
Sorption of Cd²⁺ on bone chars with or without hydrogen per-oxide treatment under various pyrolysis temperatures: Com-parison of mechanisms and performance

Qing Guo ^{1,2}, Hongmei Tang ^{1,2}, Lu Jiang ^{1,2}, Meiqing Chen ^{1,2}, Nengwu Zhu ^{1,2},

Pingxiao Wu ^{1,2,3*}

¹ School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China

² The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, PR China

³ Guangdong Provincial Key Laboratory of Solid Wastes Pollution Control and Recycling, Guangzhou 510006, PR China

*Corresponding author: pppxwu@scut.edu.cn

Tel.: +86-20-39380538;

Fax: +86-20-39383725.

E-mail address: pppxwu@scut.edu.cn

Text S1.Characterization of BCs and BCHs

The surface function groups for adsorbents before and after sorption of heavy metals were measured by a fourier transform infrared spectra (FT-IR, Spectrum Two, Perkin-Elmer, USA) within the wavenumber of 400–4000 cm^{-1} under solid potassium bromide tablets. The scanning electron microscope (SEM, Carl Zeiss, Germany) was used to observe the morphologies of the samples. Total organic carbon (TOC) was used to evaluate the dissolved organic matter of the samples. The thermogravimetric analysis (TGA) curves were obtained by heating samples from 50 °C to 900 °C at 10 °C/min on the machine (Discovery TGA, TA Instruments, New Castle, DE, USA) under N_2 flow. The specific surface area was calculated by multipoint Brunauer-Emmett-Teller (BET 3H-2000PM Beijing Co., Ltd.) at 77 K. The crystallinity of the adsorbents before and after heavy metals sorption were determined through the power X-ray diffraction (XRD, D8 advance Sox-I, Bruker Co. USA) with CuK-alpha radiation at 40 kV ($\lambda = 0.15418 \text{ nm}$). Surface elements of the samples were characterized by X-ray photoelectron-spectra (XPS, AES430S, ANELVA, Japan).The zeta potential of adsorbent samples was measurement by a Malvern zetasizer Nano ZS (Malvern Instruments, UK).

Text S2.Batch sorption experiments

The details of the experimental method are as follows:

The stock solutions (500 mg/L) of Cd^{2+} were prepared by dissolving a quantitative amount of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in deionized water, respectively. The adsorption kinetics was investigated by dispersing 100 mg adsorbents into 200 mL aqueous solution containing Cd^{2+} with different initial concentrations (i.e., 10-200 mg/L) under pH = 5.0, I = 0.01 mol/L NaNO_3 and T = 298 K.

Adsorption experiments were performed in a series of 40 mL centrifuge tubes and carried out in an orbital shaker (HNY-100B, Honour instrument shaker, Tianjin, China) with oscillation frequency of 200 rpm/min. In brief, at dosage of various adsorbents, the effect of pH values, and ionic species were investigated by varying the solution pH (2–8), NaCl, NaSO₄ and NaF concentration (10 mmol/L), and the initial Cd(II) concentrations in the aqueous solutions were 50 (with BC(H)-700-900), 100 (with BC(H)-500), 120 mg/L (with BC(H)-300-0).

The solution pH was adjusted by negligible volume of 0.001~0.1 mol/L HNO₃/NaOH solutions.

The adsorption isotherm experiments were carried out by vigorously shaking 40 mL of different cadmium solution (from 5 to 200 mg/L) mixed with 20 mg BCs and BCHs for 48 h to reach equilibrium at pH = 5.0, I = 0.01 mol/L NaNO₃ and T = 298 K.

After the sorption experiment equilibrium achieved, the supernatants were filtrated with 0.45 μm filter membrane and measured the Cd²⁺ and Ca²⁺ concentration (C_e, mg/L) by flame atomic absorption spectrometry (FAAS, AA-6880, Shimadzu, Japan). The sorption capacity (q_e, mg/g) were calculated from the initial (C₀, mg/L) and final equilibrium concentration (C_e) of metal ions as well as the adsorbents dosage (m/V, g/L) of the uptake system with the following equation: $q_e = (C_0 - C_e) \times V / m$.

