Supporting information

Spent coffee ground-calcium alginate biosorbent for adsorptive removal of methylene blue from aqueous solutions

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Section S1: Analytical instruments

Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained in the range of 4000-400 cm^{-1} on a Shimadzu IRTracer-100 spectrometer using KBr pellets. Thermal gravimetric analysis (TGA) was performed using a TA Instruments Q500HR analyzer under an N_2 atmosphere using the high-resolution mode (dynamic rate TGA) at a 2 °C min^{-1} scan rate from room temperature to 800 °C. The zeta potentials were measured using NanoPlus HD sizer equipment (Micrometrics, USA). Zeta potential values for the final composites were measured in a 2-9 pH range. A minimum of 3 measurements per sample was done at room temperature. The pH variation was carried out using 0.01 M NaOH and HNO_3 solutions. X-ray photoelectron Spectroscopy (XPS) analyses were carried out with a Thermo Scientific K-alpha X-ray photoelectron spectrometer working at 72 W and equipped with a hemispherical analyzer and a monochromatic. Survey scans were recorded using 400 μm spot size and fixed pass energy of 200 eV, whereas high-resolution scans were collected at 20 eV of pass energy. Spectra have been charged and corrected to the mainline of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV. Spectra were analyzed using CasaXPS software (version 2.3.14). Spectral backgrounds were subtracted using the Shirley method. Curve fitting procedures and elemental quantifications were performed with the CasaXPS program (version 2.3.14). MB concentration was determined by a GENESYS 150 UV-Vis spectrophotometer at the wavelength of 664 nm (Thermo Scientific, USA). The pH measurements were made using the Acorn® pH 5 Meter (OAKTON, USA). The morphology of SCG_ALG was obtained employing a variable pressure scanning electron microscope (SEM), brand FEI Co. and Quanta model FEG 250 with an EDS detector Bruker model XFlash 6160. X-ray diffraction (XRD) analysis was performed using a D5000 type equipment, Siemens, Germany. Cu radiation was used the analyzed range of diffraction angle 2θ was between 3 and 50° with a step width of 0.028°.

Nitrogen adsorption-desorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer. The sample mass was 65.0 mg. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Nitrogen isotherms were measured using UHP grade Nitrogen. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

Section S2: Materials Characterization

Table S1. Zeta potential of spent coffee grounds (SCG), alginate beads (ALG), and spent coffee grounds encapsulated in alginate beads (SCG_ALG).

SCG		ALG		SCG_ALG	
pH	ζ pot (mV)	pH	ζ pot (mV)	pH	ζ pot (mV)
10.06	-71.39	9.98	-32.96	10.21	-67.56
9.23	-68.69	9.13	-31.58	8.87	-51.03
8.15	-61.88	8.30	-29.21	7.46	-47.86
7.06	-52.53	7.38	-28.92	6.85	-40.32
5.46	-30.5	6.47	-27.92	6.32	-36.88
4.27	-20.82	5.76	-22.45	5.25	-34.6
3.99	-16.51	5.32	-21.76	4.25	-32.23
3.71	-9.97	4.54	-21.11	3.87	-19.69
3.43	-8.42	3.91	-12.86	3.56	-18.78
3.01	-0.11	3.13	-11.13	3.03	-11.36
2.07	8.04	2.03	-9.63	2.15	-7.95

Section S3: Experimental procedure

MB quantification

The determination of the MB concentration was through the lambert-beer equation expressed as:

