Supportive Information

Highly Efficient and Selective Maerua Subcordata Tuber-Derived Activated Carbon for Enhanced Removal of Methylene Blue from Wastewater Sample

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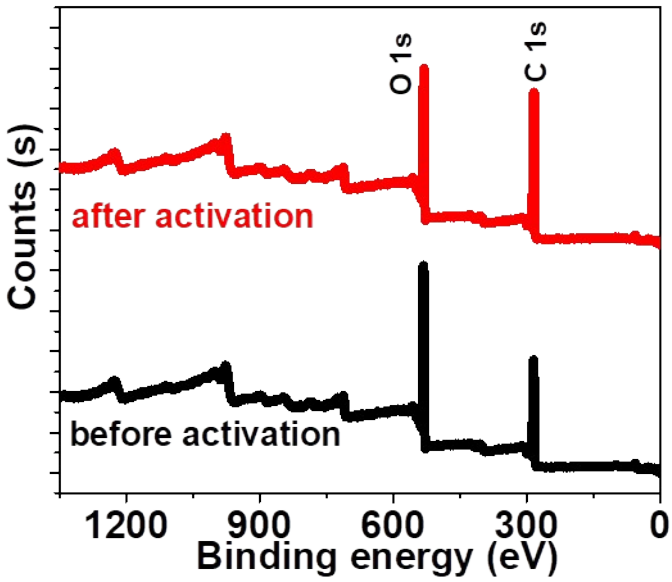


Figure S1. Survey XPS spectra, C1s and O 1s XPS spectra of as-prepared MS raw carbon sample before and after activation with Na_2CO_3.

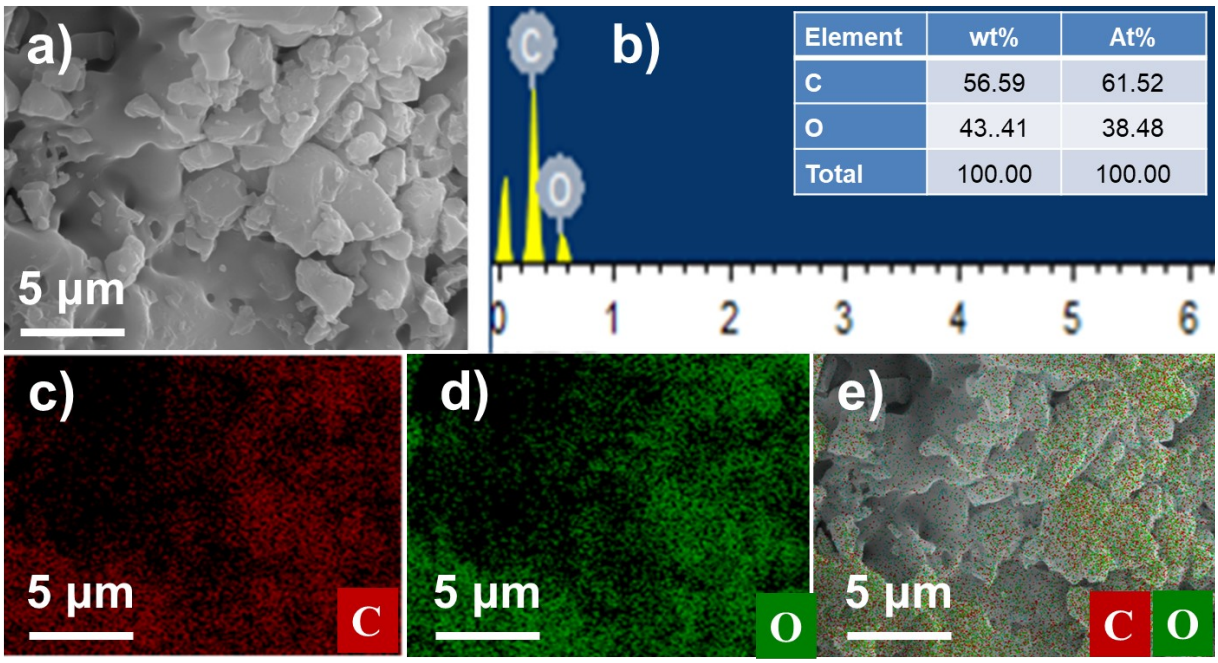


Figure S2. SEM image (a), EDX spectra (b), corresponding EDX elemental maps (c, d), and an overlay image (e) for the as-prepared MS raw carbon sample.

