water

Supplementary Materials

Single and Competitive Adsorption Behaviors of Cu^{2+}, Pb^{2+} and Zn^{2+} on the Biochar and Magnetic Biochar of Pomelo Peel in Aqueous Solution

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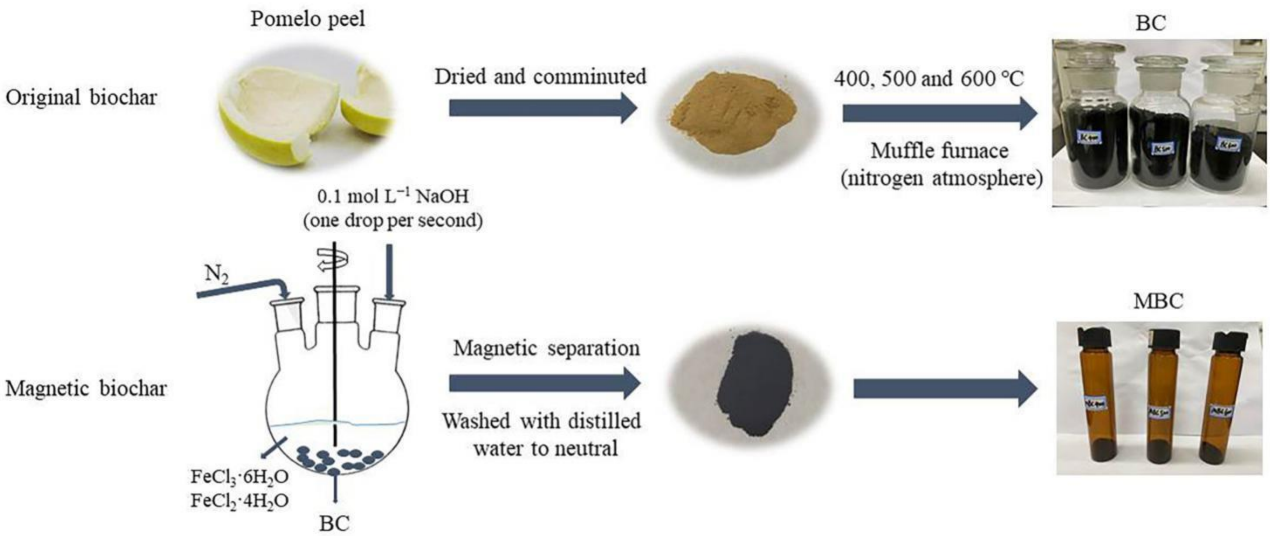

Figure S1. Preparation of biochars (BC: biochar, MBC: magnetic biochar).

