Supporting information for

Adsorption mechanism of aqueous Cr(VI) by Vietnamese corncob biochar: a spectroscopic study

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Preparation of calibration curves and Cr(VI) stock solution

For the preparation of calibration curve, Cr(VI) solutions with concentrations of 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L were prepared from a 1000 mg/L standard Cr(VI) solution (Sigma) and diluted with 0.5M HNO_3. Subsequently, a linear standard curve was generated using an AAS ZA3300 instrument, resulting in a correlation coefficient (R^2 = of 0.996). For the adsorption experiments, the desired concentration of the Cr(VI) stock solution was prepared by diluting it from the 1000 mg/L standard Cr(VI) solution in deionized water and adjusting the pH using 0.1-0.5M HNO_3 and 0.1-0.5M NaOH.

Investigation of factors influencing the adsorption process

Effect of pH*:* The pH of the Cr(VI) adsorption process was investigated at values of 2.0-11.0. Specifically, 50 mL of a Cr(VI) solution with a concentration of 85 mg/L was introduced into 100 mL glass containers, each containing 0.1 g of CCBC, at the specified pH values for adsorption. The adsorption process was carried out using a magnetic stirrer (RSM-03-10K, Germany) with a stirring speed of 250 rpm at 34 °C and t = 180 mins. After adsorption, the biochar was separated from the solution using centrifugation (6000 rpm for 30 minutes). The Cr(VI) concentration before and after adsorption was analyzed using a AAS (ZA3300, Hitachi, Japan).

Effect of contact time*:* Adsorption time was investigated in the range of 5 to 270 mins at pH = 2.0, T = 34 °C, Cr(VI) concentration of 85 mg/L (V = 50 mL), $m_{biochar}$ = 0.1 g. The adsorption process and Cr(VI) concentration analysis were conducted in a manner similar to the previously described procedure.

Effect of initial Cr(VI) concentration*:* Various Cr(VI) concentrations were investigated sequentially: 25, 50, 75, 100, 125, 150, 175, 200, and 225 mg/L to calculate isotherm adsorption models. The adsorption process was carried out with 50 mL of Cr(VI) solution at pH = 2.0, t = 180 mins, $m_{biochar}$ = 0.1 g at 34 °C, 44 °C, and 54 °C respectively.

Effect of adsorbent dosage and ionic strength*:* The influence of adsorbent dosage and ionic strength was studied under the following conditions: pH = 2.0, t = 180 mins, T = 34 °C, with a volume of 50 mL and a Cr(VI) concentration of 85 mg/L. Adsorbent dosage ranged from 0.05 to 0.15 g (0.05; 0.075; 0.1; 0.125; 0.15), and ion strength was varied from 0.0 to 18.63 x 10^3 mg/L of KCl (0.0; 3.72; 7.45; 11.18; 14.91; 18.63 x 10^3).

ANOVA Analysis for effect of pH

pH	*Count*	*Sum*	*Average*	*Variance*
2	3	172.38	57.46	7.74
3	3	123.71	41.24	47.11
4	3	96.88	32.29	5.43
5	3	78.64	26.21	2.51
6	3	63.56	21.19	1.75
7	3	51.85	17.28	3.52
8	3	28.67	9.56	40.57
9	3	31.46	10.49	1.15
10	3	45.62	15.21	6.58
11	3	34.87	11.62	9.70

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6493.37	9	721.49	57.23	2.58E-12	2.39
Within Groups	252.13	20	12.61			
Total	6745.50	29				

ANOVA Analysis for effect of Sorbent dosage

Sorbent dosage (g)	*Count*	*Sum*	*Average*	*Variance*
0.05	3	76,68	25,56	0,12
0.075	3	113,88	37,96	0,26
0.1	3	149,15	49,72	0,41
0.125	3	178,79	59,60	0,18
0.15	3	206,73	68,91	0,03

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3535,22	4	883,80	4423,59	3,45E-16	3,48
Within Groups	2,00	10	0,20			
Total	3537,21	14				

