

### Supplementary Information

#### **Recyclable chitosan–biochar biocomposite films for sustainable removal of Congo red dye pollutants from water**

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## 1. Characterization

The morphology and the elemental composition of biochars and biocomposite films were observed using a scanning electron microscope (JSM-6610, JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV. The samples were sputtered with a thin layer of gold using a Balzers SCD 040 sputter coater (Balzers Union Limited, Balzers, Liechtenstein), which serves as the channel for removing charged electrons from the material. AzTec (Springfield, NJ, USA) software was used for collecting SEM images.

The specific surface area and pore size of the samples were determined by N<sub>2</sub> adsorption-desorption isotherm at 77 K after 16 h of outgassing under high vacuum at 100 °C, using BET and BJH on Micromeritics ASAP 2420, USA.

The surface functional groups of adsorbents were determined using ATR-IR spectroscopy (Thermo Scientific Nicolet iS20, UK) from 600 to 4000 cm<sup>-1</sup> at 2 cm<sup>-1</sup> resolution. The chemical composition and the valence states were assessed by X-ray photo spectroscopy using a Thermo Scientific NEXSA-G2 XPS system (Thermo Fisher Scientific, UK) in which the surface compositions in atomic % were determined by considering the integrated peak areas of the detected atoms and the respective Scofield sensitivity factors.

The weight loss and the thermal stability of the adsorbents were determined using thermogravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA 851e device (Switzerland) at a heating rate of 10 °C/min in the temperature range of 30 – 1000 °C under a nitrogen atmosphere.

The tensile properties were measured by using an Instron 3365 (Instron, Norwood, MA, USA) universal testing machine in uniaxial deformation at a cross-head speed of 1 mm/min up to 1% deformation followed by a speed of 50 mm/min at higher deformations to determine Young's modulus, tensile stress, and Elongation at break.

The degree of swelling of biocomposite films was determined by submerging the film sample (0.5 x 1 cm) in 10 mL of water in closed vials and shaking it for 2 hours at room temperature (in triplicate). The absorbent paper was gently used to remove the excess water, and the swollen films were weighed, and the following equation was used to determine the degree of swelling <sup>1</sup>.

$$\text{Swelling degree} = \frac{m_s - m_d}{m_d} \times 100$$

Where  $m_d$  and  $m_s$  are the mass of dry and swollen samples respectively.

The solubility of films in water was determined by submerging the film sample (1 cm x 1 cm) in 10 mL of water in closed vials and shaking it for 48 hours at room temperature (in triplicate) <sup>1</sup>. The films were then oven-dried at 60 °C for 16 hours and weighed. The following equation was used to determine the solubility (dissolution) of film:

$$\text{Solubility} = \frac{m_i - m_f}{m_i} \times 100$$

Where  $m_i$  and  $m_f$  are the initial and final mass of film after 48 hours respectively.

The water contact angle measurements were carried out using a computerized apparatus for CA analysis (OCA 25, DataPhysics, Germany) in order to assess the wettability of the prepared films. The measurement was performed for each side of the biofilm.

The pH of the point of zero charge (pH<sub>pzc</sub>) of biochar samples was determined using 0.01 M NaCl solution. The pH was adjusted with either 0.1 M NaOH or HCl in the range of 3 to 11. The 10 mL of solution were mixed with 0.01 g of adsorbent, stirred for 24 hours and the pH filtrate pH was measured. The pH<sub>pzc</sub> was obtained from a plot of the initial solution pH vs the final pH <sup>2</sup>.

## 2. Adsorption model

### 2.1. Kinetic models

The kinetic data were using the nonlinear forms of Pseudo-first order, Pseudo-second order, Elovich and Intraparticle diffusion model

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

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

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

$$q_t = k_{ip} t^{0.5} + c$$

$q_t$  and  $q_e$  ( $\text{mg} \cdot \text{g}^{-1}$ ): adsorption capacity at time  $t$  and equilibrium respectively,  $t$ : time (min).  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ): constants of the pseudo-first-order and the pseudo-second-order models, respectively.  $\alpha$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) and  $\beta$  ( $\text{g} \cdot \text{mg}^{-1}$ ): constants for Elovich model model.  $k_{id}$  and  $c$ : intraparticle diffusion constants.

### 2.2. Isotherm models

The adsorption characteristic of CR onto the biocomposite films were determined using the nonlinear form of Langmuir, Freundlich, and Temkin isotherm models

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

$$q_e = K_F C_e^{1/n}$$

$$q_e = B \ln A + B \ln C_e$$

Where  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ): adsorption capacity,  $C_0$  and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ): initial and equilibrium concentrations.  $q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ): maximum adsorption capacity,  $K_L$  ( $\text{L}\cdot\text{g}^{-1}$ ): Langmuir equilibrium adsorption constant.  $K_F$  ( $\text{L}\cdot\text{g}^{-1}$ ): Freundlich constant or relative sorption capacity,  $n$ : constant indicating adsorption intensity.  $B$  is a constant related to the heat of adsorption and is defined by the expression  $B = RT/b$  where  $b$  is the Temkin constant ( $\text{J}\cdot\text{mol}^{-1}$ ),  $T$  (K) the absolute temperature,  $A$  is the Temkin isotherm constant ( $\text{L}\cdot\text{g}^{-1}$ ),  $R$  ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) the gas constant.  $R_L$  (dimensionless) separation factor based on Langmuir isotherm is used to predict the feasibility of the adsorption process to be either irreversible ( $R_L = 0$ ), linear ( $R_L = 1$ ), unfavorable ( $R_L > 1$ ), or favorable ( $0 < R_L < 1$ )

$$R_L = \frac{1}{1 + K_L C_0}$$

### 2.3. Thermodynamics model

Thermodynamic study was based on the Gibbs-Helm Holtz equation expressed as follow:

$$\Delta G^\circ = -RT \ln K_c \quad (19)$$

$$K_c = \frac{q_e}{C_e}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_c = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