Text S3. Analytical methods

Adsorption kinetics. The experimental adsorption kinetic data was fitted by pseudo-first order and pseudo-second order models to evaluate the potential sorption mechanism.

pseudo-first-order (eq S1):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (S1)$$

pseudo-second-order (eq S2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{S2})$$

Adsorption isotherm models and thermodynamics. Langmuir isotherm (eq S3) and Freundlich isotherm model (eq S4) can be described as the following non-linear equations, respectively

$$q_e = \frac{b q_{e,\max} C_e}{1 + b C_e} \quad (\text{S3})$$

$$q_e = K_F C_e^n \quad (\text{S4})$$

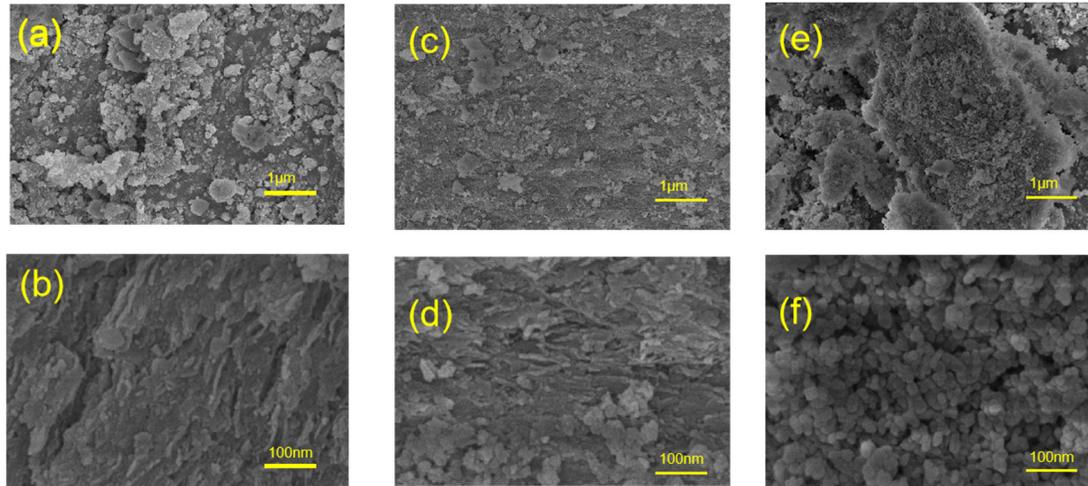


Figure S1. The SEM images of BC and BCH samples: BCH(a, b), BC-500(c, d), BC-700(e, f).