ANOVA Analysis for effect of Ionic strength

Ionic strength	*Count*	*Sum*	*Average*	*Variance*
0.05	3	161,68	53,89	0,73
0.1	3	157,80	52,60	19,21
0.15	3	149,58	49,86	8,77
0.2	3	140,17	46,72	44,82
0.3	3	131,99	44,00	149,41

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	200,99	4	50,25	1,13	0,40	3,48
Within Groups	445,86	10	44,59			
Total	646,85	14				

ANOVA Analysis for effect of adsorption time

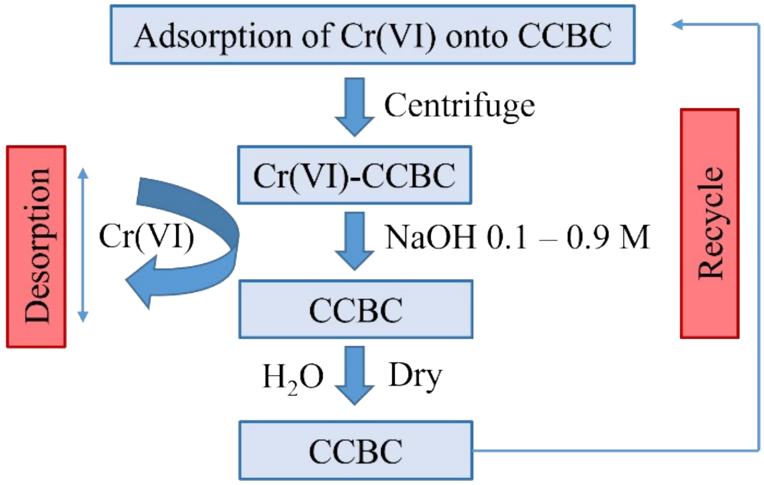
Time	*Count*	*Sum*	*Average*	*Variance*
5	3	46.03	15.34	0.29
10	3	52.11	17.37	0.39
15	3	55.37	18.46	0.24
20	3	58.62	19.54	0.08
30	3	61.54	20.51	0.06
40	3	63.91	21.30	0.03
60	3	64.8	21.60	0.00
80	3	65.6	21.87	0.23
100	3	67.29	22.43	0.16
120	3	67.9	22.63	0.15
150	3	70.77	23.59	0.13
180	3	72.51	24.17	0.05
210	3	72.14	24.05	0.10
240	3	72.4	24.13	0.03
270	3	72.05	24.02	0.05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	307.42	14	21.96	166.31	1.87E-24	2.04
Within Groups	3.96	30	0.13			
Total	311.38	44				

Table S1. Non-linear isotherm and kinetic models used in this study

	Types of models	Non-linear form	Parameters
Isotherm models (307 K)	Langmuir	$Q_e = \frac{Q_m.K_L.C_e}{1 + K_L.C_e}$	K_L (L.mg^{-1})
			Q_m (mg.g^{-1})
	Freundlich	$Q_e = K_F.C_e^{1/n}$	n
			K_F ((mg.g^{-1}).(L.mg^{-1})$^{1/n}$)
	Sips	$Q_e = \frac{Q_s.C_e^{\beta_s}}{1 + \alpha_s.C_e^{\beta_s}}$	Q_S (L.g^{-1})
			α_s (L.mg^{-1})
			β_s
	Redlich-Peterson	$Q_e = \frac{A_{RP}.C_e}{1 + K_{RP}.C_e^{\beta_s}}$	A_{RP} (mg g^{-1} min^{-1})
			K_{RP} (mg.g^{-1})
			g
Kinetic models	Pseudo-first-order	$Q_t = Q_e.(1 - e^{-k_1 t})$	$q_{e\ (cal)}$ (mg.g^{-1})
			k_1 (min^{-1})
	Pseudo-second-order	$Q_t = \frac{Q_e^2.k_2.t}{1 + k_2.Q_e.t}$	$q_{e\ (cal)}$ (mg.g^{-1})
			k_2 (g.mg^{-1}.min^{-1})
	Intraparticle diffusion	$Q_t = K_P.t^{1/2} + C$	K_P
			C
	Elovic	$Q_t = \frac{1}{\beta}.ln(1 + \alpha\beta t)$	α (mg g^{-1} min^{-1})
			β (mg.g^{-1})