Where  $\Delta G^\circ$  is the Gibbs free energy,  $K_c$  is the thermodynamic equilibrium constant. The entropy ( $\Delta S^\circ$ ) and the enthalpy ( $\Delta H^\circ$ ) of the reaction were determined by plotting  $\ln K_c$  vs.  $1/T$

**Table S1.** Summary of the apparent surface chemical composition as determined by EDS

Samples	Chemical composition (%)							
	C	O	Na	K	Ca	Mg	Fe	O/C
BC	79.83	16.49	/	1.93	1.48	0.27	/	0.21
ABC	74.21	24.78	/	0.31	0.43	0.22	/	0.33
BBC	78.00	17.70	0.91	0.50	1.95	0.54	0.40	0.23
CH <sub>2</sub> BC	59.16	39.04	0.45	0.79	0.55	/	/	0.66
CH <sub>2</sub> ABC	69.32	30.10	/	0.11	0.24	0.22	/	0.43
CH <sub>2</sub> BBC	61.25	37.00	0.81	0.15	0.63	0.16	/	0.60
CH <sub>2</sub> BBC-CR	67.00	32.64	/	/	0.21	0.15	/	0.49

**Table S2.** Apparent surface chemical composition as determined by XPS

Samples	Surface chemical composition (at. %)			
	C1s	O1s	N1s	minerals
	sp <sup>2</sup> /sp <sup>3</sup> /C-O/C=O/OCO/ $\pi$ - $\pi^*$ /NC=O	C=O/C-O/OCO	=N-/N/N+/NO <sub>3</sub>	
BC	76.0	16.4	2.3	5.3
	58.6/7.3/3.8/3.2/1.6/1.5/-	9.3/6.2/0.9	0.8/1.2/0.2/0.2	
ABC	78.0	17.4	3.7	0.9
	48.2/13.7/6.2/4.2/3.1/2.6/-	9.1/7.5/0.8	0.6/1.8/0.4/0.9	
BBC	68.7	21.7	2.4	7.2
	44.7/10.5/5.7/4.2/2.2/1.4/-	13.7/6.9/1.1	0.7/1.4/0.2/0.2	
CH	68.6	24.2	4.4	2.8
	-/40.0/18.4/3.5/1.2/-/5.5	6/18.1	0.2/3.5/0.7/-	
CH <sub>2</sub> BC	62.5	28.5	4.5	4.5
	8.8/22.2/22.4/3.1/1.3/-/4.6	9.8/18.1/0.6	0.3/3.6/0.6/0.1	
CH <sub>2</sub> ABC	64.5	29.0	5.7	0.8
	11.3/12.3/29.9/7.0/1.3/-/2.5	2.8/26.2/-	1.1/3.4/1.0/0.2	
CH <sub>2</sub> BBC	62.8	29.4	6.1	1.7
	7.5/13.9/32.3/1.0/-/8	3.9/25.5/-	0.5/4.6/0.9/0.1	
CH <sub>2</sub> BBC-CR	65.9	27.3	6.0	0.8 + S (0.3)
	10.6/25.2/20.2/7.4/-/2.5	1.8/25.6	1.7/3.4/0.9/-	

**Table S3.** Kinetic model parameters for CR adsorption onto biochar and biocomposite films

	BC	CH <sub>1</sub> BC	CH <sub>2</sub> BC	ABC	CH <sub>1</sub> ABC	CH <sub>2</sub> ABC	BBC	CH <sub>1</sub> BBC	CH <sub>2</sub> BBC
<b>PFO</b>									
q <sub>exp</sub>	4.92	10.71	10.29	3.48	7.99	10.49	5.51	10.01	12.22
(mg·g <sup>-1</sup> )									
q <sub>e</sub> (mg·g <sup>-1</sup> )	4.85	10.82	10.41	3.29	7.121	11.558	5.39	9.712	12.007
K <sub>1</sub> (min <sup>-1</sup> )	0.5124	0.0054	0.0071	0.3764	0.0113	0.0053	0.3809	0.0075	0.0071
R <sup>2</sup>	0.981	0.960	0.904	0.923	0.889	0.965	0.988	0.958	0.958
RMSE	0.192	0.730	1.183	0.264	0.941	0.728	0.173	0.734	0.902
CHI <sup>2</sup>	0.083	5.612	16.81	0.233	12.173	6.204	0.061	6.958	9.465
<b>PSO</b>									
q <sub>e</sub> (mg·g <sup>-1</sup> )	4.86	14.498	12.793	3.36	8.263	15.773	5.48	12.424	15.476
K <sub>2</sub> (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	0.8076	0.0003	0.0006	0.2854	0.0018	0.0003	0.2019	0.00058	0.00044
R <sup>2</sup>	0.978	0.967	0.916	0.931	0.911	0.969	0.992	0.969	0.967
RMSE	0.207	0.652	1.065	0.251	0.790	0.665	0.139	0.618	0.775
CHI <sup>2</sup>	0.097	3.879	10.523	0.210	6.267	4.559	0.040	4.454	6.305
<b>Elo</b>									
α (mg·g <sup>-1</sup> ·min <sup>-1</sup> )	2.29E+	0.089	0.174	24.25E+	0.264	8.91E-02	2.27E+1	0.129	0.147
	33			5			0		
β (g·mg <sup>-1</sup> )	17.423	0.236	0.328	6.4177	0.575	0.211	5.617	0.299	0.237
R <sup>2</sup>	0.972	0.975	0.933	0.955	0.944	0.975	0.991	0.980	0.977
RMSE	0.234	0.555	0.894	0.205	0.580	0.589	0.148	0.482	0.626
CHI <sup>2</sup>	0.125	2.231	4.537	0.145	1.979	2.878	0.047	2.239	3.397
<b>IPD</b>									