$$A = \varepsilon \cdot b \cdot C$$

Where A is the absorbance of the solution, b is the cell's longitude (cm), C is the dye concentration in the solution (mg L^{-1}), and ε is the extinction coefficient ((mg L^{-1})$^{-1}$ cm^{-1}). A UV-vis scan from 200-900 nm was performed on the MB solution (**Figure S1a**), where the maximum absorptivity wavelength was determined at 664 nm, at which the experimental readings were performed. Moreover, a calibration curve from 0.1 to 10.0 mg L^{-1} of MB was performed, which determined the molar absorptivity coefficient from the slope after linear fit (**Figure S1b**).
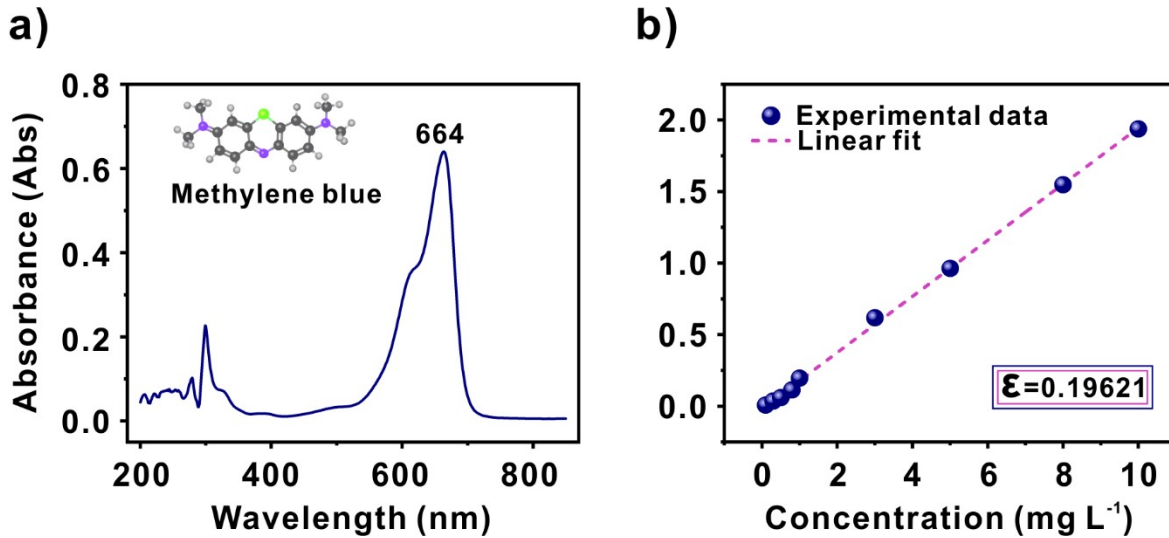

Figure S1. a) MB UV-vis scan absorption spectra; b) MB calibration curve.

The MB adsorption efficiency was determined through the concentration difference method. The following equation was used to estimate the percent uptake by the adsorbent.

$$Removal\ efficiency\ (\%) = \left(\frac{(C_0 - C_e)}{C_e} \right) \times 100$$

Where C_0 (mg L^{-1}) is the initial concentration, and Ce (mg L^{-1}) is the concentration in the equilibrium. Adsorption capacity Q_e (mg g^{-1}) was calculated by the following equation.

$$Q_e = \left(\frac{(C_0 - C_e) \times V}{m} \right)$$

Where V (L) is the volume of the solution, and m (g) is the adsorbent mass.

Effect of adsorbent amount

The effect of adsorbent mass over the adsorption process was evaluated by adding 5, 10, 20, 30, 40, and 50 mg of *SCG_ALG* to 20 ml solution with 50 mg L^{-1} of MB under stirring for 180 min.

Influence of pH in the adsorption

To study the effect of solution pH, adsorption experiments were carried out at pH 2, 4, 6, 8, and 10 by adding 10 mg of *SCG_ALG* to 20 mL (50 mg L^{-1}) of MB solution, under stirring for 180 min. The pH values were adjusted using 0.1 mol L^{-1} HNO_3/NaOH.

Influence of contact time

For evaluating the effect of contact time, 40 mg of *SCG_ALG* were placed in 80 ml with 50 mg L^{-1} of MB for 1440 min under stirring. 2 ml aliquots were collected during the experiment.

Effect of initial concentration

The variation of initial concentration of MB was valued at 10, 20, 40, 50, 80, 100, 300, 500, 800, and 1200 mg L^{-1}. 10 mg of *SCG_ALG* were added to 20 ml of MB solution under stirring for 180 min.

