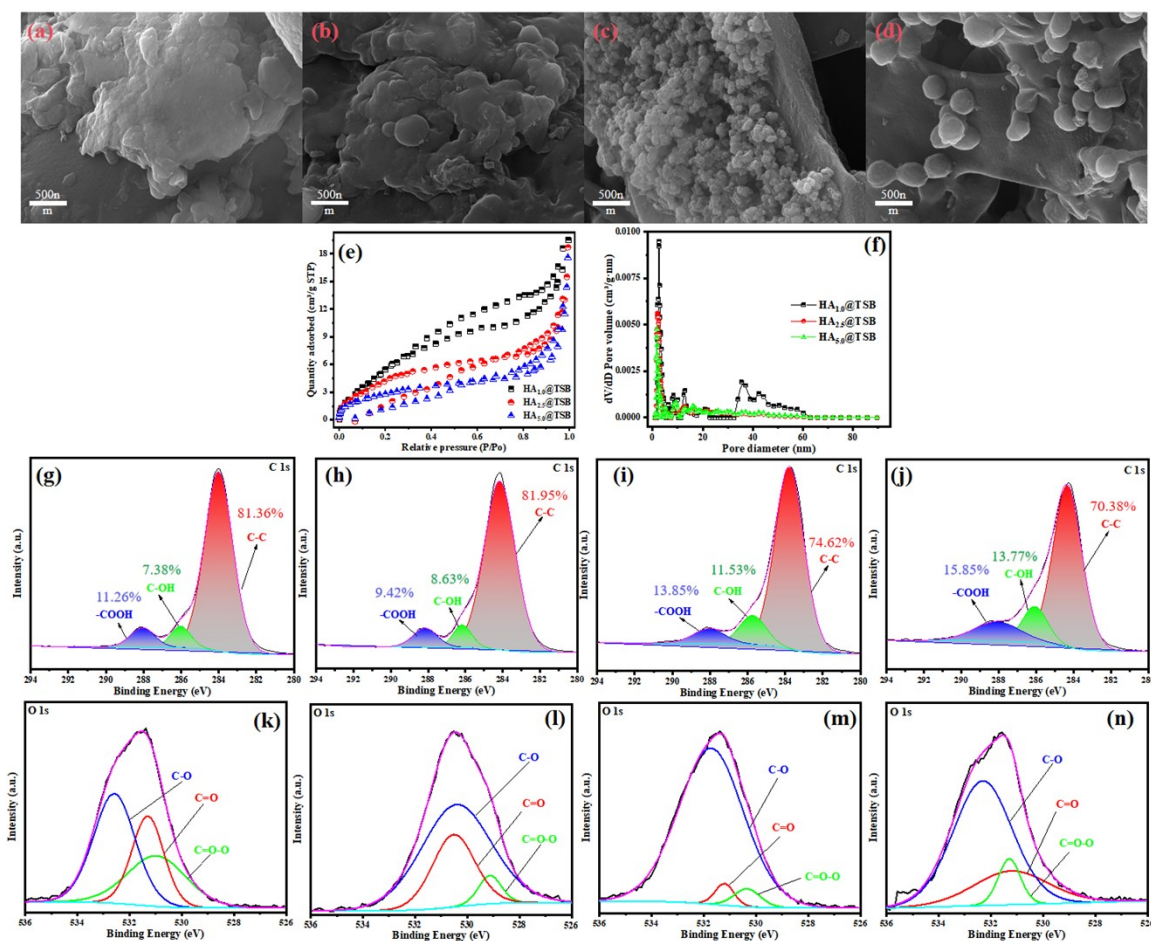
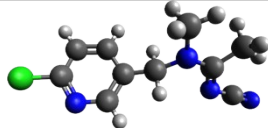
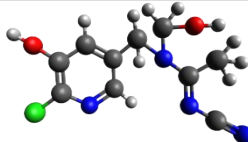
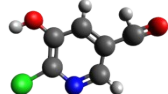
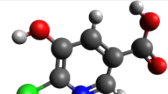
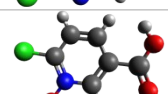
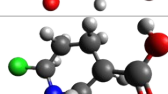
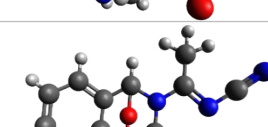
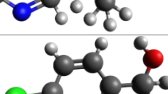
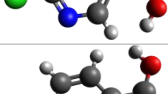
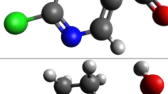
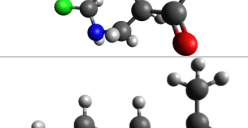
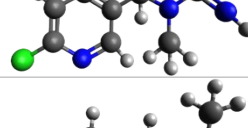