$k_{id}$ ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$ )	-0.0036	0.4968	0.4701	0.0397	0.3322	0.529	0.0355	0.4756	0.5808
$c$ ( $\text{mg}\cdot\text{g}^{-1}$ )	4.8538	-0.2402	0.707	2.8358	1.1001	-0.3095	4.9492	0.2236	0.2104
$R^2$	0.0098	0.9891	0.9743	0.6317	0.9939	0.9853	0.5741	0.9976	0.9954

**Table S4.** Isotherm model parameters for CR adsorption onto biocomposite films

	CH <sub>1</sub> BC	CH <sub>2</sub> BC	CH <sub>1</sub> ABC	CH <sub>2</sub> ABC	CH <sub>1</sub> BBC	CH <sub>2</sub> BBC
<b>Langmuir</b>						
Q <sub>m</sub>	48.951	55.258	28.943	44.718	32.983	62.234
K <sub>L</sub>	0.010	0.014	0.042	0.011	0.041	0.008
R <sub>L</sub>	0.869-	0.826-	0.615-	0.858-	0.619-	0.893-
	0.222	0.169	0.064	0.206	0.065	0.263
R <sup>2</sup>	0.827	0.922	0.744	0.924	0.738	0.842
RMSE	4.690	3.718	4.223	3.002	4.499	5.184
CHI <sup>2</sup>	49.214	21.018	23.740	16.103	43.290	18.445
<b>Freundlich</b>						
K <sub>f</sub>	3.318	4.118	5.431	2.644	7.831	2.345
1/n	0.432	0.435	0.305	0.466	0.254	0.523
R <sup>2</sup>	0.934	0.983	0.937	0.968	0.954	0.918
RMSE	2.894	1.725	2.097	1.940	1.888	3.721
CHI <sup>2</sup>	12.259	1.711	7.745	5.191	9.528	3.826
<b>Temkin</b>						
A	0.721	0.501	1.524	0.304	3.998	0.294
B	2.356	3.249	1.795	2.809	1.704	3.296
R <sup>2</sup>	0.811	0.882	0.861	0.889	0.887	0.810
RMSE	4.902	4.563	3.108	6.620	2.951	5.586

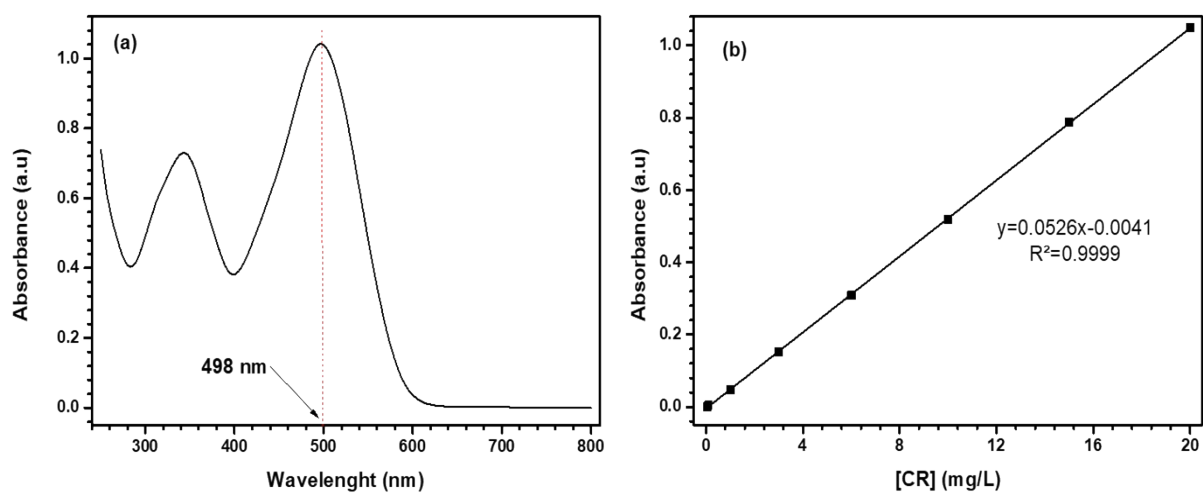
CHI<sup>2</sup>      25.103      10.031      13.309      14.752      14.995      11.783

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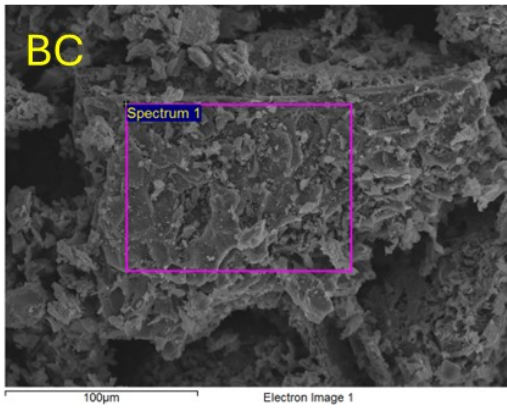
**Table S5.** Thermodynamic parameters of CR adsorption

Sample	Temperature (K)	Van't Hoff equation	$\Delta G^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta H^\circ$ (kJ·mol <sup>-1</sup> )
CH <sub>1</sub> BC	303	$y = -5765.9x + 18.395$	+1.338		
	308	$R^2 = 0.8741$	+1.016	+0.153	47.938
	313		+0.510		
	318		-1.068		
CH <sub>2</sub> BC	303	$y = -9291.1x + 29.985$	+1.182		
	308	$R^2 = 0.8417$	+0.930	+0.249	+77.246
	313		-0.056		
	318		-2.695		
CH <sub>1</sub> ABC	303	$y = -5890.9x + 18.516$	+2.292		
	308	$R^2 = 0.9759$	+1.723	+0.154	+48.976
	313		+0.586		
	318		+0.108		
CH <sub>2</sub> ABC	303	$y = -11341x + 36.37$	+2.179		
	308	$R^2 = 0.8784$	+1.495	+0.302	+94.289
	313		+0.512		
	318		-2.583		
CH <sub>1</sub> BBC	303	$y = -6887.7x + 21.903$	+2.158		
	308	$R^2 = 0.9657$	+1.225	+0.182	+57.264
	313		-0.057		