Effect of temperature

The effect of temperature over the adsorption process was carried out at 25, 40, 50, and 60 °C for 60 min by adding 10 mg of *SCG_ALG* to 20 mL MB solution at 50 mg L^{-1} under stirring.

Regeneration studies

The effect of regeneration was evaluated by 3 cycles with 20 mL of MB solution 50 mg L^{-1} of concentration with 10 mg of *SCG_ALG* under stirring for 180 min. For desorption, 20 ml of ethanol

were employed, and the exhausted *SCG_ALG* were placed under stirring for 180 min for each desorption step.

Well, lake and tap water studies

The adsorption experiment of MB removal employing water from a natural source, such as tap, lake, and well water, was carried out to evaluate the performance of the adsorbent material in more real and practical applications. In these experiments, 10 mg of *SCG_ALG* were added to 20 ml of MB solution at 50 mg L^{-1} under stirring for 180 min.

Table S2. Water sources pH-values.

Water source	pH
Deionizaded water	5.15
Well water	6.01
Lake water	5.84
Tap water	6.10

Section S3: Kinetics models, isotherms models, thermodynamic parameters data modeling.

Table S3. Langmuir adsorption capacities reported from other bioadsorbents.

Bioadsorbent	Q_{max} (mg·g^{-1})	Reference
Actived carbon	13.35	[1]
Actived carbon	413	[2]
Actived carbon	602.4	[3]
Zeolite	45	[4]
Zeolite	22	
Peanut hull	161.3	[5]
Pomelo peel	218.5	[6]

Banana peel	20.8	7
Orange peel	18.6	
Rice husk	40.58	8
Rice husk/alginate composite	274.9	9
Nano-silica	511.04	10
Spent coffee grounds	18.7	11
SCG_ALG	1601.85	This work

Table S4. Kinetic model equations and parameters.

Model	Non-linear equation	Parameters
Pseudo-first-order	$Q_t = Q_e\left(1 - e^{-k_1 t}\right)$	Q_e: adsorption capacities at equilibrium (mg g^{-1}); Q_t: adsorption capacities at a time (mg g^{-1}); k_1: pseudo-first-order rate constant for the kinetic model (mg g^{-1} min^{-1}); t: time (min)
Pseudo-second-order	$Q_t = \dfrac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$ $h = k_2 \times Q_e^2$	Q_t: adsorption capacities at time t (mg g^{-1}); Q_e: adsorption capacities at equilibrium (mg g^{-1}); k_2: pseudo-second-order rate constant of adsorption (mg g^{-1} min^{-1}); h: initial adsorption rate (mg g^{-1} min^{-1})
Elovich	$Q_t = \dfrac{1}{\beta}\ln\left(1 + \alpha\beta t\right)$	Q_t: adsorption capacities at time t (mg g^{-1}); α: adsorption equilibrium constant (mg g^{-1} min^{-1}); β:

		equilibrium constant desorption (g mg^{-1})
Intraparticle diffusion	$Q_t = K_{id}t^{0.5} + C_i$	Q_t: adsorption capacities at time t (mg g^{-1}); K_{id}: rate parameter of stage i (mg g^{-1} min$^{-1/2}$); C_i: intercept of stage i that gives an idea about of the thickness of boundary layer (mg g^{-1}).