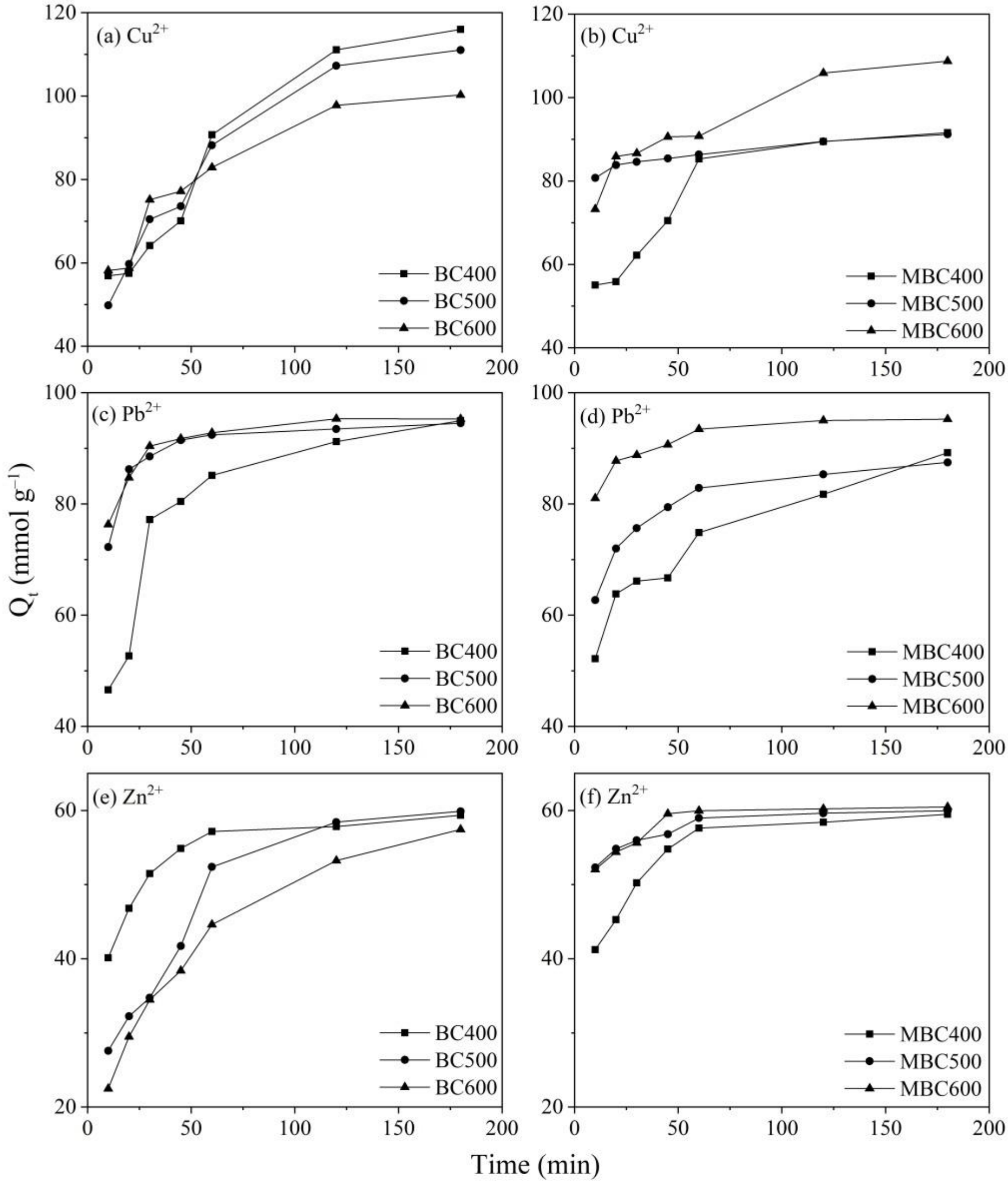

Figure S2. Adsorption kinetics of Cu^{2+} (**a**,**b**), Pb^{2+} (**c**,**d**) and Zn^{2+} (**e**,**f**) on BCs and MBCs.