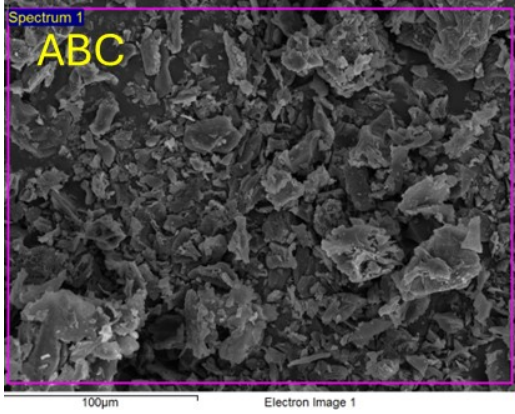
	318		-0.438		
	303	$y = -10220x + 33.103$	+1.797		
CH <sub>2</sub> BBC	308	$R^2 = 0.9786$	-17.063	+0.275	+84.969
	313		-1.401		
	318		-2.309		



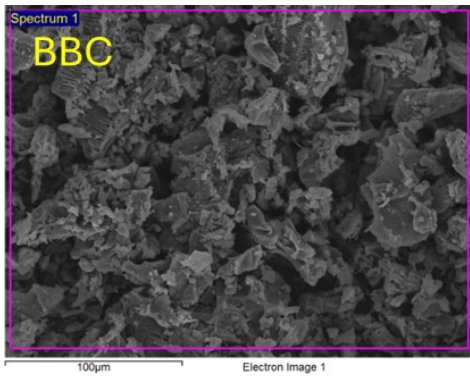
**Fig. S1.** UV-vis spectrum of CR at 20 mg/L (a) and calibration curve (b)



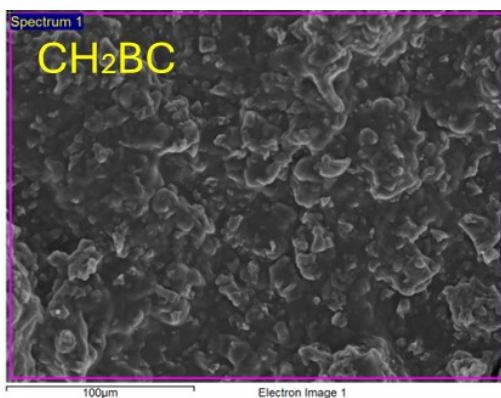
Spectrum	In stats.	C	O	Mg	K	Ca	Total
Spectrum 1	Yes	79.83	16.49	0.27	1.93	1.48	100.00
Mean		79.83	16.49	0.27	1.93	1.48	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	
Max.		79.83	16.49	0.27	1.93	1.48	
Min.		79.83	16.49	0.27	1.93	1.48	



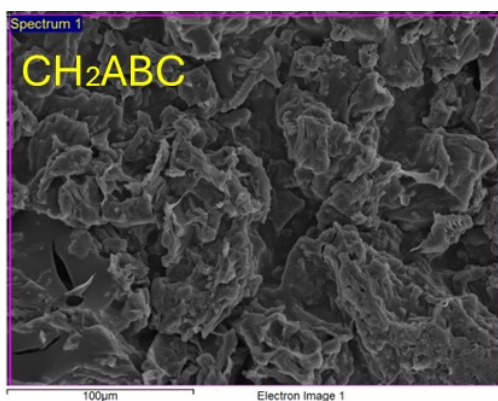
Spectrum	In stats.	C	O	Mg	K	Ca	Total
Spectrum 1	Yes	74.21	24.78	0.22	0.37	0.43	100.00
Mean		74.21	24.78	0.22	0.37	0.43	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	
Max.		74.21	24.78	0.22	0.37	0.43	
Min.		74.21	24.78	0.22	0.37	0.43	



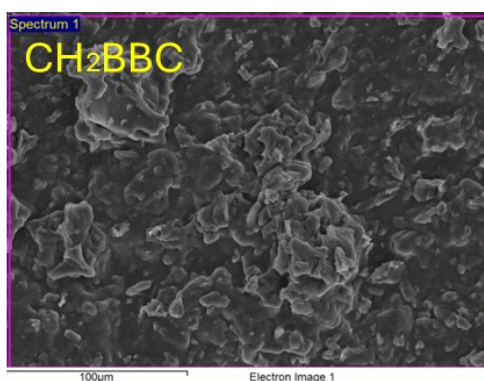
Spectrum	In stats.	C	O	Na	Mg	K	Ca	Fe	Total
Spectrum 1	Yes	78.00	17.70	0.91	0.54	0.50	1.95	0.40	100.00
Mean		78.00	17.70	0.91	0.54	0.50	1.95	0.40	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		78.00	17.70	0.91	0.54	0.50	1.95	0.40	
Min.		78.00	17.70	0.91	0.54	0.50	1.95	0.40	



Spectrum	In stats.	C	O	Na	K	Ca	Total
Spectrum 1	Yes	59.16	39.04	0.45	0.79	0.55	100.00
Mean		59.16	39.04	0.45	0.79	0.55	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	
Max.		59.16	39.04	0.45	0.79	0.55	
Min.		59.16	39.04	0.45	0.79	0.55	

