

Supplementary Material

A Novel Adsorbent of Attapulgite & Carbon Composites Derived from Spent Bleaching Earth for Synergistic Removal of TC and Cu(II) in Water

Yuxin Ke ^{1,2}, Xiaoli Zhu ^{1,2,*}, Shaocheng Si ^{1,2}, Ting Zhang ^{1,2}, Junqiang Wang ^{1,3} and Ziyi Zhang ³

1 College of Urban and Environmental Science, Northwest University, Xi'an, 710127, China

2 Shaanxi Key Laboratory of Earth Surface System and Environment Carrying Capacity, Xi'an, 710127, China;

3 Xi'an Jinborui Ecological Tech. Co., Ltd. Xi'an, 710065, China

* Correspondence: xiaolizhu@nwu.edu.cn

Text S1

The characterization corresponding to mechanism analysis of A&Cs was conducted as follows. The micro-morphology, structure and surface elemental composition of A&Cs were analyzed by SEM-EDS (HITACHI SU8010, Japan). The specific surface area was calculated through the BET method, while FTIR (BRUKER Invenio, Germany) and XPS (ULVAC -PHI - 5000VPIII, Japan) were applied to investigate the chemical states of surface elements and the functional groups of A&Cs. The XRD (Bruker D8, Germany) was used to reflect the types and structure of crystals in A&Cs. The determination of pH_{pzc} (the pH value for sorbent at the point of zero charges) for A&Cs were conducted through the pH drift method, in which the pH values were measured by the pH meter (Mettler Toledo FE28, Switzerland).

Eq. S1 Removal efficiency:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (S1)$$

Eq. S2 Adsorption capacity:

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (S2)$$

Where η (%) and Q_e (mg/g) represent removal rate and the adsorption capacity at equilibrium state, respectively; C_0 and C_e (mg/L) are the concentration before and after adsorption, respectively.

Eq. S3 Pseudo-first-order (PFO) kinetic model:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (S3)$$

Eq. S4 Pseudo-second-order (PSO) kinetic model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (S4)$$

Where q_t and q_e (mg/g) are the adsorption capacity of A&C500 for TC or Cu(II) at the time t (h) and equilibrium stage; K_1 (min⁻¹) and K_2 (g/(mg·min)) refer to the constant of pseudo-first-order and pseudo-second-order kinetic model, respectively.

Eq. S5 Intra-particle diffusion (IPD) kinetic model:

$$q_t = K_i \cdot t^{0.5} + C_i \quad (S5)$$

Where K_i (mg/(g·h)) refers to the constant of intra-particle diffusion kinetic model; and C_i is the constant corresponding to the thickness of the boundary layer.

Eq. S6 Langmuir isotherm model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (S6)$$

Eq. S7 Freundlich isotherm model:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (S7)$$

Where q_e (mg/g) is the adsorption capacity of TC or Cu(II) at equilibrium state, q_m (mg/g) is the maximum sorption capacity of A&C500 for TC or Cu(II); KL (L/mg) is the Langmuir constant that relates to the free energy of sorption; K_F is the Freundlich constant related to sorption capacity; n is an empirical parameter which varies with the degree of heterogeneity of adsorbing sites.