Scheme S1. Desorption and reusable of corn cob biochar

Table S2. Efficiency of converting corn cob biomass to biochar

Sample	Weight of biomass (g)	Weight of product (g)	Yield of conversion (%)
CCBC-500-15	10.01	2.62	26.21
CCBC-500-30	10.06	2.48	24.70
CCBC-500-45	10.03	2.45	24.44
CCBC-600-15	10.00	2.27	22.78
CCBC-600-30	10.08	2.24	22.29
CCBC-600-45	10.03	2.21	22.06
CCBC-700-15	10.05	2.20	21.96
CCBC-700-30	10.00	2.11	21.16
CCBC-700-45	10.04	2.02	20.14

Yield = $[(m_{biochar} / m_{biomass}) \times 100\%]$ [1]

Table S3. The porosity of biochar samples synthesized from raw corn cob

Materials	**Pyrolysis condition (°C)**	**Ssa[a] (m^2/g)**	**S_{micro} (m^2/g)**	**S_{ext}[b] (m^2/g)**	**Pore volume (cm^3/g)**	**Refs**
Corn cob biochar	500	6.7	3.8	2.9	0.002	This study
Corn cob biochar	600	262	245	17	0.113	This study
Corn cob biochar	700	443	416	27	0.194	This study
Corn cob activated carbon	500	25.3	21.7	3.6	-	[2]
Corn cob activated carbon	600	30.9	-	-	0.011	[3]
Cassava Stems biochar	700	200.5	-	-	0.122	[4]
Sugarcane bagasse biochar	800	60	-	-	0.090	[5]
Spent coffee ground biochar	500	11	-	-	0.010	[6]
Pomelo fruit peel biochar	500	40.6	-	-	-	[7]

[a]Calculated with the BET model. [b]Determined by the t-plot method, $S_{ext} = Ssa - S_{micro}$. Ssa = Specific surface area.

Table S4. Percentage removal of Cr(VI) from water on CCBC samples synthesized under different pyrolysis conditions.

Pyr. condition (°C, mins)	Biochar (g)	Ads. time (mins)	Ads. temp. (°C)	% Removal
700, 15	0.1	180	34	57.6 ± 2.1
600, 15				42.5 ± 2.3
500, 15				31.3 ± 2.4
700, 30	0.1	180	34	56.5 ± 2.0
600, 30	0.1	180	34	43.1 ± 2.2
500, 30	0.1	180	34	32.5 ± 2.2
700, 45	0.1	180	34	55.3 ± 2.0
600, 45	0.1	180	34	43.7 ± 1.9
500, 45	0.1	180	34	32.9 ± 2.0

Pyr. = pyrolysis; Ssa = Specific surface area; Temp. = temperature; Ads. = adsorption.

