Supplementary material for

Adsorption of Methylene Blue onto clay/carbon composite: Kinetics and isotherms study

Freeman Madhau^{a,c}, Zhenjun Wu^{a,b}, Yahui Shi^{a, b}, Dongjin Wan^{a, b, *}, Shepherd Tichapondwa^d, Yangyang Wang^a, Jiekai Wang^a, Heyu Wan^a

^a College of Environmental Engineering, Henan University of Technology, Zhengzhou, Henan 450001, China

^b Zhengzhou Key Laboratory of Water Safety and Water Ecology Technology, Zhengzhou, Henan 450001, China

[°] Department of Water Resources Engineering, Bulawayo Polytechnic, P.O. Box1392, Bulawayo, Zimbabwe

^d Water Utilization and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa

* Corresponding author: djwan@haut.edu.cn

Supplementary material (Text)

Text 1. Analysis methods.

All experiments were at least performed in triplicates and average values were used. Values in the column chart are the standard deviation. The one-way ANOVA was utilized to test whether there was a significant difference among different groups. Identical letters represent no significant differences at a significance level of P < 0.05 in the column charts.

MB concentrations were measured at 664 *nm* using a UV-visible spectrophotometer (TU-1900, China). All samples were filtered before analysis using a 0.45 μ m membrane supplied by Shanghai Xin Ya Purification Equipment Co., Ltd China. A ZEISS GeminiSEM 300 (Germany) instrument was used for both Energy-Dispersive X-ray spectroscopy (EDS) analysis and Scanning Electron Microscopy (SEM) imaging. The elements C, H, O, and N were measured using a vario MICRO select elemental analyzer (Elementar, Germany). The specific surface area and other physical properties of the samples were determined using the Brunauer-Emmet-Teller (BET) method with a Micrometrics ASAP 2460 (China) instrument. Fourier transform infrared (FTIR) spectra of 4,000-400 cm⁻¹ were obtained using a Nexus 670 (USA) spectrometer. X-ray diffraction (XRD) spectra were acquired on a D8 Advanced diffractometer (USA) using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed using Thermo Escalab 250SXI (USA). Dissolved organic carbon (DOC) amounts were determined by a total organic carbon analyzer (TOC-LCPN, Japan).

Supplementary material (tables)

Table S1. Characteristic of MB dye

Parameter	Value
Chemical structure	H ₃ C, N CH ₃ CH ₃ Ci
Chemical formula	$C_{16}H_{18}CIN_3S$
Molecular weight (g/mol)	319.85
Solubility in water (25 °C)	10%

Table S2. The comparison of maximum adsorption capacities of different activated materials forMB adsorption.

Operating condition	ons	Activating	Adsorbent			
	Activation	Temperature	dosage	Co	Q_m	
Adsorbent	process	(°C)	(g/L)	(mg/L)	(mg/g)	Reference
Rosa canina seeds	Chemical	500	2	20-100	47.20	(Jawad et al., 2016)
Coconut leaves	Chemical	-	0.5-2.5	30-400	126.6	(El-Sayed, Yehia and Asaad, 2014)
Corncob	Chemical	400	2	5-50	28.65	(Ren et al., 2011)
Corncob	Chemical	500	2	5-50	17.57	(Zhang, Zhang and Li, 2018)
SBE@C(500 °C)	Physical	500	0.6	10-60	29.54	This study
SBE	Physical	25	0.6	10-60	10.62	This study

Table S3: Thermodynamic parameters for MB adsorption onto SBE@C (500 °C).

Adsorbent	T(°C)	ΔG° (kJ/mol)	$\Delta \mathrm{H}^{\circ}$ (kJ/mol)	$\Delta \mathrm{S}^{\circ}$ (J/mol)
	25	-9.96		
SBE@C(500 °C)	35	-10.30	26.39	121.00
	45	-12.38		

	Atomic percent (%)			
Element	SBE	SBE@C(500 °C)	SBE after adsorption	SBE@C(500 °C) after adsorption
С	49.56	58.25	50.66	59.64
О	42.33	35.21	40.25	35.04
Al	1.97	1.79	2.17	1.14
Si	6.01	4.65	6.83	4.11
S	0.10	0.08	0.02	0.07
Cl	0.03	0.01	0.07	0

Table S4. EDS of SBE, SBE@C (500 °C), SBE after adsorption, and SBE@C (500 °C) after adsorption.

Table S5. BET analysis results for SBE and SBE@C (500 °C).