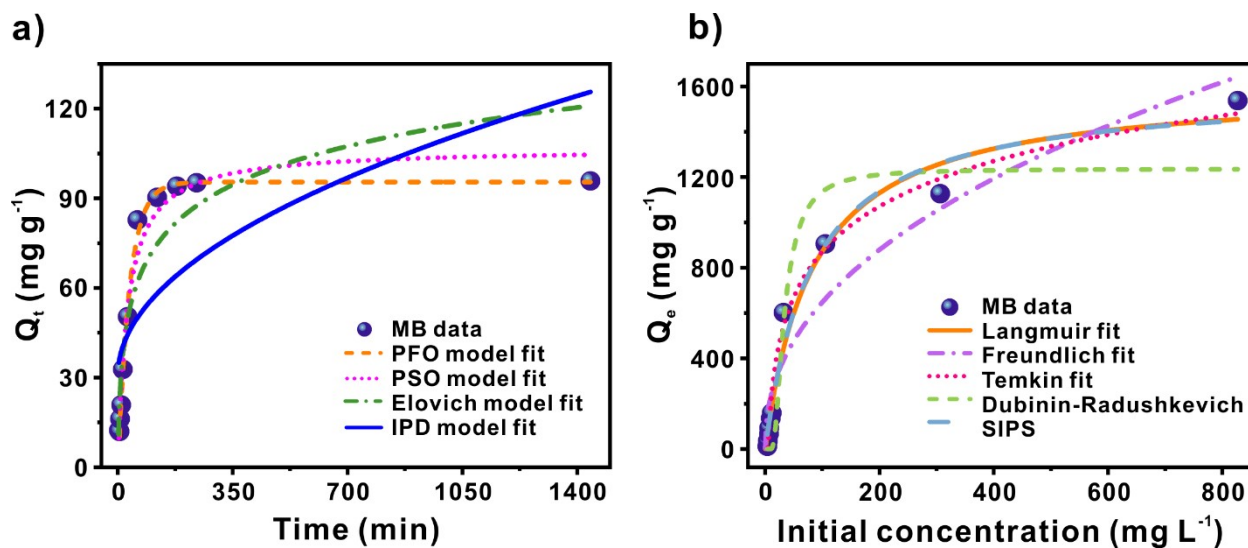**Figure S2.** a) Kinetics fits, Pseudo-first-order (PFO); Pseudo-second-order (PSO); Elovich; and Intra-particle diffusion (IPD) ([MB]=50 mg L^{-1}; SCG_ALG=40 mg, volume=80 ml, time=1400 min, pH=6, room temperature), and b) isotherms fits, Langmuir, Freundlich, and Temkin model fit for MB adsorption ([MB]=10-1200 mg L^{-1}; SCG_ALG=10 mg, volume=20 ml, time=180 min, pH=6, room temperature).

Table S5. Adsorption isotherm equation and parameters.

Model	Non-linear equation	Parameters

Langmuir	$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + K_L \times C_e}$$ $$R_L = \frac{1}{1 + K_L \times C_o}$$ $$\Delta G = -RT ln\,(K_O)$$ $$Ko = K_L \times MM \times 10^3$$	Q_m: is maximum adsorption capacity (mg g^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); K_L: is adsorption intensity or Langmuir coefficient (L mg^{-1}); C_e: is the concentration of absorbate at equilibrium (mg L^{-1}); R_L: is separation factor; ΔG: free Gibbs energy (kJ mol^{-1}); T: temperature (K); R: molar gas constant (J K^{-1} mol^{-1}); MM: Molar mass (g mol^{-1})
Freundlich	$$Q_e = K_F \times C_e^{\,1/n}$$	K_F: is the constant indicative of the relative adsorption capacity (L g^{-1}); n: is indicative of the intensity
Temkin	$$Q_e = \frac{RT}{b_t} ln\,(A_t \times Ce)$$ $$B = \frac{RT}{b_t}$$	A_t: Temkin isotherm equilibrium binding constant (L g^{-1}); b_t: Temkin isotherm constant; B: Constant related to the heat of sorption (J mol^{-1})
Dubinin-Radushkevich	$$Q_e = Q_s e^{\left(-K_d \times \varepsilon^2\right)}$$ $$\varepsilon = RT ln\left(1 + 1/C_e\right)$$	Q_s is a constant in the Dubinin-Radushkevich isotherm model which are related toadsorption capacity (mg P g^{-1}); K_d is a constant in related to the mean free energy of adsorption (mol^2 k^{-1}J^{-1});R is the

		gas constant (J mol⁻¹K⁻¹); and T is the absolute temperature (K)
Sips	$$Q_e = \frac{K_s \times C_e^n}{1 + Q_s \times C_e^n}$$	K_s is a SIPS isotherm model constant (L g⁻¹); n is the SIPS isotherm model exponent; Q_s is the adsorption cacacity (mg g⁻¹)

Table S6. Adsorption isotherm parameters from the non-linear fitting for MB adsorption.