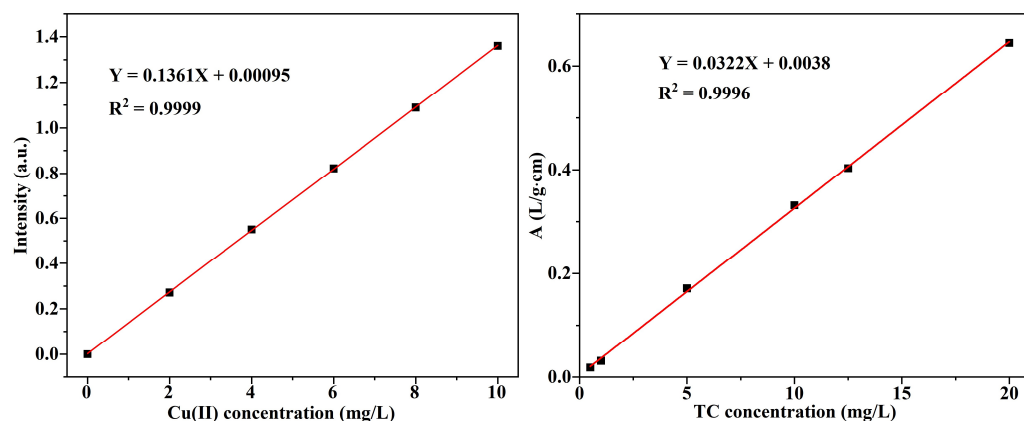


Figure S1 Standard curves for Cu(II) and TC

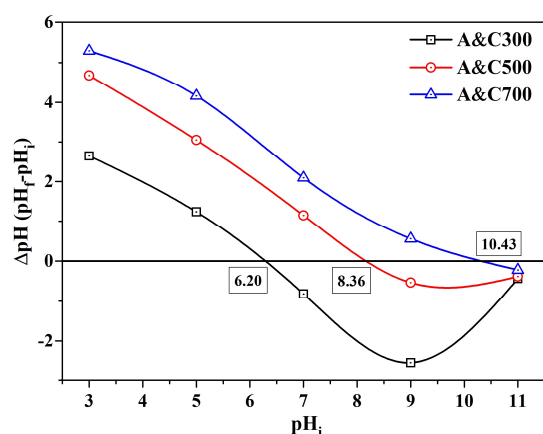


Figure S2 The pH at point of zero charges (pH_{pzc}) for A&C300, A&C500 and A&C700.

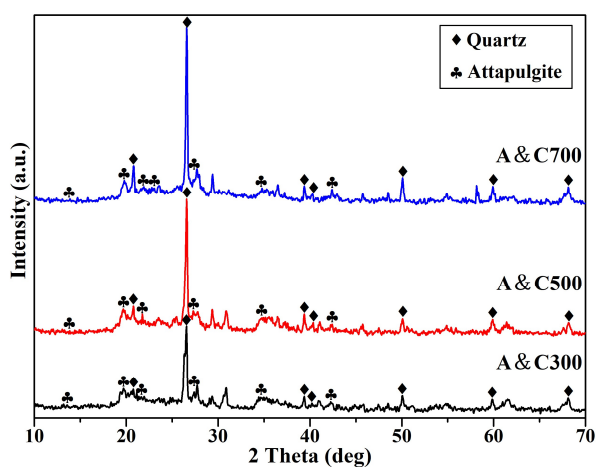


Figure S3 X-ray diffraction plots of A&C300, A&C500 and A&C700.

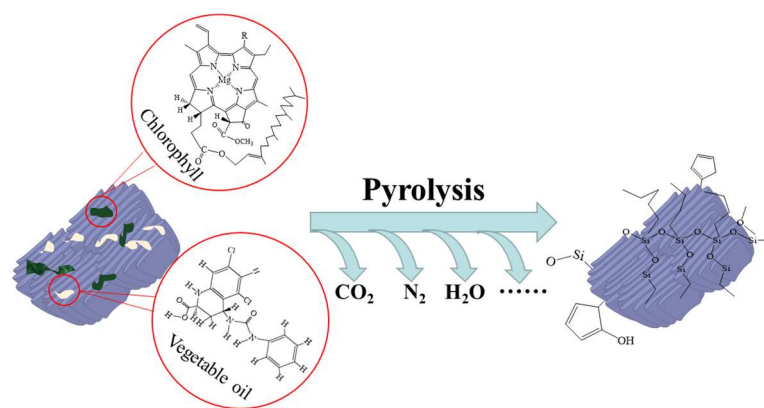


Figure S4 The pyrolysis process of SBE.