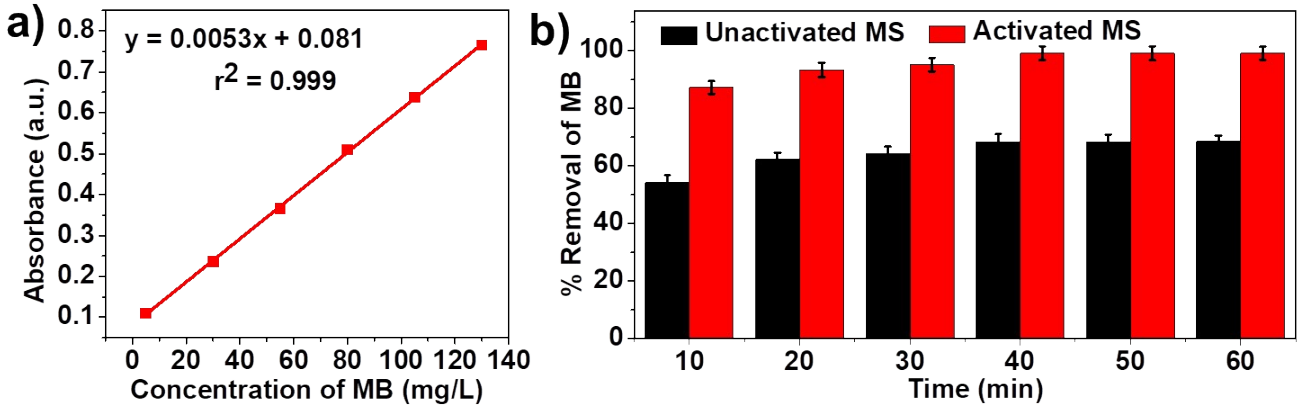


Figure S3. a) Calibration curve for the MB standard solution at 665 nm. b) Percentage removal of MB before and after activation of the MS adsorbent: C_o 100 mg/l, pH = 8, adsorbent dose = 75 mg, temperature = 298 K, and agitation speed = 120 rpm.

Table S1. Order of methylene blue selectivity in mixed dyes compared to previous reports.

S.N	**Adsorbent Material**	**Dye Selectivity Order**	**Dominant Mechanism**	**Ref.**
1	[1] cluster	MB > RhB >MO>CR	Electrostatic interaction + π–π interactions	[1]
2	AC-derived from papaya plant	MB > ARS (Alizarin red s)	Electrostatic interaction + π–π interactions	[2]
3	Porous Carbon Material (PC-900)	MB > MO	Electrostatic interaction + π–π interaction + pore diffusion	[3]
4	Biocarbons developed from waste	MB > MO	Electrostatic interaction + π–π interactions + molecular size	[4]
5	Nano-Carbon Adsorbent	MB > RB19	Electrostatic interaction + π–π interactions + hydrogen bonding	[5]
6	ZMPLB-800	MB > CR > acid fuchsin > tetracycline > MO	Electrostatic interaction + π–π interactions + molecular size	[6]
7	Cu-BTC	MB > RhB > MO	Hydrophobicity + electrostatic attraction	[7]
8	*AC-derived from Maerua subcordata* tuber	MB > RhB > PBB > MO	Electrostatic + π–π interactions + molecular size	This study

Adsorption isotherm studies

To examine the adsorption behavior of MB on MS-AC, we conducted adsorption isotherm studies using various concentrations of MB ranging from 10 to 160 mg/L at 25 °C, pH 8, a stirring speed of 120 rpm, an adsorbent dosage of 75 mg, and a contact time of 40 minutes. Four adsorption isotherms—Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich—were employed to fit the data. The mathematical equations, the meaning of the individual terms, and a summary of the relevant physical quantities for each isotherm model are provided in the supplementary information.