Model	Parameter	Material
		SCG_ALG
Freundlich	K_F (L g⁻¹)	85.35
	n	2.27
	χ^2	25202.58
	R^2	0.925
Langmuir	Q_m (mg g⁻¹)	1601.85
	K_L (L mg⁻¹)	0.012
	R_L	0.97-0.81
	ΔG (kJ mol⁻¹)	-20.44
	χ^2	7514.065
	R^2	0.977
Temkin	A_t (L g⁻¹)	0.20
	b_t	8.59
	B (kJ mol⁻¹)	0.29

	χ^2	4660.67
	R^2	0.986
Dubinin-Radushkevich	Q_s (mg P g^{-1})	1236.36
	K_d (mol^2 k^{-1}J^{-2})	1.39E-4
	χ^2	27203.67
	R^2	0.919
SIPS	Q_s (mg g^{-1})	0.011
	K_s (L mg^{-1})	17.93
	n	1.02
	χ^2	8577.07
	R^2	0.977

Table S7. Thermodynamics equations and parameters.

Parameter	Equation	Parameters
Entropy	$\Delta S° = nR$ $K_C = \dfrac{Q_e}{C_e}$	n: intercept from a linear fit of plotting ln(K$_c$) × T^{-1}; Q$_e$: amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); C$_e$: concentration of absorbate in the equilibrium (mg L^{-1}); T: temperature (K); R: molar gas constant (kJ K^{-1} mol^{-1})
Enthalpy	$\Delta H° = mR$	

	$$K_C = \frac{Q_e}{C_e}$$	
Free energy	$\Delta G° = \Delta H° - (T\Delta S°)$	$\Delta H°$: enthalpy (J mol^{-1}); $\Delta S°$: entropy (J mol^{-1} K^{-1})
	$$K_C = \frac{Q_e}{C_e}$$	

Table S8. Thermodynamic parameters for MB adsorption.

Material	T (K)	Function			R^2
		$\Delta S°$	$\Delta H°$	$\Delta G°$	
		(kJ mol^{-1} K^{-1})	(kJ mol^{-1})	(kJ mol^{-1})	
SCG_ALG	298	-0.0396	-16.44	-4.65	0.951
	313			-4.05	
	323			-3.66	
	333			-3.26	

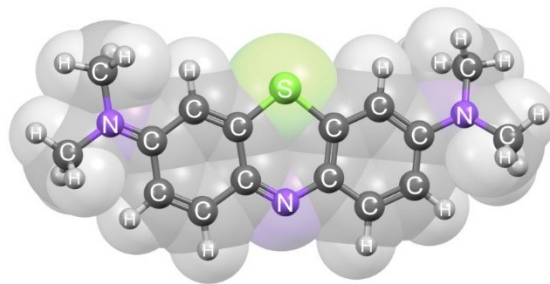**Section S4: X-ray photoelectron spectroscopy (XPS)**

Figure S3. MB structure

Table S9. XPS survey data (atomic percentage) for the most concentrated elements in the materials.

Samples	Elements (At. %)				
	C 1s	O 1s	Ca 2p	N 1s	S 2p
SCG_ALG	84.9	13.8	0.8	0.4	-
SCG_ALG + MB	88.8	9.8	0.4	0.9	0.2

Table S10. The peak-fitting results of O 1s high-resolution signal of materials.

Samples	Assignment	E_B (eV)	FWHM (eV)	At. %
SCG_ALG	O1s $_{C=O}$	531.2	1.5	11.5
	O1s $_{C-O}$	532.2	1.6	48.5

	O1s C-O-C=O	533.5	1.7	40.0
SCG_ALG + MB	O1s C=O	531.2	1.4	14.1
	O1s C-O	532.4	1.5	42.9
	O1s C-O-C=O	533.7	1.7	43.0

Table S11. The peak-fitting results of C 1s high-resolution signal of materials.