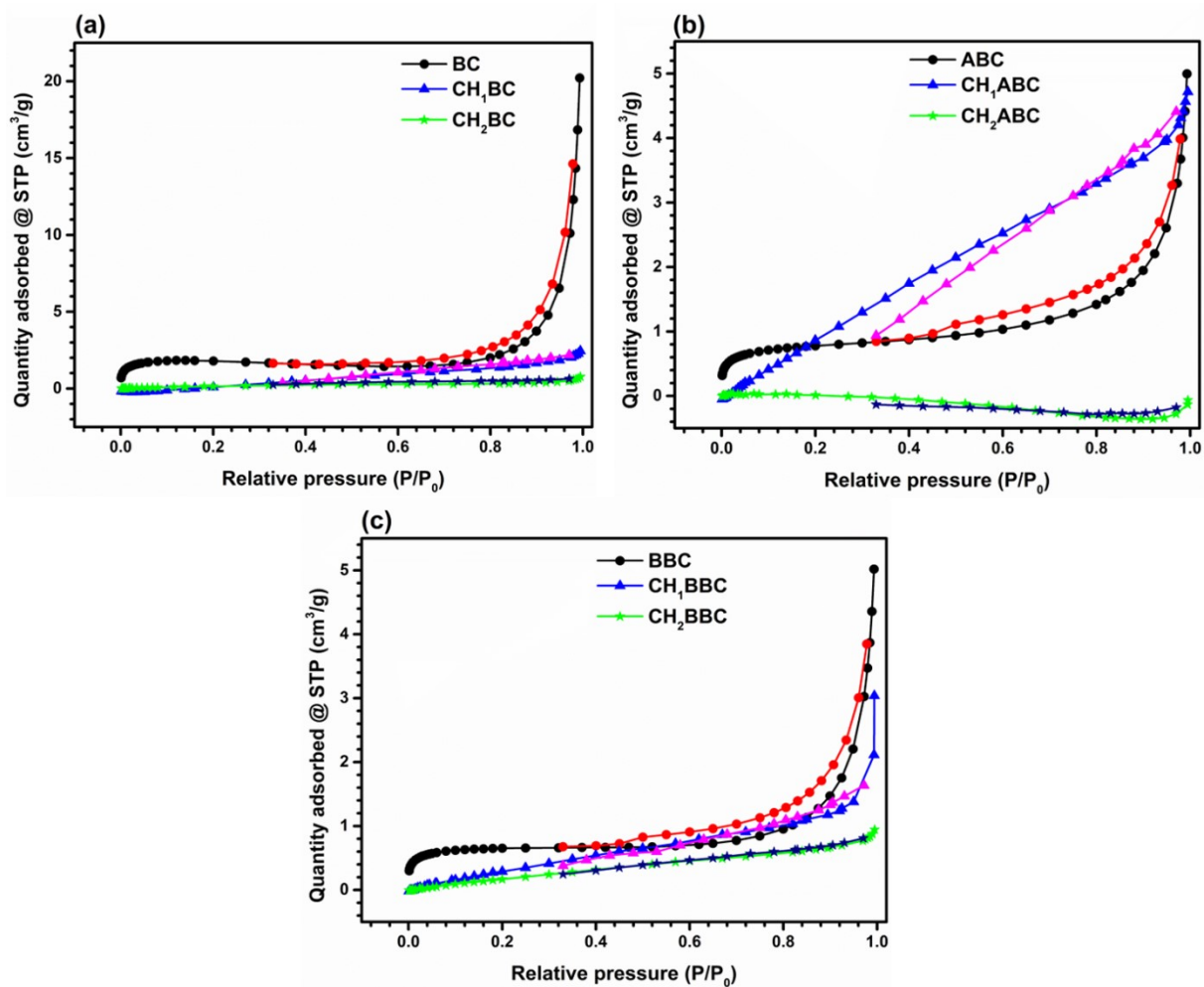


Spectrum	In stats.	C	O	Mg	K	Ca	Total
Spectrum 1	Yes	69.32	30.10	0.22	0.11	0.24	100.00
Mean		69.32	30.10	0.22	0.11	0.24	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	
Max.		69.32	30.10	0.22	0.11	0.24	
Min.		69.32	30.10	0.22	0.11	0.24	

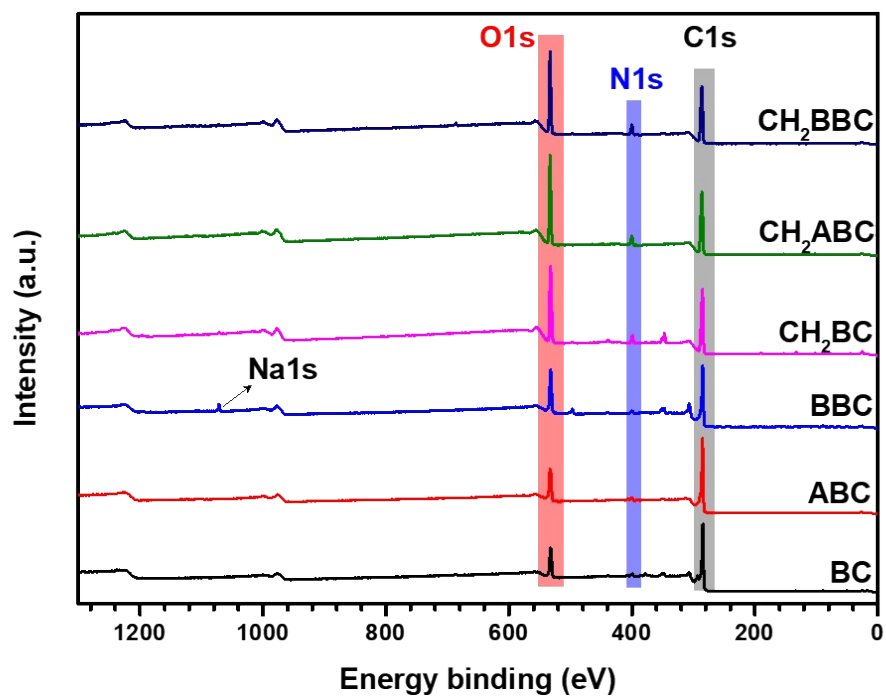


Spectrum	In stats.	C	O	Na	Mg	K	Ca	Total
Spectrum 1	Yes	61.25	37.00	0.81	0.16	0.15	0.63	100.00
Mean		61.25	37.00	0.81	0.16	0.15	0.63	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	
Max.		61.25	37.00	0.81	0.16	0.15	0.63	
Min.		61.25	37.00	0.81	0.16	0.15	0.63	

