

Supplementary material

Citric acid modified sepiolite as an efficient and sustainable adsorbent for the removal of methylene blue

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S1. Characterization methods

The powder X-ray diffraction (XRD, Bruker D8 Advance, Bruker Corporation, Billerica, MA, USA) measurements were performed on a diffractometer with Cu $K\alpha$ radiation with $\lambda = 1.5406 \text{ \AA}$. The prepared CA-SEP powders were prepared by compressing in the cassette sample holder. Data were collected from $2\theta = 5^\circ$ - 60° with scan step 0.02° . FTIR characterization was performed on a Nicolet iS5 spectrometer (ThermoFisher, USA) with resolution of 4 cm^{-1} in the frequency range of 4000 - 400 cm^{-1} . The sample was prepared by the KBr pellet method. The structure and morphologies of CA-SEP samples were determined by scanning electron microscopy equipped with an energy-dispersive x-ray spectrometer (SEM-EDS, JEOL-7800F, Japan). The Brunauer-Emmett-Teller (BET) surface area and porosity of the samples were determined with a nitrogen adsorption-desorption instrument (Micromeritics ASAP2460, USA).

The point zero charge (pH_{PZC}) of the CA-SEP adsorbent was determined using a common pH drift method. For this, 0.1 g of adsorbent was added into different vials containing 50 mL each of 0.1 M NaNO_3 solution applied as an inert electrolyte. The initial pH values ($\text{pH}_{\text{initial}}$) were adjusted within the range of 2 - 11 using 0.1 M HNO_3 or 0.1 M NaOH . The resulting suspension was agitated at 200 rpm in a shaker incubator for 24 h at room temperature to reach an equilibrium pH. After 24 h , the final pH values (pH_{final}) of the suspensions were measured and plotted against the $\text{pH}_{\text{initial}}$. The pH_{PZC} values were obtained from the plateaus of the pH_{final} versus $\text{pH}_{\text{initial}}$ plots.

S2. Mathematical models

To study the kinetics of MB adsorption, pseudo-first-order (PFO) (1), and pseudo-second-order (PSO) (2), and Weber-Morris (W-M, or intraparticle diffusion) kinetic models (3) were used to fit the adsorption data. The intraparticle diffusion model was also used to analyze and elucidate the diffusion mechanism. These models are expressed as:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (2)$$

$$q_t = k_d t^{0.5} + C \quad (3)$$

where q_e and q_t (mg/g) denote the amounts of adsorbed MB on CA-SEP at equilibrium and time t , respectively; k_1 (1/min) and k_2 (g/(mg·min)) values are the rate constants. k_d is the diffusion rate constant within the particle, and C is the constant involving thickness and boundary layer.

In this study, Langmuir model (5) Freundlich model (6), and Sips model (7) were used to study the adsorption process of MB. The isothermal adsorption models are as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$q_e = q_m \frac{(K_S C_e)^{\frac{1}{n}}}{1 + (K_S C_e)^{\frac{1}{n}}} \quad (6)$$

where, q_e is the equilibrium adsorption amount (mg/g); C_e is the equilibrium concentration of adsorbate (mg/L), K_F is the Freundlich distribution coefficient, (mg/g(L/mg)^{1/n}); N is the surface heterogeneity factor; q_m is Langmuir saturated adsorption capacity, mg/g; K_L is Langmuir adsorption constant, L/mg. K_S is Sips equilibrium constant (L/mg), and n is the heterogeneous parameter of the adsorbent.

To further investigate the possible adsorption mechanisms involved in MB removal, Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) were determined by using the following equations:

$$\ln \frac{1}{C_e} = \frac{-\Delta H^0}{RT} + \ln K_0 \quad (7)$$

$$\Delta G^0 = -nRT \quad (8)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (9)$$

where C_e (mg/L) is the equilibrium aqueous MB concentration; n is the fitting constant of Freundlich exponent; R is the universal gas constant (8.314 J/(mol·K)); T is the temperature in Kelvin, and K_0 is the

thermodynamic equilibrium constant. Enthalpy (ΔH^0) was determined from the slope of the plots of $\ln 1/C_e$ versus $1/T$ (Fig. 8d).

Table S1. The main experimental materials and chemicals used in this study.