Samples	Assignment	E_B (eV)	FWHM (eV)	At. %
	C1s C=C aromatic	284.4	1.2	21.9
SCG_ALG	C1s C-C, C-CH	285.0	1.2	51.4
	C1s C-N/C-O	286.4	1.4	17.1
	C1s C=O	288.5	1.7	9.6
	C1s C=C aromatic	283.9	1.4	10.3
SCG_ALG + MB	C1s C-C, C-CH	285.0	1.5	67.2
	C1s C-N/C-O	286.6	1.6	14.4
	C1s C=O	288.7	1.8	8.1

Table S12. The peak-fitting results of Ca $2p_{3/2}$ high-resolution signal of materials.

Samples	Assignment	E_B (eV)	FWHM (eV)	At. %
SCG_ALG	Ca $2p_{3/2}$ Ca(II)	347.5	1.7	100

Samples	Assignment			
SCG_ALG + MB	Ca 2p$_{3/2}$ Ca(II)	347.4	1.7	100

Table S13. The peak-fitting results of N 1s high-resolution signal of materials.

Samples	Assignment	E$_B$ (eV)	FWHM (eV)	At. %
SCG_ALG + MB	N 1s R-N=R (R: aromatic), Iminie	398.4	1.6	23.7
	N 1s Amine	399.9	1.8	76.3

Table S14. The peak-fitting results of S 2p$_{3/2}$ high-resolution signal of materials.