To obtain better understanding about the interaction of MS-AC and MB, the equilibrium data were fitted to Langmuir, Temkin, Dubinin–Radushkevich (D–R), and Freundlich isotherm models (Figure 5). The results were obtained at a dosage of 75 mg, a pH of 8, a contact time of 40 minutes, an MB concentration of 100 mg/L, a temperature of 298 K, and a mixing speed of 120 rpm.

Langmuir isotherm

The Langmuir isotherm is an important model that assumes monolayer adsorption takes place on a uniform surface. The linear representation of this model can be expressed by equation (1):

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q^m} \quad (1)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (2)$$

Where K_L (L/mg) is the Langmuir adsorption equilibrium constant related with the affinity of the binding site of adsorbent, q_m (mg/g) is the maximum adsorption capacity when the monolayer surface of the adsorbents is completely coated with adsorbate, q_e (mg/g) is the adsorption capacity adsorbed at equilibrium, C_e and C_o are the equilibrium and initial concentration of MB (mg/L); and R_L is the separation factor within the range 0–1 used to determine whether the adsorption process is favorable or unfavorable. If R_L >1.0, the sorption isotherm is unfavorable, R_L = 1.0 (linear), 0 < R_L < 1.0 (favorable), and R_L = 0 (irreversible). The $1/q_e$ versus $1/C_e$ plot provides a straight line with a slope of $1/q_m K_L$ and intercept of $1/q_m$.

Freundlich isotherm

The Freundlich isotherm is an empirical model that assumes multilayer adsorption on heterogeneous systems. The linear form of the Freundlich isotherm is given by equation (3):

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (3)$$

Where K_f is a Freundlich constant related to the adsorption capacity, q_e is the amount adsorbed at equilibrium (mg/g), $1/n_f$ is the adsorption intensity, and Ce is the equilibrium concentration (mg/L). An n_f value in the range of $1 < n_f < 10$ indicates a satisfactory adsorption process. The larger the n_f value is within these limits, the more effective the adsorption becomes. The $\ln q_e$ versus $\ln C_e$ provides a straight line with a slope of 1/n and intercept of $\ln K_f$.

Temkin isotherm

The Temkin isotherm is to study the interaction between 2,4-D and adsorbent surfaces In the Temkin isotherm model, it is assumed that the adsorption heat decreases linearly rather than logarithmically as in the Langmuir isotherm. The linear form of Temkin isotherm equation is given by:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (4)$$

$$q_e = \mathrm{B} \ln A + B \ln C_e \quad (5)$$

Where constant B = RT/b is related to the heat of sorption, R is the universal gas constant (KJ/mol K), T is temperature (K), b is the variation of sorption energy (J/mol) and A is the equilibrium binding constant (L/mg) corresponding to maximum binding energy. The Temkin isotherm constants B and A can be obtained from the slope and intercept of the plot of q_e versus $\ln C_e$, respectively.

Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm is used to carry out differentiation between physical adsorption and chemisorption process. The linear form of Dubinin–Radushkevich isotherm equation is given by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

Where q_e is the amount of 2,4-D adsorbed on per unit weight of adsorbent (mg/g), q_m is the maximum sorption capacity (mg/g), β is the activity coefficient related to adsorption mean free energy (mol^2/kJ^2) and ε is the Polanyi potential described as:

$$\varepsilon = RT\ ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

where R is the gas constant 0.008314 kJ/mol K, T is the temperature in Kelvin and C_e is the equilibrium concentration of the 2,4-D in solution (mg/L). The mean free energy of adsorption can be determined by:

$$E = \frac{1}{\sqrt{-2\beta}} \quad ()$$

The Dubinin–Radushkevich constants β and q_m can be obtained from the slope and the intercept of the plot of $\ln q_m$ versus ε^2, respectively. The value of E smaller than 8 kJ mol^{-1} indicates the adsorption process proceeds physically while its value ranging from 8 to 16 kJ mol^{-1} corresponds to a chemical ion-exchange process.

Table S2. Isotherm models for MB adsorption using MS-AC at 298 K.

