Supplementary Material

Biosourced choline-functionalized sawdust for dual dye removal: ion-exchange versus multifactorial adsorption mechanisms

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Fig. S1. Point of zero charge (pHpzc) of alkaline-treated sawdust (ATS) and choline-functionalized sawdust (CFS), determined by the drift method.

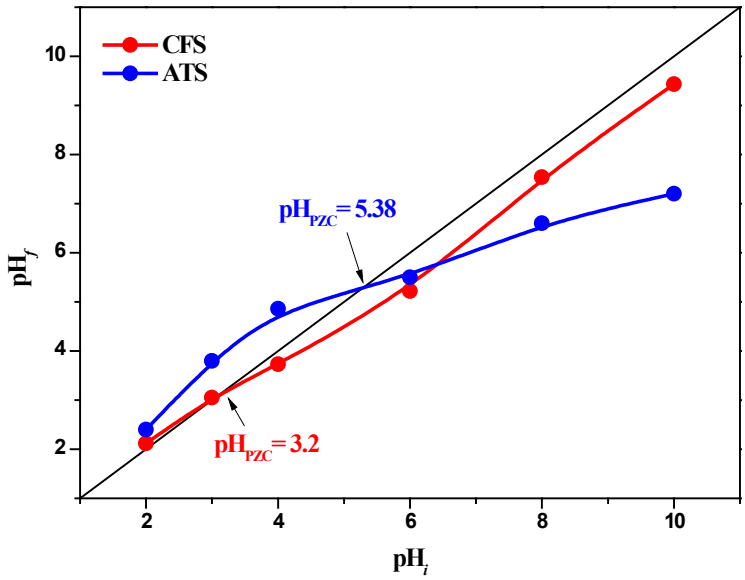


Fig. S2. Differential scanning calorimetry (DSC) curves of ATS (a) and CFS (b). Exothermic peaks correspond to cellulose degradation and char combustion, with CFS showing an additional exothermic event at ~200–250 °C due to quaternary ammonium groups and a more intense high-temperature exotherm, confirming modified degradation pathway and improved thermal stability.

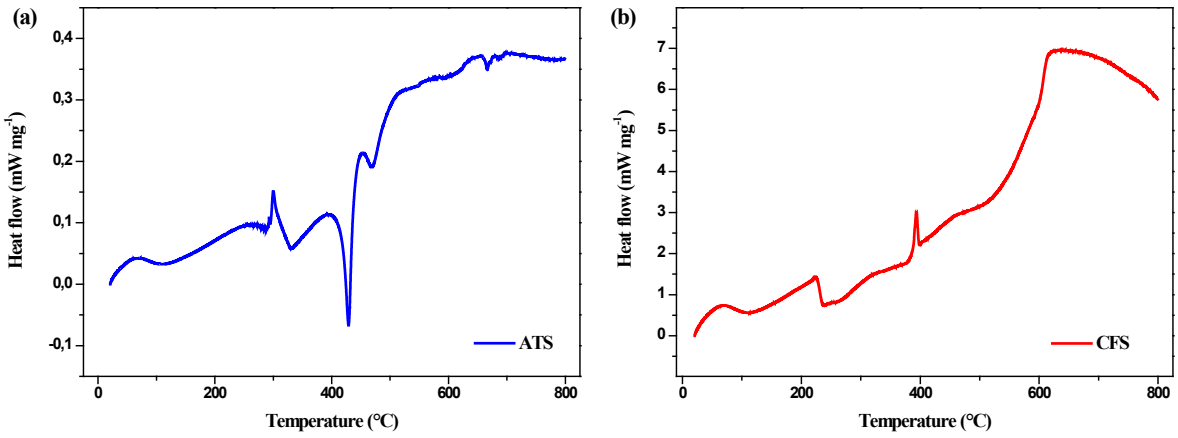
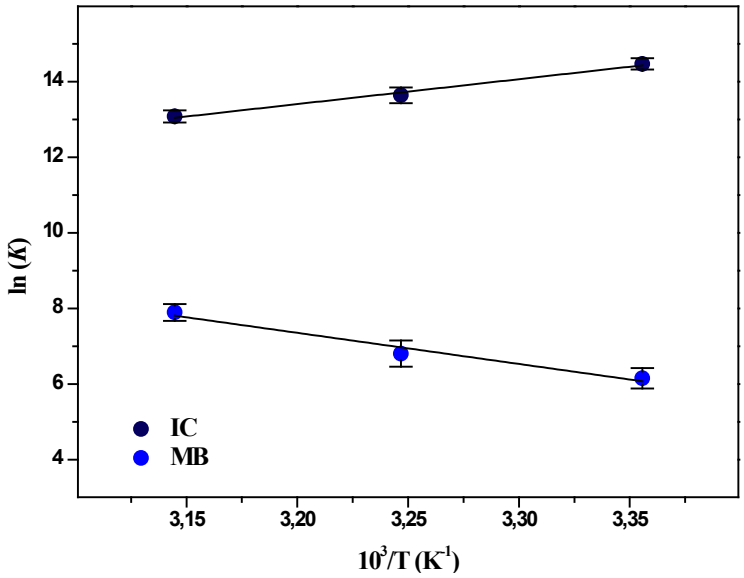