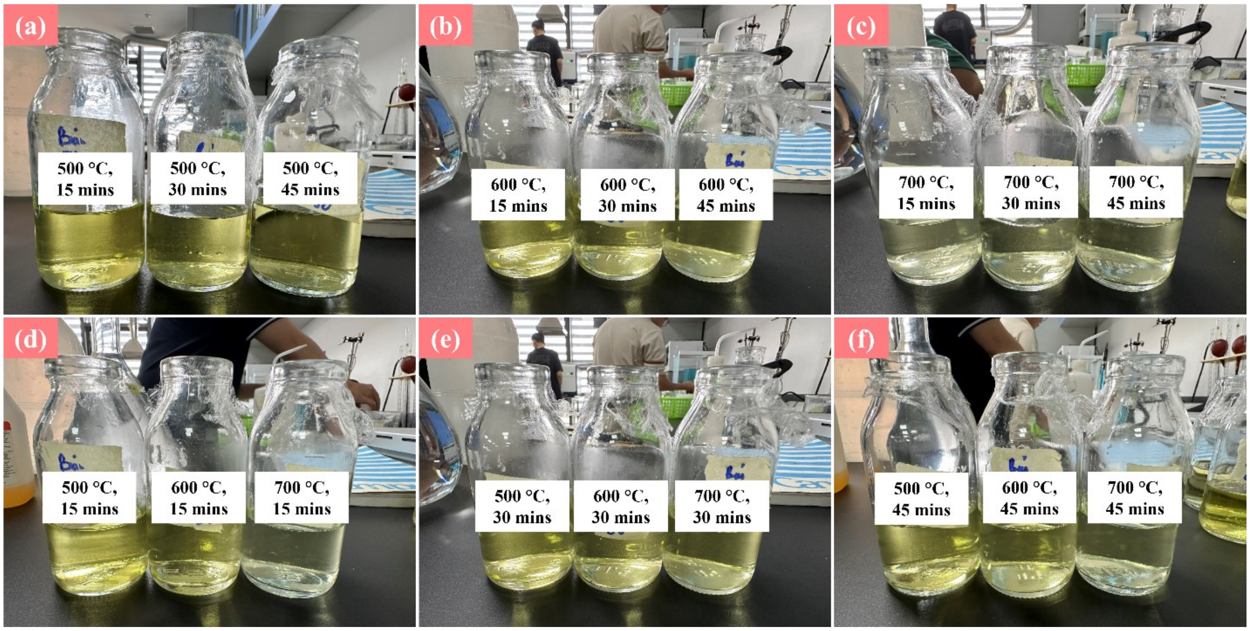


Fig. S1. The solution after Cr(VI) adsorption onto CCBC synthesized at different pyrolysis condition (C_o = 85 mg/L, pH = 2.0, T = 34 °C, t = 180 mins).

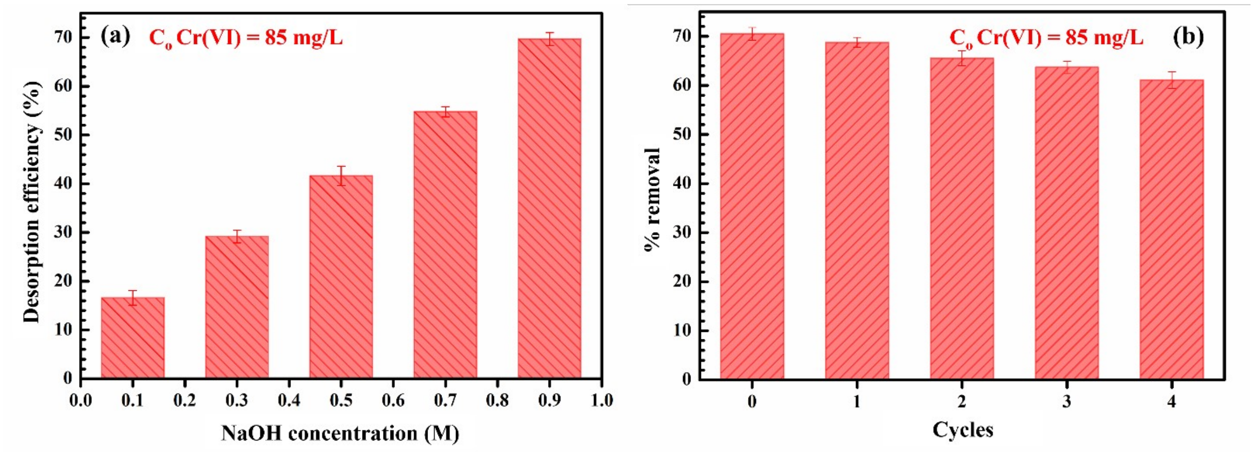


Fig. S2. The desorption efficiency (a) and recycle numbers (b) of CCBC for Cr(VI) removal from aqueous solution

Table S5. The parameters of non-linear isotherm models at 34 °C

Types of models	Parameters	34 °C
Langmuir	K_L (L.mg^{-1})	0.06
	q_m (mg.g^{-1})	38.13
	RMSE	2.25
	R^2	0.93
	χ^2	2.72
Freundlich	n	3.30
	K_F ((mg.g^{-1}).(L.mg^{-1})$^{1/n}$)	8.04
	RMSE	1.23
	R^2	0.98
	χ^2	0.43
Sips	Q_S (L.g^{-1})	6.98
	α_s (L.mg^{-1})	0.09
	β_s	0.46
	RMSE	1.06
	R^2	0.98
	χ^2	0.33
Redlich-Peterson	K_{RP} (L.g^{-1})	0.73
	A_{RP} (L.mg^{-1})	0.43
	g	16.28
	RMSE	6.96
	R^2	0.33
	χ^2	21.39