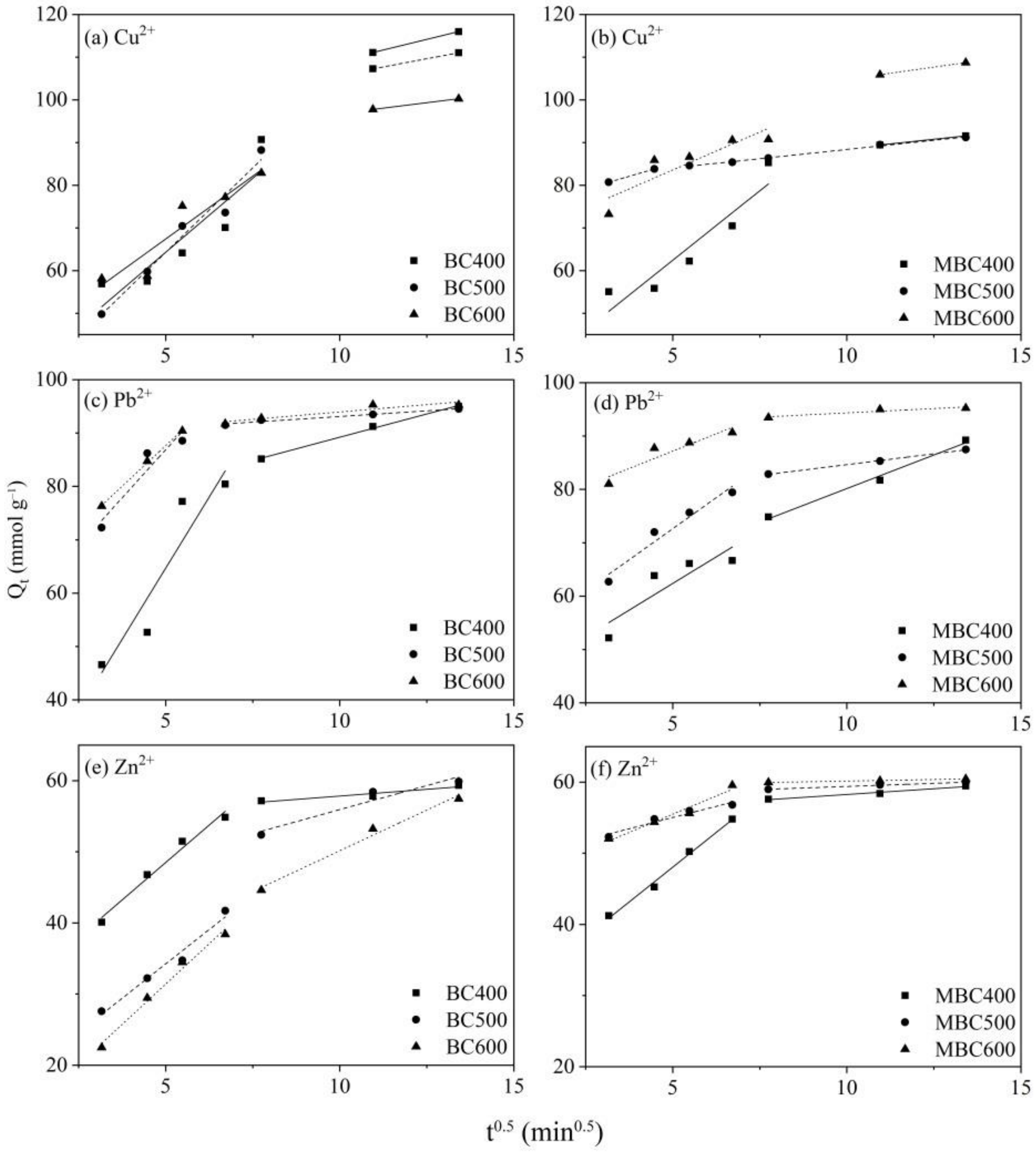

Figure S3. Intraparticle diffusion plots of adsorption for Cu^{2+} (**a**,**b**), Pb^{2+} (**c**,**d**) and Zn^{2+} (**e**,**f**) on BCs and MBCs.