Table S1 Thermodynamic parameters for MB and IC adsorption onto CFS. MB uptake is endothermic and entropy driven, becoming more favorable with increasing temperature, whereas IC adsorption is exothermic with negative entropy change, reflecting strong spontaneity but slight inhibition at elevated temperatures.

Dye	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J/mol^{-1}·K^{-1})	$\Delta G°$ (kJ mol^{-1})		
			298 K	308 K	318 K
IC	–54.74	–63.71	–35.75	–35.12	–34.48
MB	+68.34	+279.85	–15.05	–17.85	–20.65

Fig S3. van't Hoff plots for IC and MB adsorption onto CFS, constructed from equilibrium data at 25, 35, and 45 °C. Conditions: IC at natural pH with 50 mg biosorbent in 25 mL of 100 mg·L^{-1} solution; MB at pH 8 with 75 mg biosorbent in 25 mL of 50 mg·L^{-1} solution. Experiments were stirred for 120 min at ambient temperature.



Figs. S4. FTIR spectra of CFS before and after adsorption of Indigo Carmine (IC) and Methylene Blue (MB). Dye uptake induced characteristic spectral modifications: disappearance of the lignin carbonyl shoulder (~1743 cm^{-1}), shifts in quaternary ammonium C–N^{+} stretching bands (from 1595/1497 to 1601/1504 cm^{-1}) and loss of the ~949 cm^{-1} shoulder upon IC adsorption, confirming sulfonate–ammonium ion exchange. For MB, reduced O–H intensity (~3420 cm^{-1}) and perturbations in aromatic C=C (~1600 cm^{-1}) and carbonyl regions corroborate multifactorial binding involving hydrogen bonding, π–π stacking, and dipolar interactions. Minor band shifts (Δν ±2–3 cm^{-1}) collectively support the involvement of hydroxyl and carbonyl groups in dye binding.