Samples	Assignment	E$_B$ (eV)	FWHM (eV)	At. %
SCG_ALG + MB	S 2p$_{3/2}$ C-S=C	163.7	1.7	100
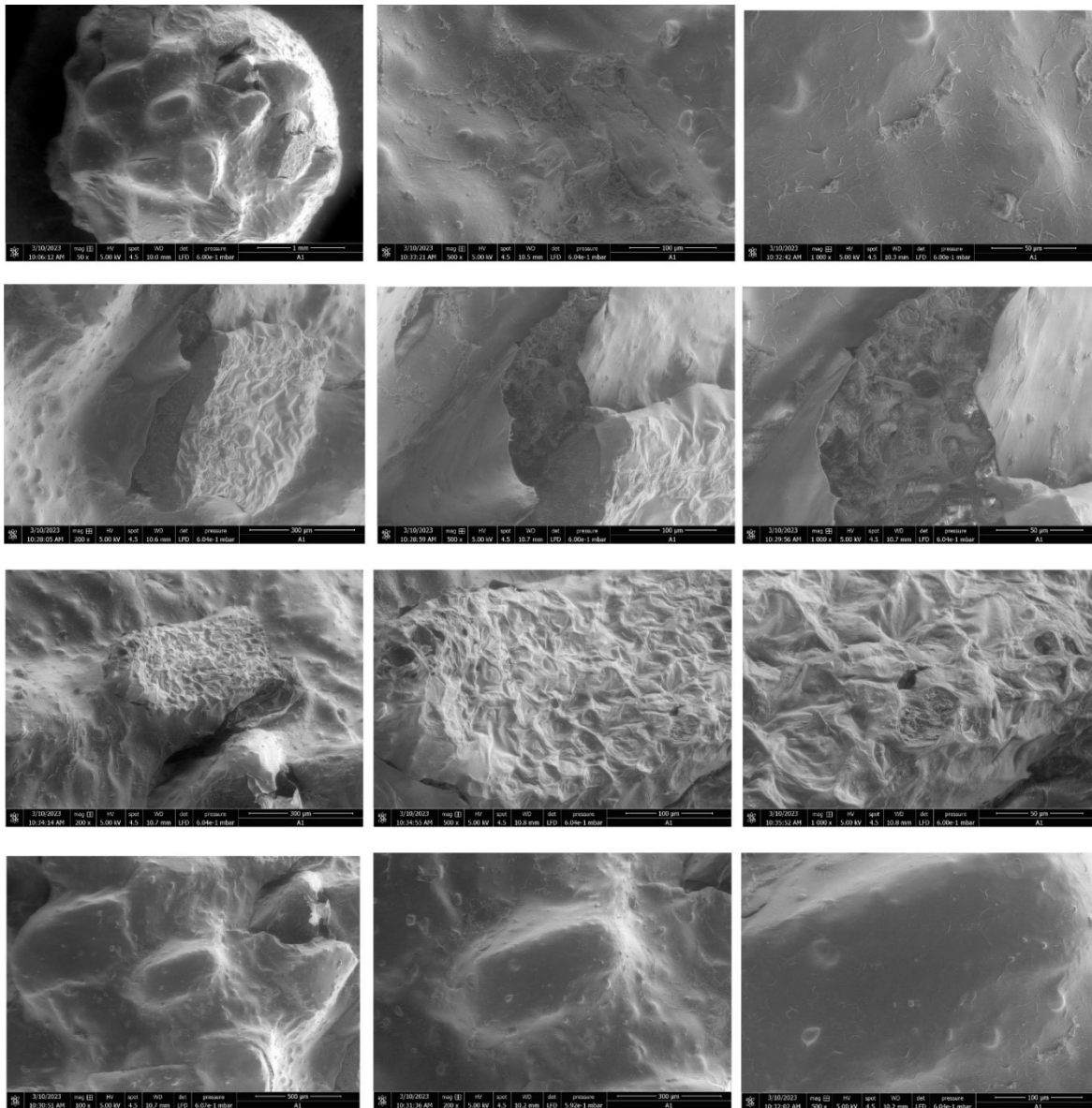
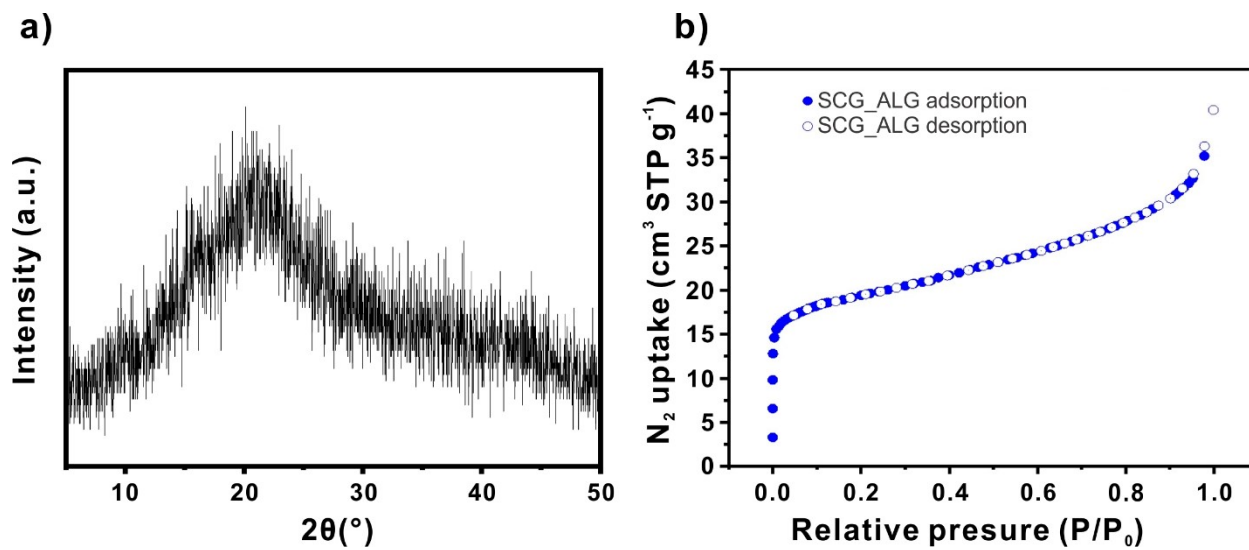**Figure S4.** SEM micrographs of SCG_ALG before MB adsorption.