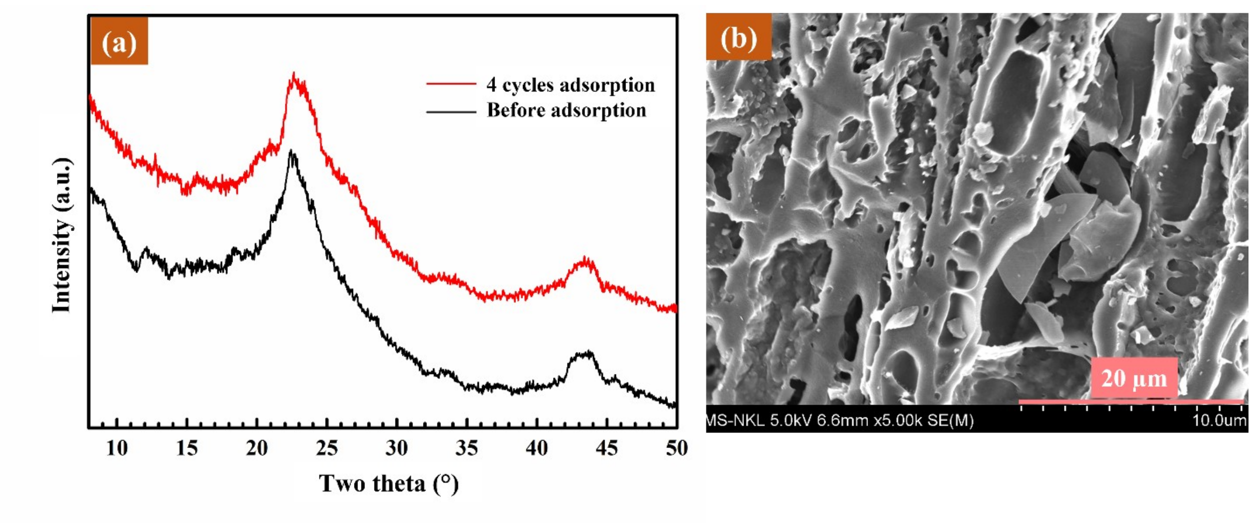
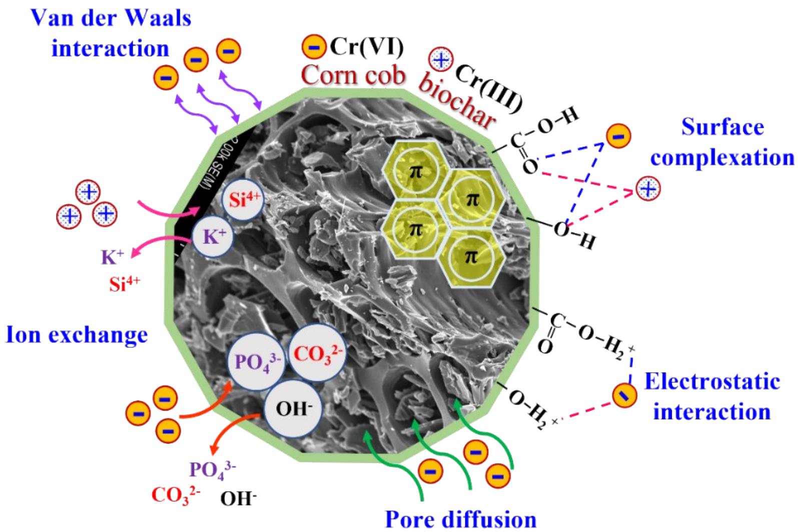


Fig. S3. XRD pattern (a); and SEM image (b) of CCBC before 4th cycles of Cr(VI) adsorption.



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103 **Fig. S4.** Possible interaction mechanism between Cr(VI) and CCBC

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