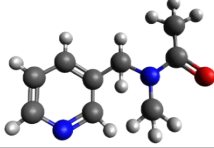

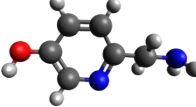
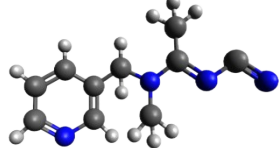
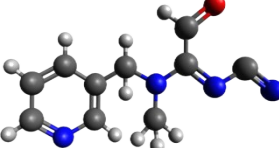
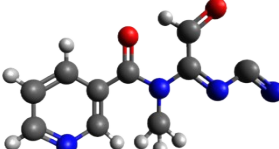
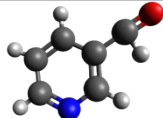
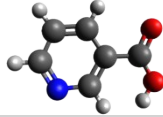
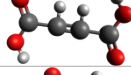

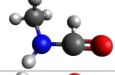
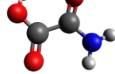


Fig. S2. The SEM images of different samples: (a) HA₁@TSB, (b) HA_{2.5}@TSB, (c) HA₅@TSB, (d) HA₅@TSB after use. (e) N₂ adsorption-desorption isotherms, (f) corresponding pore size distributions. XPS spectra of HA_x@TSB before and after use: C 1s spectra of (g) HA₁@TSB, (h) HA_{2.5}@TSB, (i) HA₅@TSB, (j) HA₅@TSB after use, O 1s spectra of (k) HA₁@TSB, (l) HA_{2.5}@TSB, (m) HA₅@TSB, (n) HA₅@TSB after use.

Table S1 BET parameters of HA₁@TSB, HA_{2.5}@TSB and HA₅@TSB.

Materials	BET surface area (m ² /g)	Average pore size (nm)	Total pore volume (cm ³ /g)
HA ₁ @TSB	63.58	135.98	0.09
HA _{2.5} @TSB	113.67	124.54	0.14
HA ₅ @TSB	235.88	68.65	0.25

Table S2 During the degradation of Ace by HA₅@TSB, the intermediate products were identified by LC-MS.

Compound	m/z	Molecular structure	Ball-and-stick models
Ace	223	C ₁₀ H ₁₁ ClN ₄	
P1	239	C ₁₀ H ₁₁ ClN ₄ O	
P2	158	C ₆ H ₄ ClNO ₂	
P3	174	C ₆ H ₄ ClNO ₃	
P4	174	C ₆ H ₄ ClNO ₃	
P5	165	C ₆ H ₁₀ ClNO ₂	
P6	239	C ₁₀ H ₁₁ ClN ₄ O	
P7	160	C ₆ H ₆ ClNO ₂	
P8	158	C ₆ H ₄ ClNO ₂	
P9	165	C ₆ H ₁₀ ClNO ₂	
P10	198	C ₉ H ₁₂ ClN ₃	
P11	199	C ₉ H ₁₁ ClN ₂ O	

P12	164	$C_9H_{12}N_2O$	
P13	166	$C_8H_{10}N_2O_2$	
P14	136	$C_6H_8N_2O$	
P15	187	$C_{10}H_{11}N_4$	
P16	201	$C_{10}H_9N_4O$	
P17	215	$C_{10}H_7N_4O_2$	
P18	107	C_6H_5NO	
P19	123	$C_6H_5NO_2$	
P20	116	$C_4H_4O_4$	
P21	90	$C_2H_2O_4$	
P22	59	C_2H_5NO	
P23	89	$C_2H_3NO_3$	
P24	64	$C_2H_4O_2$	
P25	46	CH_2O_2	
P26	48	CH_4O_2	