Type of isotherms	Model equation	Parameters	Corresponding values
Langmuir	$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$	K_L(L/mg)	2.25
		q_m (mg/g)	158.7
		R^2	0.999
Freundlich	$q_e = K_F C_e^{1/n}$	K_f	85.93
		$1/n_f$	0.561
		R^2	0.983
Temkin	$q_e = Bln(AC_e)$	A (L/mg)	52.83
		B	21.37
		b (J/mol)	115.94
		R^2	0.991
Dubinin-Radushkevich	$q_e = q_{max}e^{-\beta\varepsilon^2}$	$q_{max}\ (mg/g)$	96.44
		$\beta\ (mol^2J^2)$	0.289×10^{-8}
		E (J/mol)	13,132

		R^2	0.994

Table S3. Kinetic studies revealing MB adsorption over MS-AC.

Type of kinetic model	Model equation	Parameters	Values
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	q_e (mg/g)	101.7
		k_1 (min)	0.0013
		R^2	0.862
Pseudo-second-order	$\frac{t}{q} = \left[\frac{1}{k_2 q_e^2} + \frac{t}{q^e}\right]$	q_e (mg/g)	67.6
		k_2 (g/mg min)	0.0066
		R^2	0.999
Intraparticle diffusion	$q_t = kt^{0.5} + C$	k (mg/g $min^{0.5}$)	1.627
		C (mg/g)	52.591
		R^2	0.930
Boyd kinetic equations	$Bt = \ln(1 - F) - 0.4997$	$F = \frac{q_t}{q_e}$	

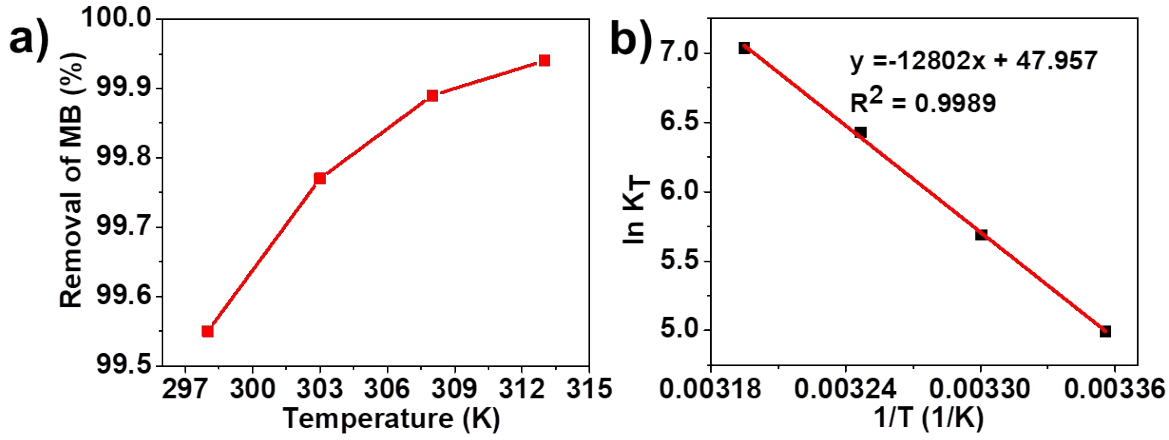


Figure S4. (a) Effect of temperature on the removal of MB dye and (b) van't Hoff plot.

Table S4. Thermodynamic studies of MB adsorption over MS-AC.

T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298	-12.4		
303	-14.3	106.4	398.8
308	-16.5		
313	-18.3		