**Fig. S2.** EDS data of BC, ABC, BBC, CH<sub>2</sub>BC, CH<sub>2</sub>ABC, and CH<sub>2</sub>BBC



**Fig. S3.** Nitrogen physisorption isotherm of BC, CH<sub>2</sub>BC and CH<sub>1</sub>BC (a), ABC, CH<sub>2</sub>ABC and CH<sub>1</sub>ABC (b), and BBC, CH<sub>2</sub>BBC and CH<sub>1</sub>BBC (c)



**Fig. S4.** XPS full-scan spectra of biochars and biocomposite chitosan-biochars

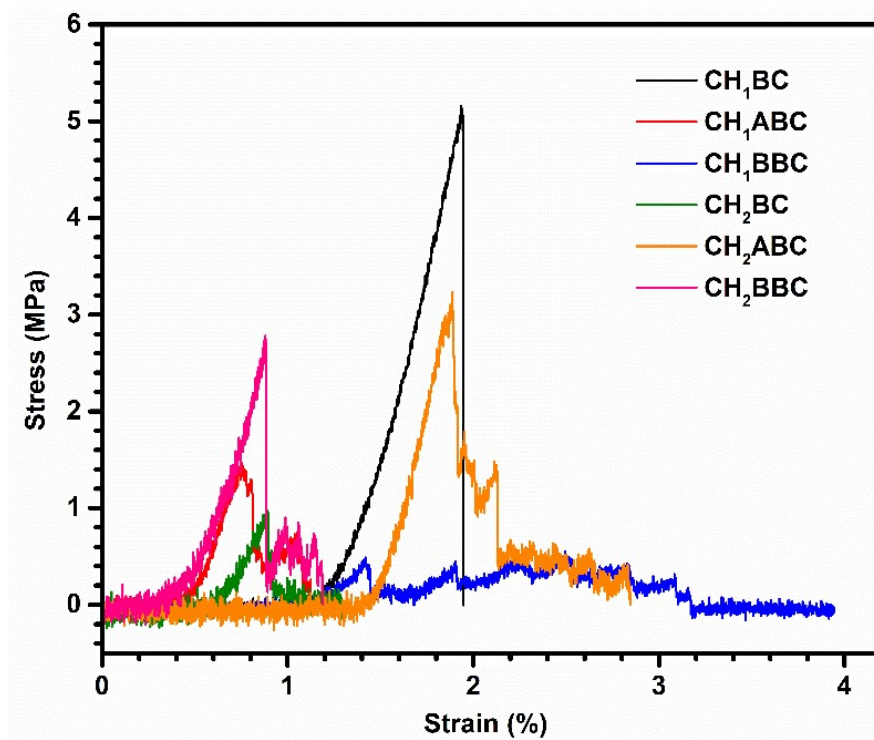
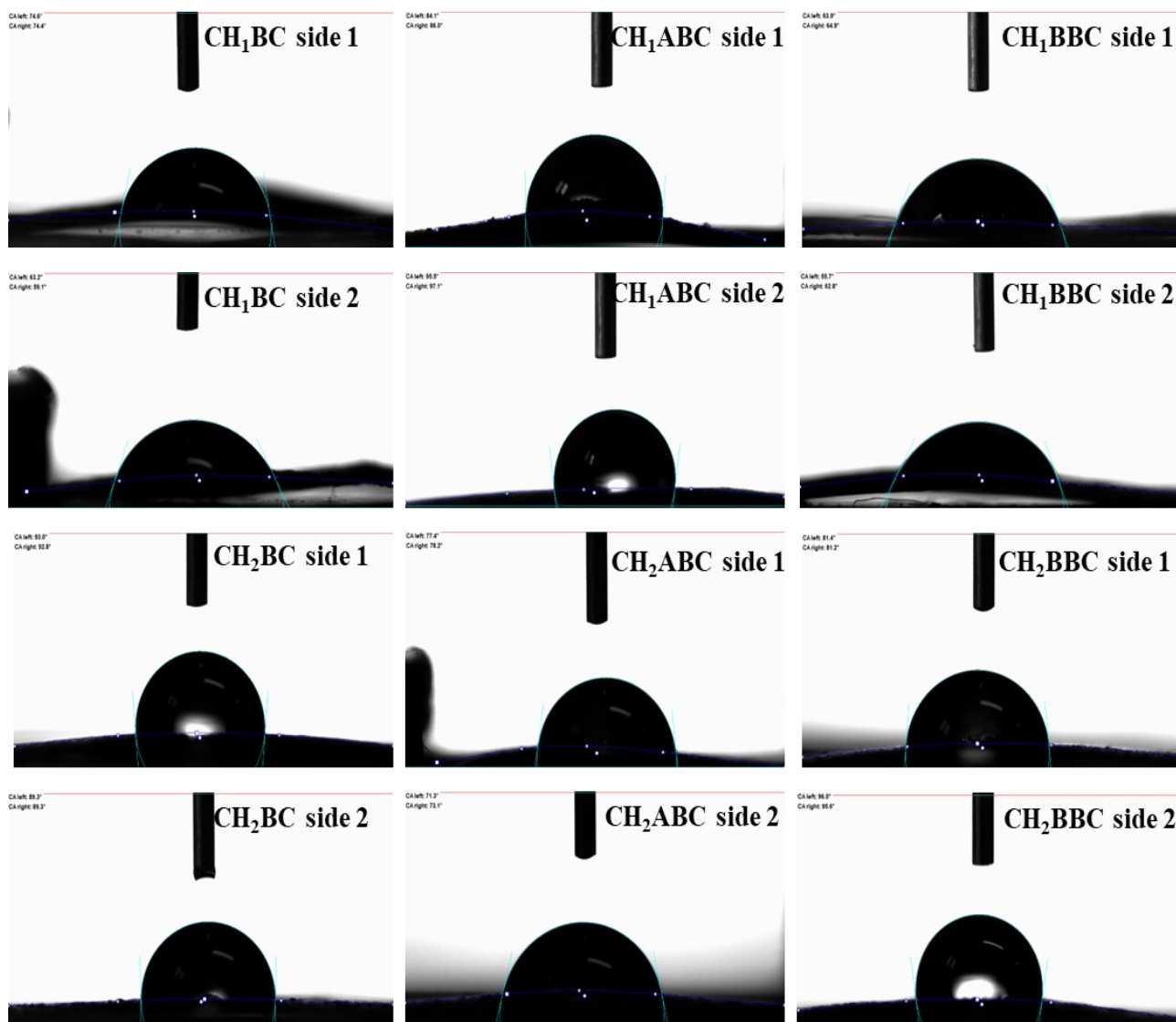