Materials/chemicals	Fineness	Origin
Natural sepiolite	/	Fuhong Mineral Products Co., Ltd, China
Citric acid	AR	Tianjin Kemio Chemical Co., Ltd., China
Methylene blue	AR	Shanghai Sinopharm Chemical Reagent Company, China
Hydrochloric acid	AR	Nanjing Chemical Reagent Company, China
Sodium hydroxide	AR	Nanjing Chemical Reagent Company, China
Sodium chloride	AR	Nanjing Chemical Reagent Company, China
Calcium chloride	AR	Nanjing Chemical Reagent Company, China

Table S2. BET surface area, pore volume and pore diameter values of the SEP, 0.1CA-SEP, and 0.5CA-SEP.

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
SEP	3.2727	0.016505	11.8101
0.1CA-SEP	2.8908	0.009352	12.9240
0.5CA-SEP	2.6304	0.008258	13.0522

Table S3. Kinetic model constants for MB adsorption by CA-SEP at different initial concentrations.

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	PFO model			PSO model			W-M model					
		$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/(mg·min))	R^2	Surface diffusion			Equilibrium		
								k_{d1} (mg/(g·min ^{0.5}))	C_1 (mg/g)	R^2	k_{d2} (mg/(g·min ^{0.5}))	C_2 (mg/g)	R^2
50	17.38	17.37	0.0109	0.9039	21.95	5.06442E-4	0.9225	1.0217	0.4368	0.9893	0.2643	12.93	0.7432
100	22.72	22.75	0.01813	0.9577	27.34	7.18377E-4	0.9672	1.8027	-0.4046	0.9935	0.0408	22.03	0.8567

Table S4. Parameters of the isotherm models for MB adsorption on CA-SEP.

Fitting models	Parameters	Temperature (K)		
		283	298	313
Langmuir	q_m (mg/g)	39.66	40.41	40.61
	K_L (L/mg)	0.0103	0.0174	0.0232
	R^2	0.9554	0.9632	0.9822
Freundlich	K_F (mg/g (L/mg) ^{1/n})	0.7723	1.6188	2.2533
	$1/n$	0.7126	0.6005	0.5564
	R^2	0.9063	0.8872	0.9201
Sips	q_m (mg/g)	30.49	33.26	33.74
	K_S (L/mg)	0.0385	0.0527	0.1577
	$1/n$	1.7671	1.8902	3.1383
	R^2	0.9831	0.9841	0.9965

Table S5. The thermodynamic parameters for adsorption of MB onto CA-SEP at various adsorption capacities and temperatures.

Adsorption capacity (q_e , mg/g)	ΔH° (kJ/mol)	ΔG° (kJ/mol)			ΔS° (J/(mol·K))		
		283 K	298 K	313 K	283 K	298 K	313 K
5	29.28				115.16	109.36	104.12
10	22.54	-3.31	-4.13	-4.68	94.24	89.50	85.21
20	15.81				72.40	68.76	65.46

Table S6. Comparison with other materials for MB adsorption.

Adsorbents	q_m (mg/g)	pH	Reference
Natural zeolite	0.204	7.0	[52]
Artificial zeolite	0.3326	7.0	[52]
Bagasse-montmorillonite composite	11.94	5.7	[60]
Synthetic zeolite	19.53	7.0	[21]
Bentonite	22.131	7.0	[22]
Magnetic chitosan/organic rectorite	24.69	6.0	[61]
CuO nanoparticles	26.738	8.0	[14]
Chabazite	28.9	5.0	[62]
Chitosan modified zeolite	37.04	5.1	[63]
NiO/sepiolite composite	22.73-50.00	*	[64]
CuO-acid modified SEP	38.6-64.5	*	[65]
CA-SEP	40.61	8.0	This work
Chitosan/SEP composite	40.986	6.0-8.0	[59]
Multi-walled carbon nanotubes	55.18	6.0	[15]
Silver nanoparticles decorated SEP	101	8.0	[1]
g-C ₃ N ₄ -modified Na-Ca-magnesium silicate adsorbent	420	*	[66]

* Not available.

Table S7. Physicochemical characteristics of the real wastewater.

Parameters	Sample 1	Sample 2
pH	11.8	8.2
$\lambda_{\max}$	620	665
BOD ₅ (mg/L)	108	35.6
COD _{Cr} (mg/L)	1265	94.9
Total suspended solid (TSS, mg/L)	184	60
Chroma (dilution)	500	25