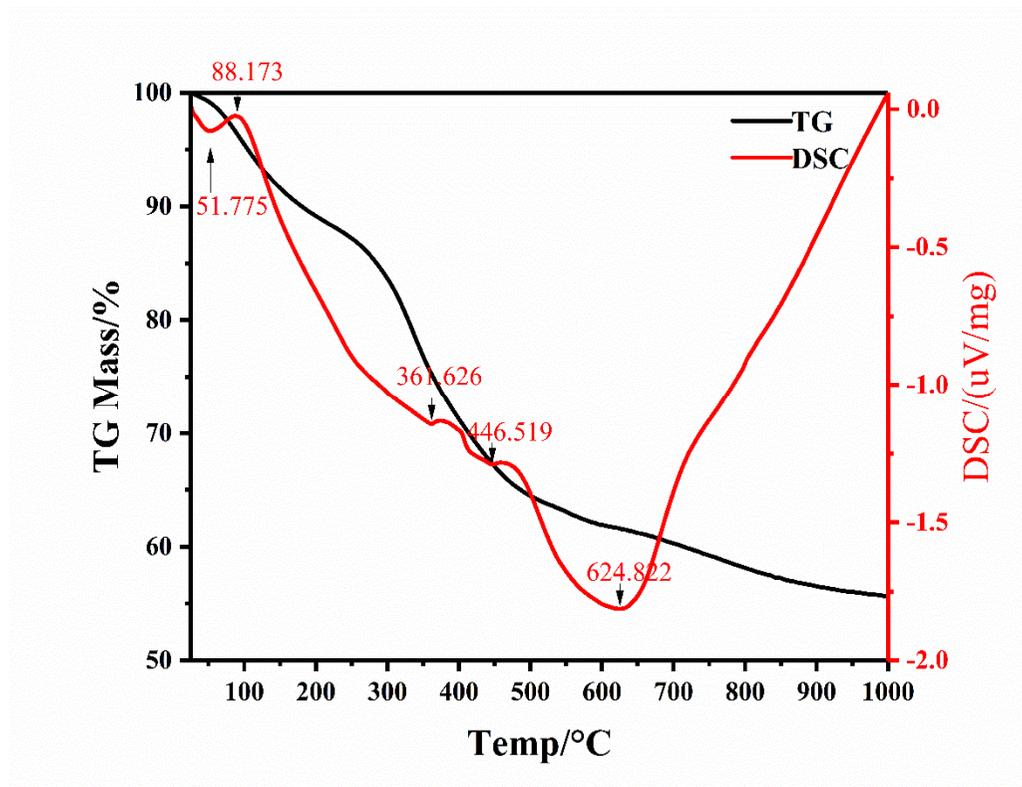


Figure S2.DTA/TGA analysis of bone sample.

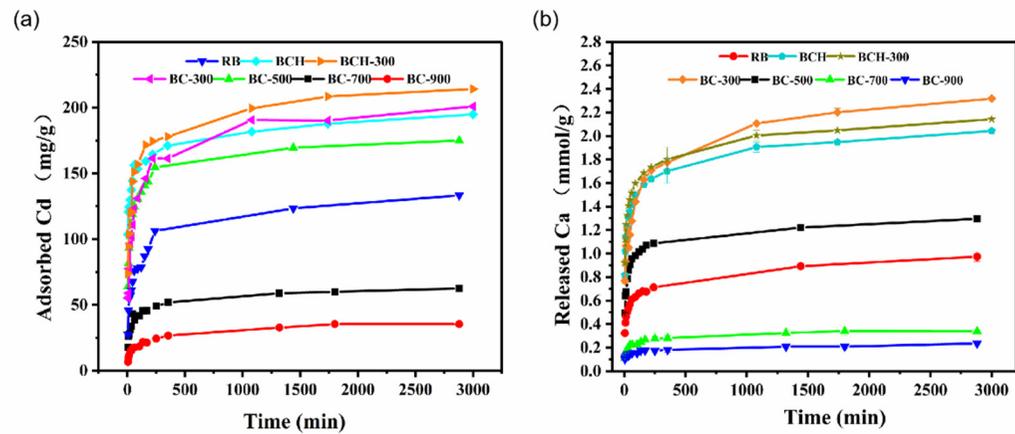


Figure S3. Effect of contact time on amounts of Cd^{2+} adsorbed (a) and Ca^{2+} released from adsorbents (b).