Fig. S5. Tensile strain





**Fig. S6.** Water contact angle

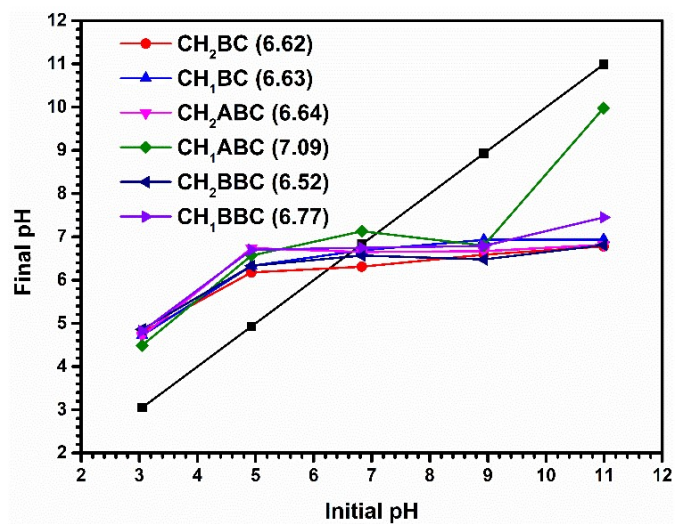
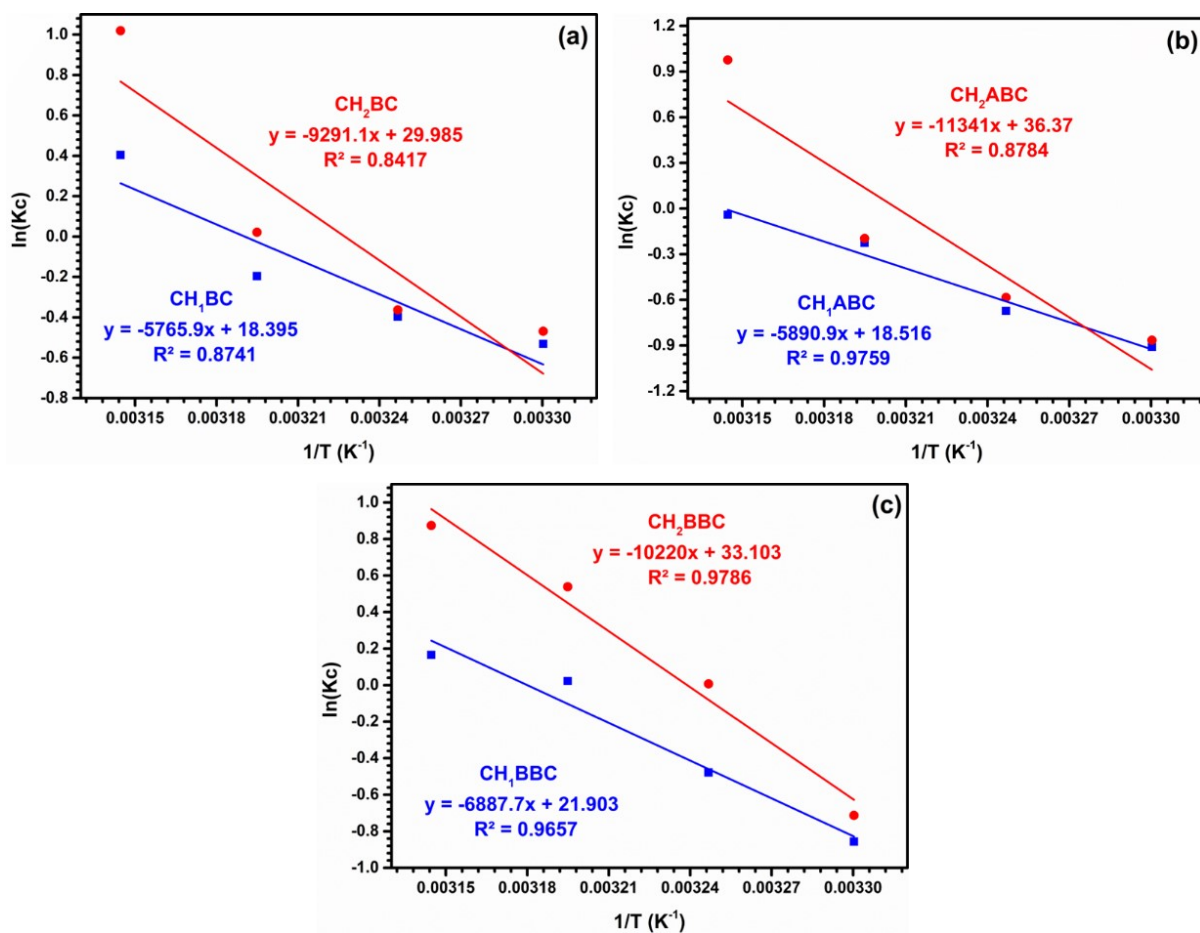
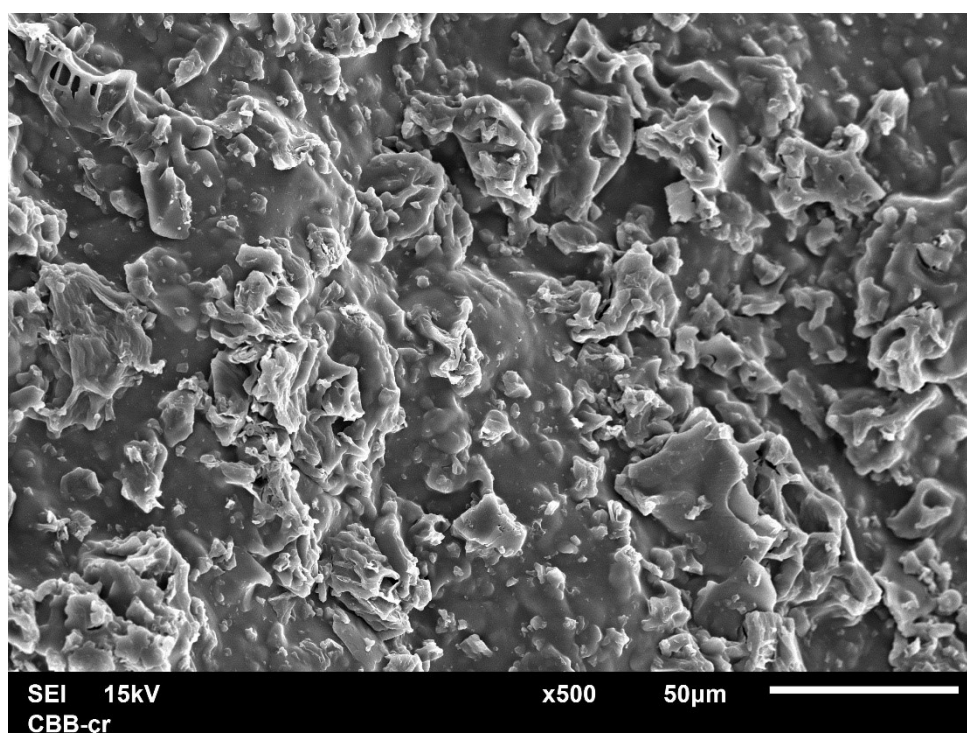
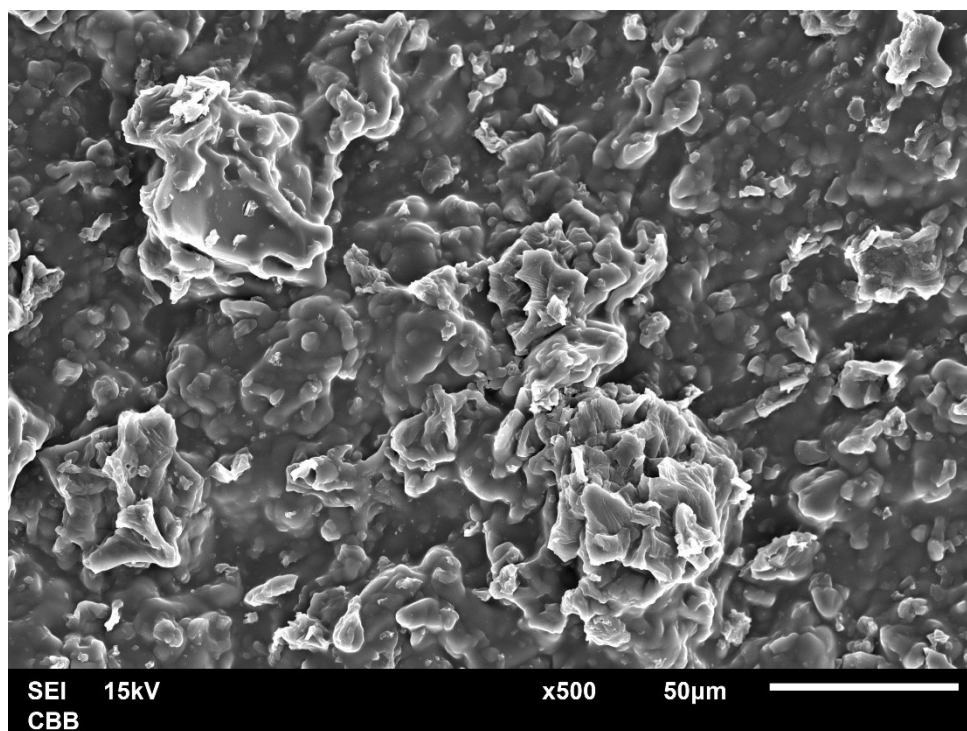


Fig. S7. Determination of pH point of zero charge biocomposite films



**Fig. S8.** Van't Hoff plots for the adsorption of  $CH_2BC$  and  $CH_1BC$  (a),  $CH_2ABC$  and  $CH_1ABC$  (b), and  $CH_2BBC$  and  $CH_1BBC$  (c)



**Fig. S9.** SEM of CH<sub>2</sub>BBC before and after CR adsorption

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