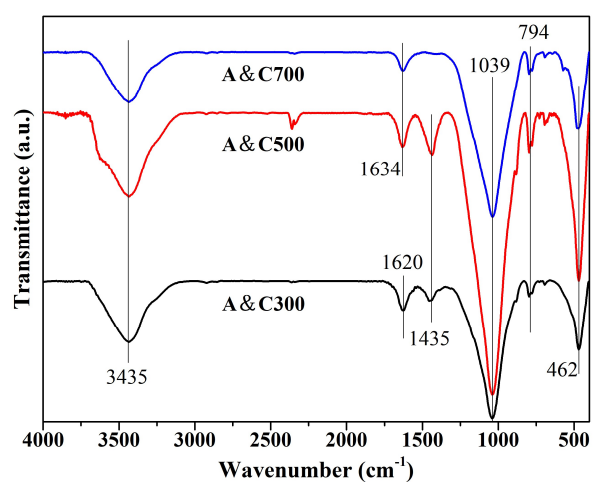


Figure S5 The FTIR spectra of A&C300, A&C500 and A&C700.

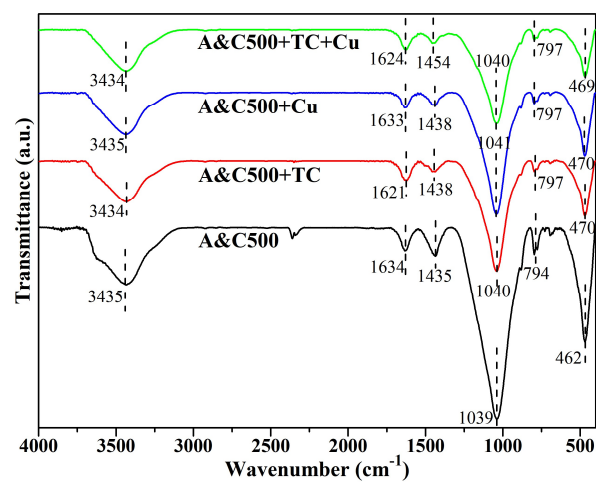


Figure S6 The FTIR spectroscopy of A&C500.

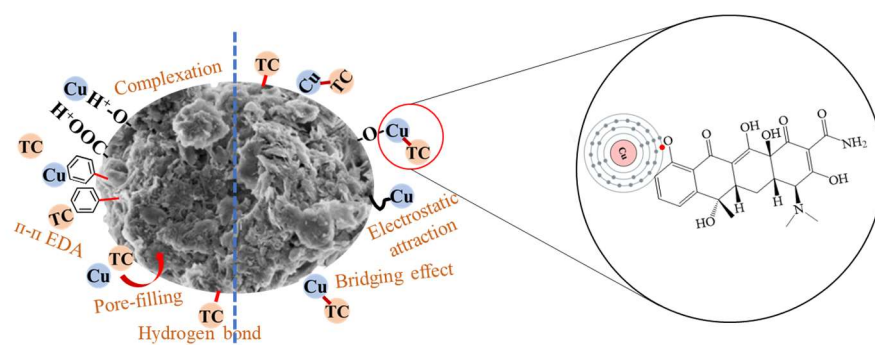


Figure S7 Adsorption mechanisms of Cu(II) and TC on A&C500

Table S1 Physicochemical properties of A&Cs

Adsorbent	Specific surface area	Total volume	Average pore size	pH	Ash content	Yield	pH _{pzc}
	m ² /g	cm ³ /g	nm		%	%	
A&C300	29.71	0.0630	43.660	6.64	76.82	84.34	6.20
A&C500	77.729	0.1024	43.754	9.03	84.41	74.02	8.36
A&C700	79.24	0.1741	43.944	9.71	87.15	70.30	10.43

Table S2 Main functional groups observed for A&Cs

	Wavenumber (cm ⁻¹)	3435	1634	1620	1435	1039	794	462
A&C500	Functional groups	-OH	C=C	C=O	C-H	C-O-C Si-O-Si	Si-O C-O	Si-O-Al