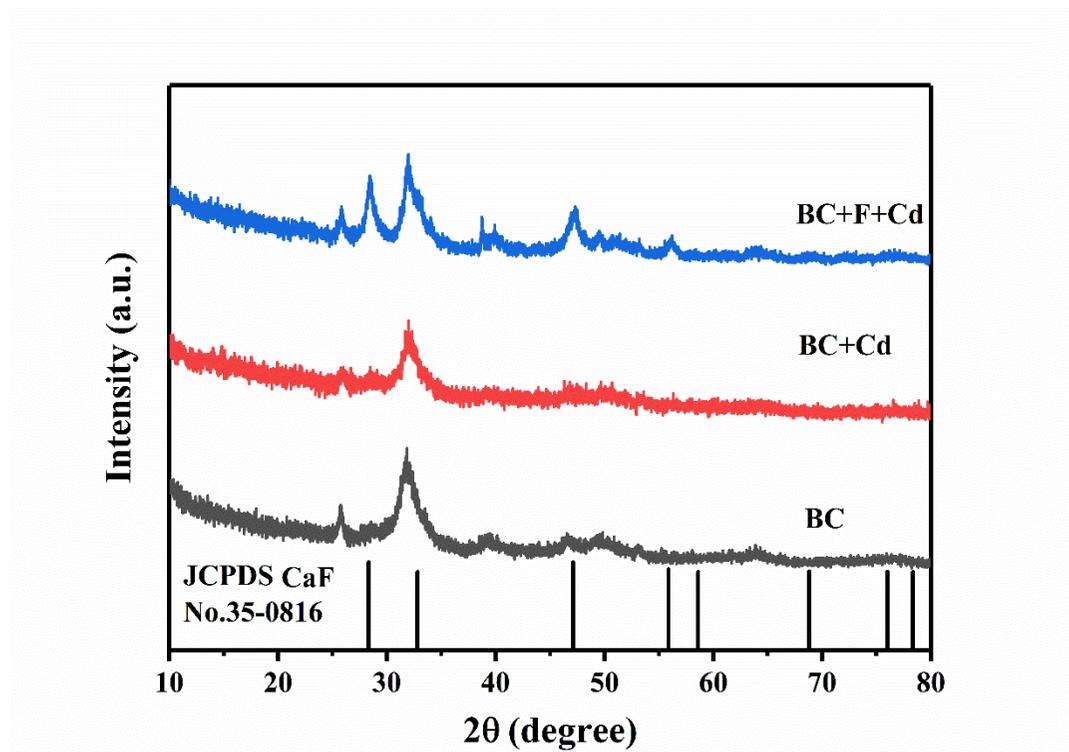


Figure S4. The XRD spectra of adsorbent after adsorbed Cd^{2+} with 10mmol/L NaF.

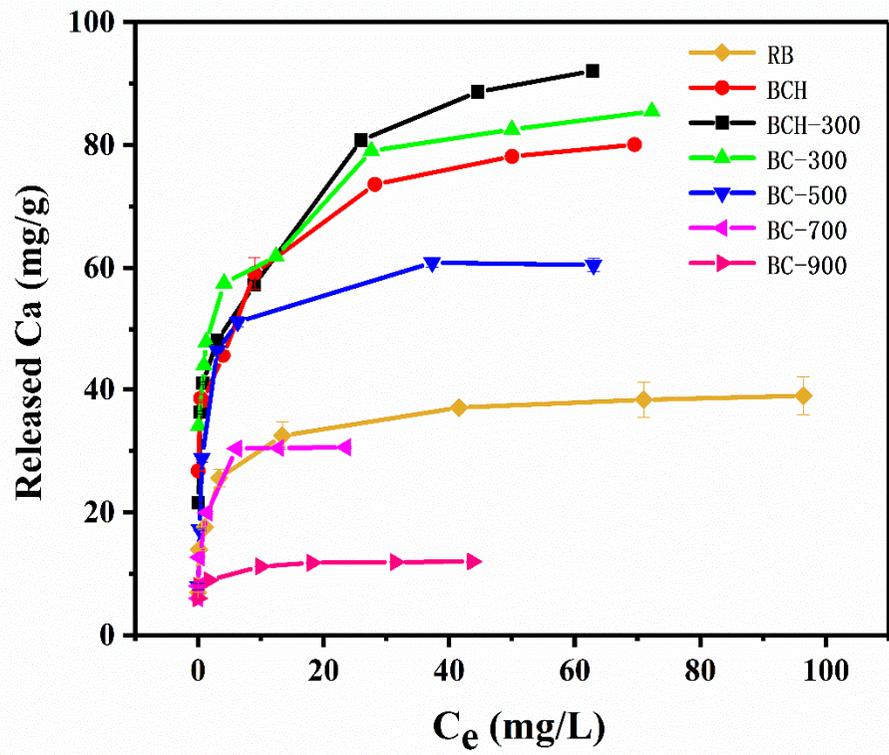


Figure S5. The relationships between equilibrium Cd²⁺ concentrations and the amounts of Ca²⁺ released from adsorbents.