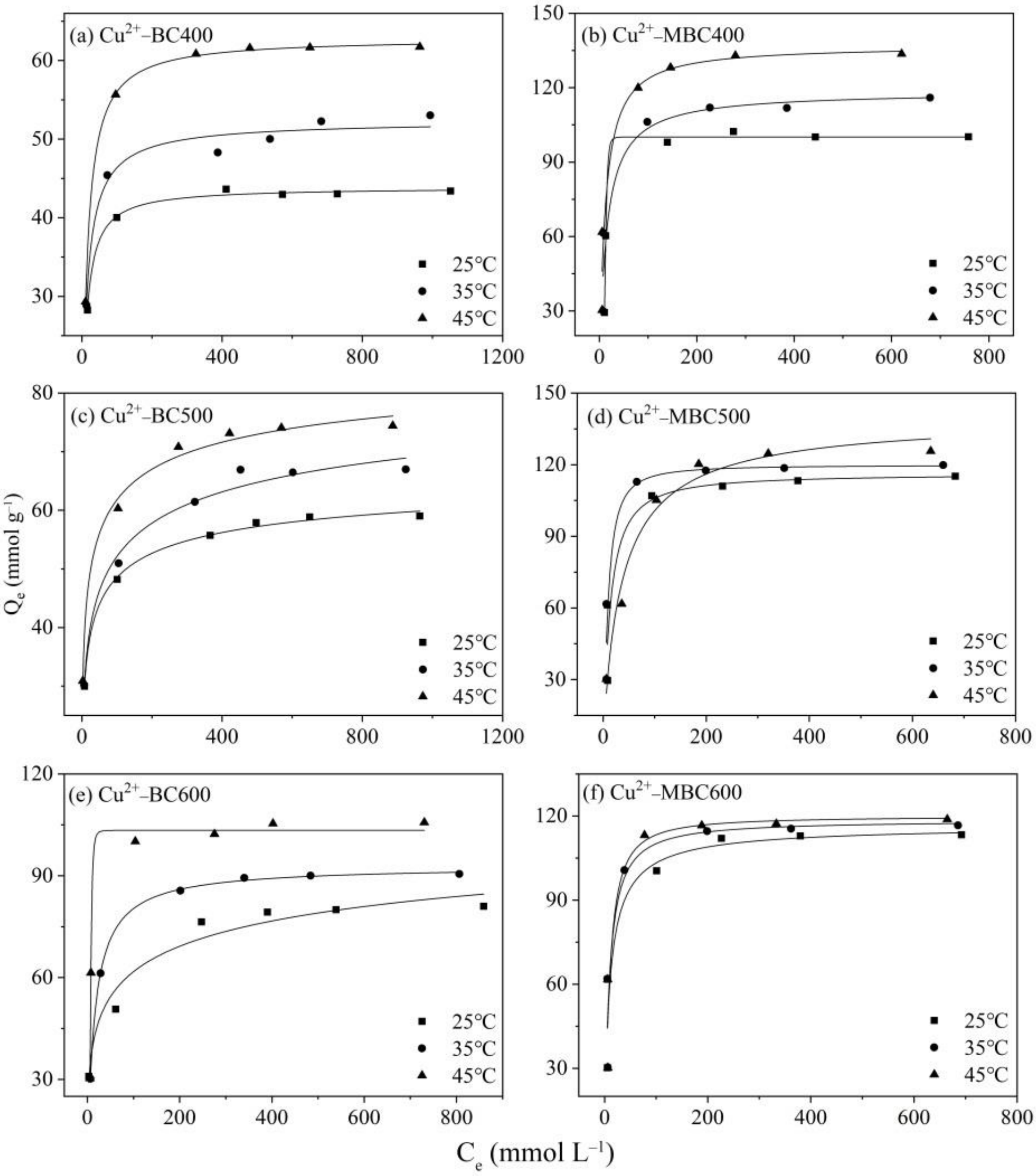

Figure S4. Adsorption thermodynamics of Cu^{2+} on BCs (**a,c,e**) and MBCs (**b,d,f**).

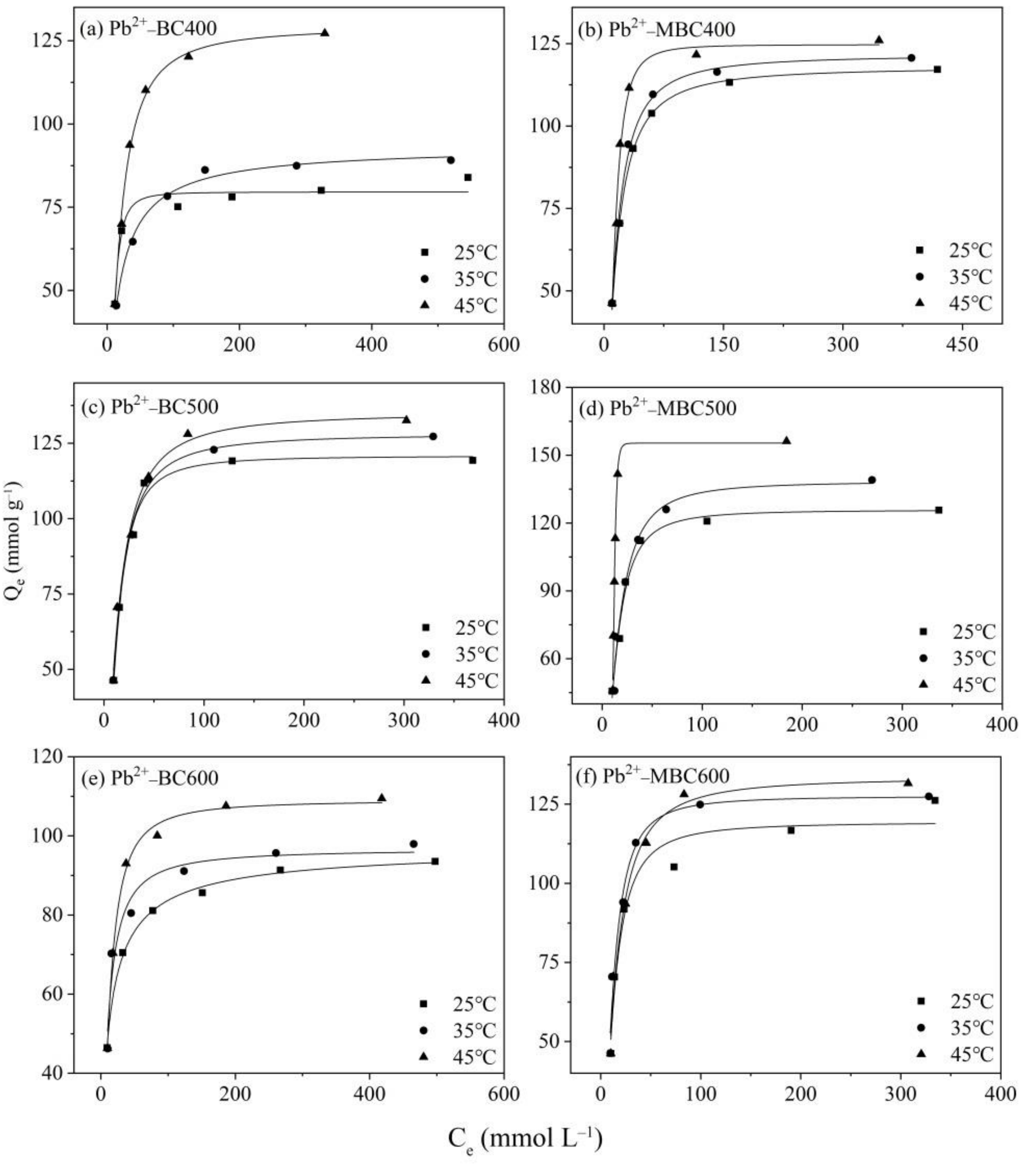

Figure S5. Adsorption thermodynamics of Pb^{2+} on BCs (**a,c,e**) and MBCs (**b,d,f**).