Table S3 The fitted parameters of pseudo-first-order and pseudo-second-order kinetic model

	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
	q_e	q_{48h}	K_1	R^2	q_e	q_{48h}	K_2	R^2
	mg/g	mg/g	min ⁻¹		mg/g	mg/g	g/(mg·min)	
TC	12.3	37.5	0.037	0.439	36.9	37.5	0.023	0.989
TC-BS-10	27.5	74.2	0.111	0.821	75.0	74.2	0.016	0.999
TC-BS-5	45.2	97.0	0.093	0.834	98.2	97.0	0.008	0.999
TC-BS-2	51.3	90.8	0.099	0.978	92.9	90.8	0.006	0.996
Cu	12.3	22.7	0.145	0.981	23.2	22.7	0.036	0.999
Cu-BS-10	12.4	27.3	0.097	0.964	27.7	27.3	0.029	0.998
Cu-BS-5	11.1	25.3	0.072	0.916	25.5	25.3	0.028	0.996
Cu-BS-2	11.1	26.2	0.069	0.901	26.4	26.2	0.027	0.996

Note: The q_e refers to the modeled equilibrium adsorption capacity of A&C500 for TC or Cu(II) through pseudo-first-order kinetic model, while the q_{48h} is the adsorption capacity of A&C500 at the contact time of 48h.

Table S4 The fitted parameters of intra-particle diffusion model

	Ki1	C1	R^2	Ki2	C2	R^2	Ki3	C3	R^2
	mg/(g·h)			mg/(g·h)			mg/(g·h)		
TC	9.182	14.929	0.842	3.405	21.630	0.839	2.084	22.378	0.702
TC-BS-10	9.608	35.305	0.971	13.481	29.001	0.927	1.102	66.308	0.835
TC-BS-5	32.393	15.933	0.891	9.544	54.284	0.999	3.367	73.713	0.999
TC-BS-2	19.507	23.307	0.839	10.594	39.167	0.594	4.545	60.538	0.811
Cu	6.954	4.637	0.996	4.493	7.002	0.999	0.621	18.617	0.628
Cu-BS-10	5.422	10.089	0.888	3.558	12.558	0.971	1.209	19.253	0.792
Cu-BS-5	4.857	9.433	0.933	3.261	11.035	0.999	1.160	17.262	0.999
Cu-BS-2	3.479	11.514	0.987	2.559	13.358	0.930	1.089	18.544	0.960

Table S5 The fitted parameters of Langmuir and Freundlich isotherm model

	Langmuir isotherm model			Freundlich isotherm model		
	q_m	K_L	R^2	n	K_F	R^2
TC	44.9	0.148	0.949	3.058	10.8	0.991
TC+10Cu	50.9	0.050	0.213	6.289	19.2	0.886
TC+30Cu	99.0	0.039	0.921	1.965	9.0	0.948
TC+50Cu	59.2	0.575	0.936	3.814	33.3	0.986
Cu	14.7	2.629	0.847	8.621	10.0	0.961
Cu+10TC	13.1	1.051	0.914	8.264	8.4	0.802
Cu+25TC	15.1	1.006	0.954	6.849	9.0	0.906
Cu+50TC	15.6	1.182	0.946	6.993	9.5	0.910

Table S6 Binding energy lookup table for signals from C1s, O1s and Cu2p of A&C500

Elements		A&C500	A&C500+TC	A&C500+Cu(II)	A&C500+TC+Cu(II)
		Binding Energy			
C1s	C-H/C=C	284	284.5	284.2	284.52
	C-O	286.6	286.85	286.5	286.7
O1s	O-H/C-O-C	533.35	533.7	533.7	533.5
	C=O	531.5	531.9	531.8	531.56
Cu2p	Cu2p _{3/2}			933.68	933.11
				941.78	939.20
	Cu2p _{1/2}			-	943.33
				953.49	953.00