Sample	Specific surface area (m ² /g)	Mesopore Volume (cm ³ /g)	Average Pore diameter (nm)
SBE	0.17	5.82×10^{-4}	13.83
SBE@C (500 °C)	68.28	3.40 ×10 ⁻¹	19.93

Supplementary material (Figures)

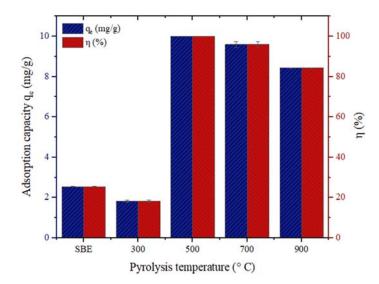


Figure S1. Adsorption capacity of MB in solution by SBE@C at different pyrolysis temperatures $(C_o = 10 \text{ mg/L}, \text{ dosage} = 1 \text{ g/L}, \text{ solution volume} = 100 \text{ mL}, \text{ rotation speed} = 150 \text{ rpm}, \text{ temperature} = 25 ^{\circ}C, 120 \text{ minutes}).$

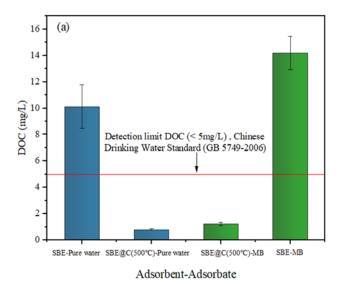


Figure S2. (a) DOC of pure water and MB solution ($C_0 = 10 \text{ mg/L}$, dosage = 0.6 g/L and V= 100 mL) after adsorption by SBE and SBE@C (500 °C) at 25 °C.

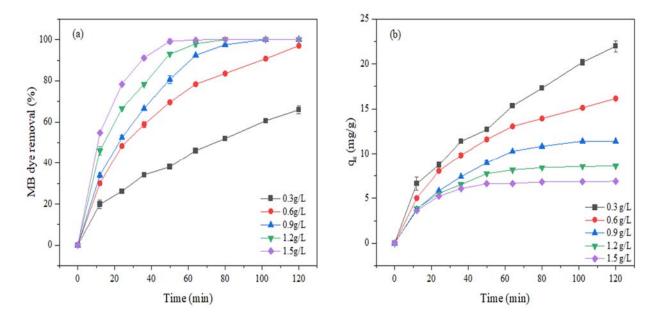


Figure S3. Effects of SBE@C (500 °C) dosage on (a) removal efficiency (%) and (b) adsorption capacity (mg/g), ($C_0=10 \text{ mg/L}$, rotation speed = 150 rpm and V= 100 mL).

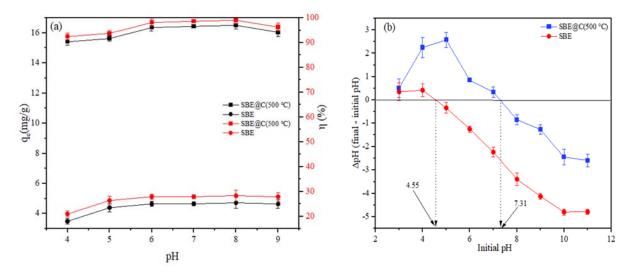


Figure S4. (a) Effect of pH on the adsorption of MB by SBE and SBE@C (500 °C), and (b) pH of zero point charge (pH_{pzc}) plots of SBE and SBE@C (500 °C).

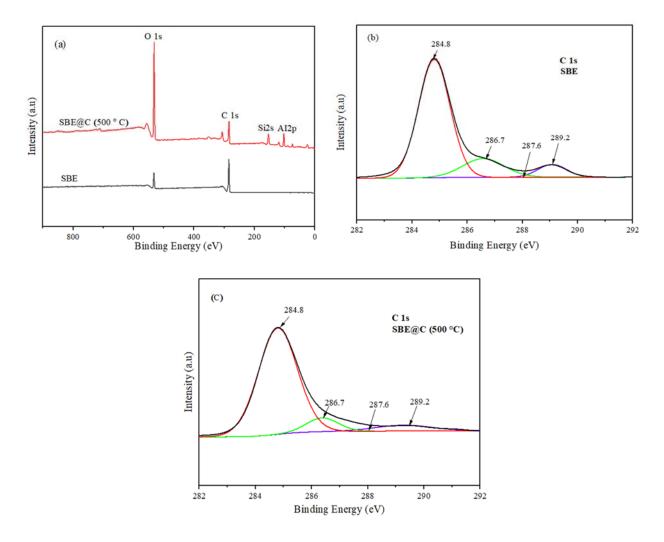


Figure S5. (a) Survey scan, C1s XPS spectra of (b) SBE, and (c) SBE@C (500 °C).

References

El-Sayed, G.O., Yehia, M.M. and Asaad, A.A. (2014) 'Assessment of activated carbon prepared from corncob by chemical activation with phosphoric acid', *Water Resources and Industry*, 7–8. doi:10.1016/j.wri.2014.10.001.

Jawad, A.H. *et al.* (2016) 'Adsorption of methylene blue onto activated carbon developed from biomass waste by H2SO4 activation: kinetic, equilibrium and thermodynamic studies', *Desalination and Water Treatment*, 57(52). doi:10.1080/19443994.2016.1144534.

Ren, L. *et al.* (2011) 'Preparation and evaluation of cattail fiber-based activated carbon for 2,4dichlorophenol and 2,4,6-trichlorophenol removal', *Chemical Engineering Journal*, 168(2). doi:10.1016/j.cej.2011.01.021.

Zhang, X., Zhang, L. and Li, A. (2018) 'Eucalyptus sawdust derived biochar generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal', *Journal of Environmental Management*, 206. doi:10.1016/j.jenvman.2017.11.079.