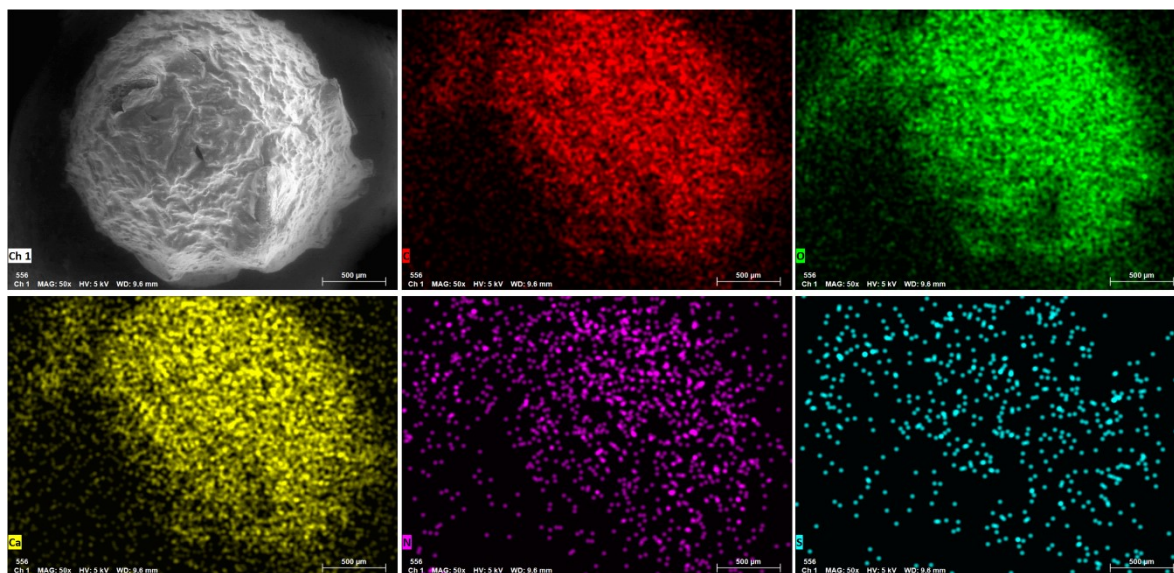**Figure S5.** a)PXRD and b) N_2 adsorption of SCG_ALG.

Figure S6. SEM micrograph and mapping of SCG_ALG after MB adsorption.
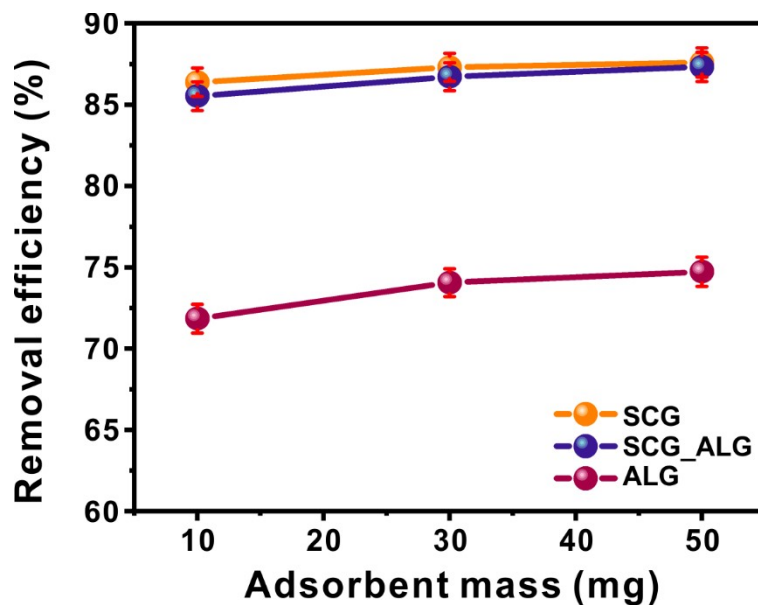
Figure S7. Control experiment of adsorbent mass influence with spent coffee grounds (SCG), SCG_ALG and alginate beads (ALG) over removal efficiency of MB adsorption.

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