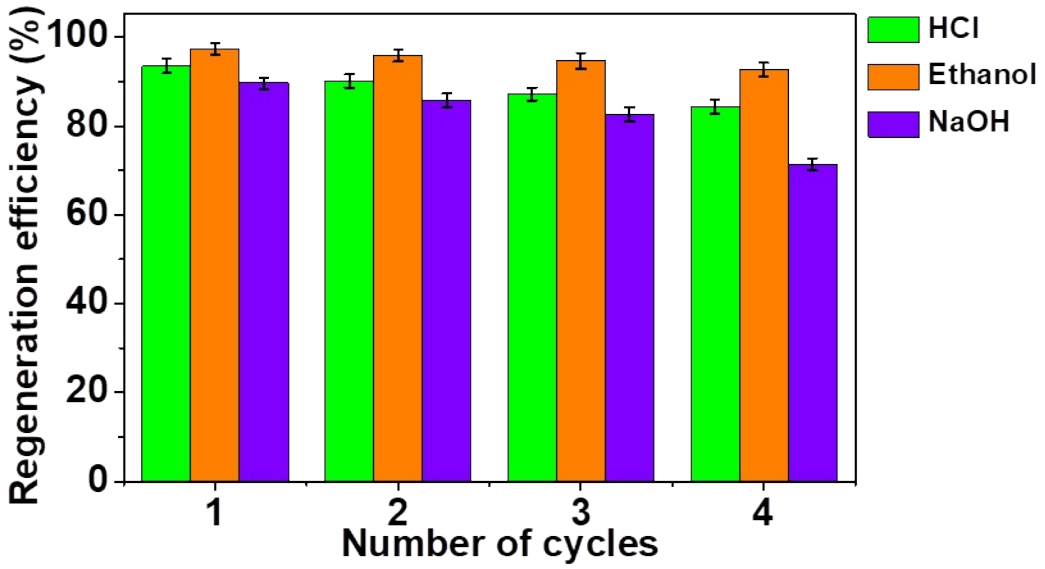
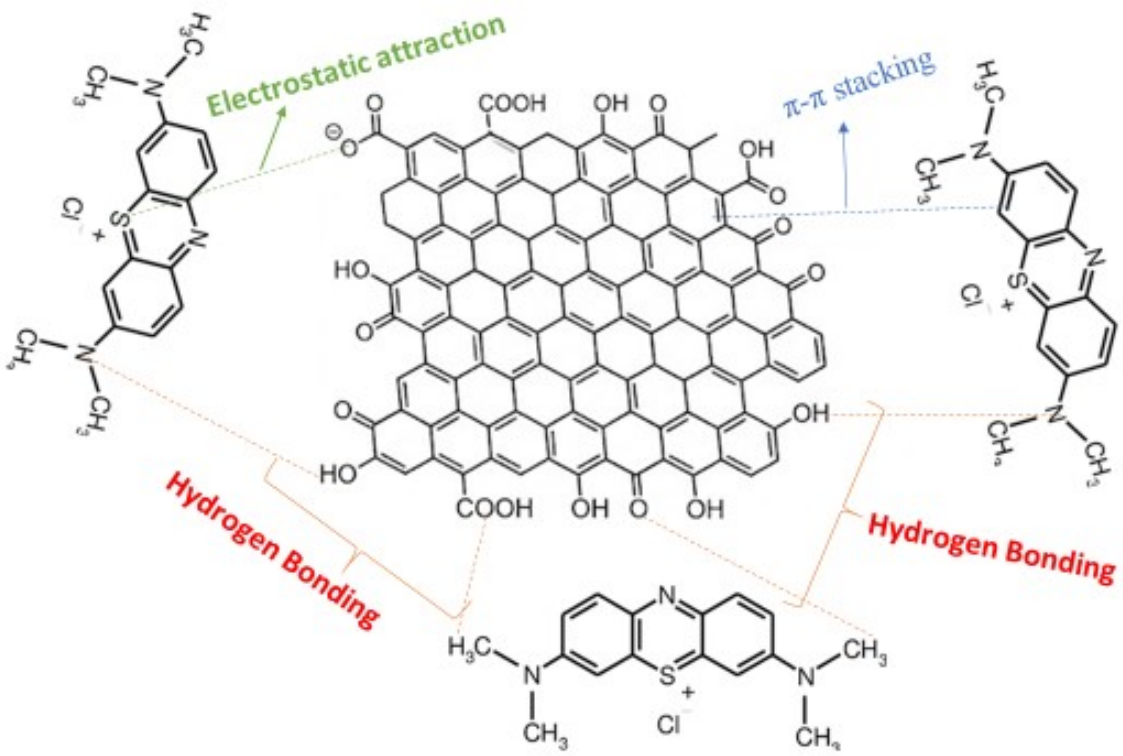


Figure S5. Reusability efficiencies of MS-AC for MB adsorption by using ethanol, HCl, and NaOH as eluents.



Scheme S1. Proposed mechanism for MB adsorption by MS-AC.

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