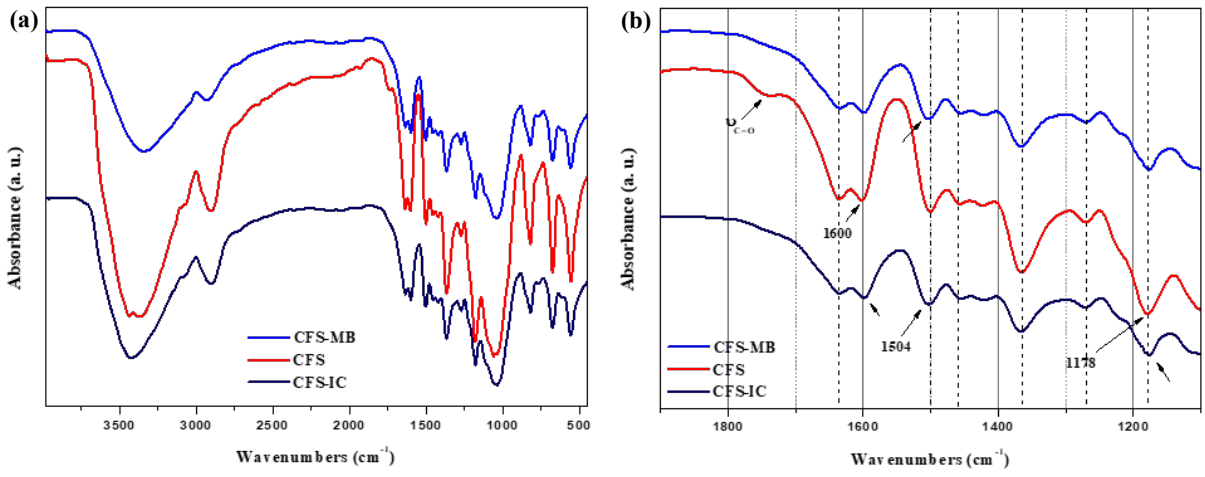


Table S2. Nonlinear kinetic and equilibrium isotherm model equations applied to the adsorption of methylene blue (MB), Congo red (CR), and Cu(II) ions on raw artichoke hay (RAH). The table summarizes the mathematical formulations, parameters, and units for each model. These models were employed to interpret adsorption kinetics, surface heterogeneity, diffusion regimes, and adsorbate–adsorbent interactions.

Model type	Model name	Equation	Parameters	Notes
Kinetics	Pseudo-first-order (PFO)	$q_t = q_e(1 - e^{-k_1 t})$	q_e (mg g^{-1}) k_1 (min^{-1})	Simple rate law
	Pseudo-second-order (PSO)	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	q_e (mg g^{-1}) k_2 (g mg^{-1} min^{-1})	Highlights chemisorption
	Elovich	$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t)$	α (mg g^{-1} min^{-1}) β (g mg^{-1})	Surface heterogeneity
	Intraparticle diffusion (ID)	$q_t = k_{id} t^{1/2} + C$	k_{id} (mg g^{-1} min$^{-1/2}$) C (mg g^{-1})	Diffusion into pores
	Liquid Film Diffusion	$q_t = q_e(1 - e^{-k_f t^{\alpha}})$	q_e (mg g^{-1}) k_f (min^{-1}) α (dimensionless)	Describes external diffusion control
	General Fractional Order	$q_t = q_e\left[1 - (1 + (n-1) \times k_f t))^{\frac{1}{1-n}}\right]$	q_e (mg g^{-1}) k_f (min^{-1}) n (dimensionless)	Captures non-integer kinetic orders
	Avrami	$q_t = q_e(1 - e^{-k_{av} t^n})$	q_e (mg g^{-1}) k_A (min^{-n}) n_A (dimensionless)	Multi-mechanistic regimes
Isotherms	Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	q_{max} (mg g^{-1}) K_L (L mg^{-1})	Monolayer adsorption
	Freundlich	$q_e = K_F C_e^{1/n}$	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$ n (dimensionless)	Heterogeneous surfaces
	Temkin	$q_e = \frac{RT}{b_T}\ln(K_T C_e)$	K_T (L g^{-1}) b (J mol^{-1})	Adsorbate–adsorbent interactions
	Dubinin–Radushkevich (D–R)	$q_e = q_{max} e^{-K_{DR}\varepsilon^2}$ $\varepsilon = RT\, ln\left(1 + \frac{1}{C_e}\right)$	q_{max} (mg g^{-1}) K_{DR} (mol^2 J^{-2}) E (kJ mol^{-1})	Energy of adsorption
	Sips	$q_e = \frac{q_{max}(K_S C_e^n)}{1 + K_S C_e^n}$	q_{max} (mg g^{-1}) K_S (L mg^{-1}) n (dimensionless)	Hybrid Langmuir–Freundlich
	Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}}$	K_{RP} (L g^{-1}) a_{RP} (L mg^{-1}) β (dimensionless)	Empirical hybrid model
	Toth	$q_e = \frac{q_{max} K_T C_e}{(1 + (K_T C_e)^t)^{1/t}}$	q_{max} (mg g^{-1}) K_T (L mg^{-1}) t (dimensionless)	Heterogeneity correction