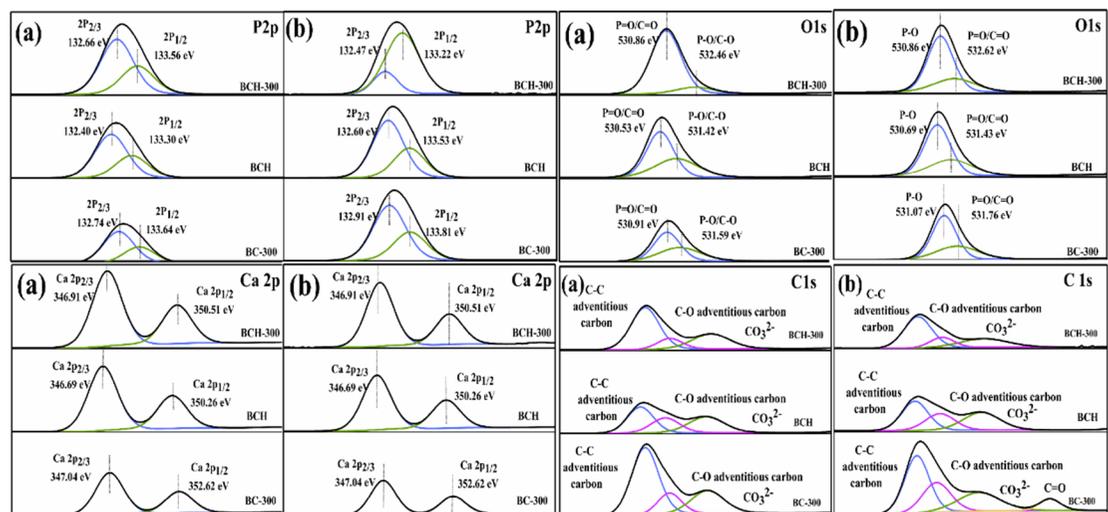


Figure S6. The spectra of BCs before and after adsorbed Cd: XPS spectra: (a) P 2p spectra, (b) O 1s spectra, (c) Ca 2p spectra, (d) C 1s spectra.

Table S1. Properties and adsorption capacity of bone char samples

Adsorbents	Cd ²⁺ uptake, mg/g	Degree of crystallinity	Specific surface area	Zeta potential (pH=6)	Organic parameters			Other elements		
					Doc	C (w.t%)	Ca (w.t%)	P (w.t%)	O (w.t%)	
RB	105.02	0.26	10.347	-7.21	60.25±0.35	47.12	4.19	5.18	43.51	
BCH	208.56	0.27	171.664	-19.76	1.92±0.12	22.37	12.22	10.14	55.27	
BCH-300	228.73	0.27	172.926	-23.11	1.32±0.14	16.40	14.06	22.60	46.94	
BC-300	196.35	0.27	50.247	-25.21	30.25±0.35	42.26	6.92	6.75	44.07	
BC-500	170.92	0.36	77.313	-19.76	11.73±0.07	33.25	12.14	9.69	44.92	
BC-700	82.35	0.38	158.478	-25.14	4.11±0.01	15.32	15.17	11.21	58.30	
BC-900	47.71	0.67	108.248	-23.11	3.67±0.11	13.22	17.18	10.21	59.39	

Table S2. Pseudo-first-order and pseudo-second-order kinetic parameters for Cd²⁺ adsorbed on adsorbents form aqueous solution.

Adsorbents	Pseudo-first order			Pseudo-second order		
	k ₁ (1/min)	q _{e,cal} (mg/g)	R ²	k ₂ (g/mg min)	q _{e,cal} (mg/g)	R ²
RB	0.101	105.02	0.957	0.0018	104.21	0.999
BCH	0.202	208.56	0.986	0.0015	208.18	0.999
BCH-300	0.211	228.73	0.954	0.0017	228.68	0.999
BC-300	0.153	196.35	0.978	0.0019	197.77	0.999
BC-500	0.128	170.92	0.986	0.0021	168.77	0.999
BC-700	0.075	82.35	0.957	0.0055	82.96	0.998
BC-900	0.061	47.71	0.987	0.0064	47.25	0.999

Table S3. Langmuir and Freundlich parameters for Cd²⁺ adsorbed on adsorbents from aqueous solution.

Adsorbents	Langmuir constants			Freundlich constants		
	K _i (L/mg)	q _{max} (mg/g)	R ²	K _F (mg/g) (L/mg) ^{1/n}	n	R ²
RB	1.76	113.43	0.991	3.33	0.605	0.969
BCH	0.51	276.70	0.992	5.76	0.568	0.972
BCH-300	0.46	293.31	0.994	10.4	0.533	0.959
BC-300	0.43	247.33	0.995	6.05	0.594	0.912
BC-500	1.14	197.34	0.988	3.24	0.566	0.975
BC-700	0.53	108.23	0.995	5.98	0.562	0.969
BC-900	0.58	82.77	0.997	3.33	0.605	0.957