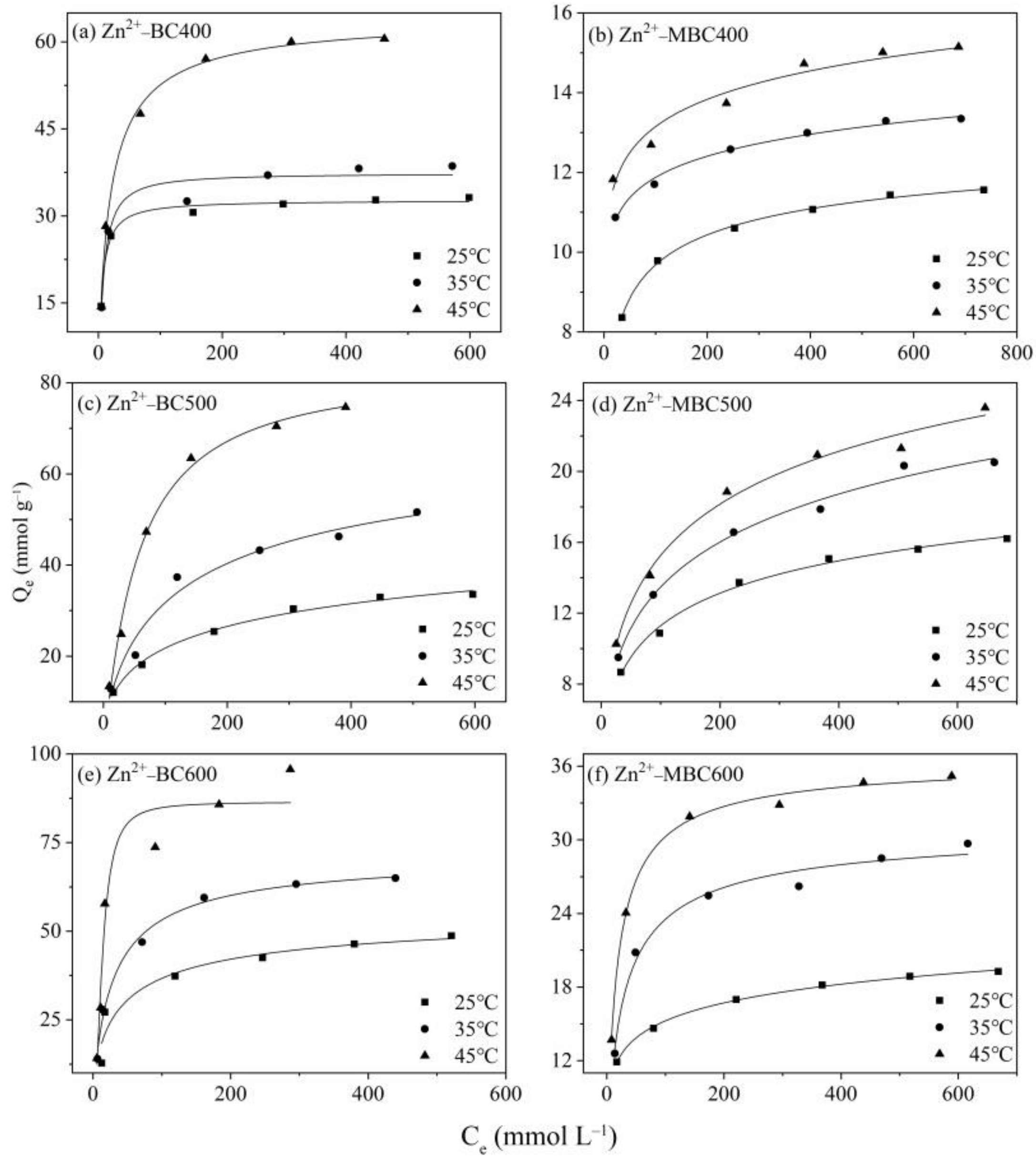

Figure S6. Adsorption thermodynamics of Zn^{2+} on BCs (**a,c,e**) and MBCs (**b,d,f**).

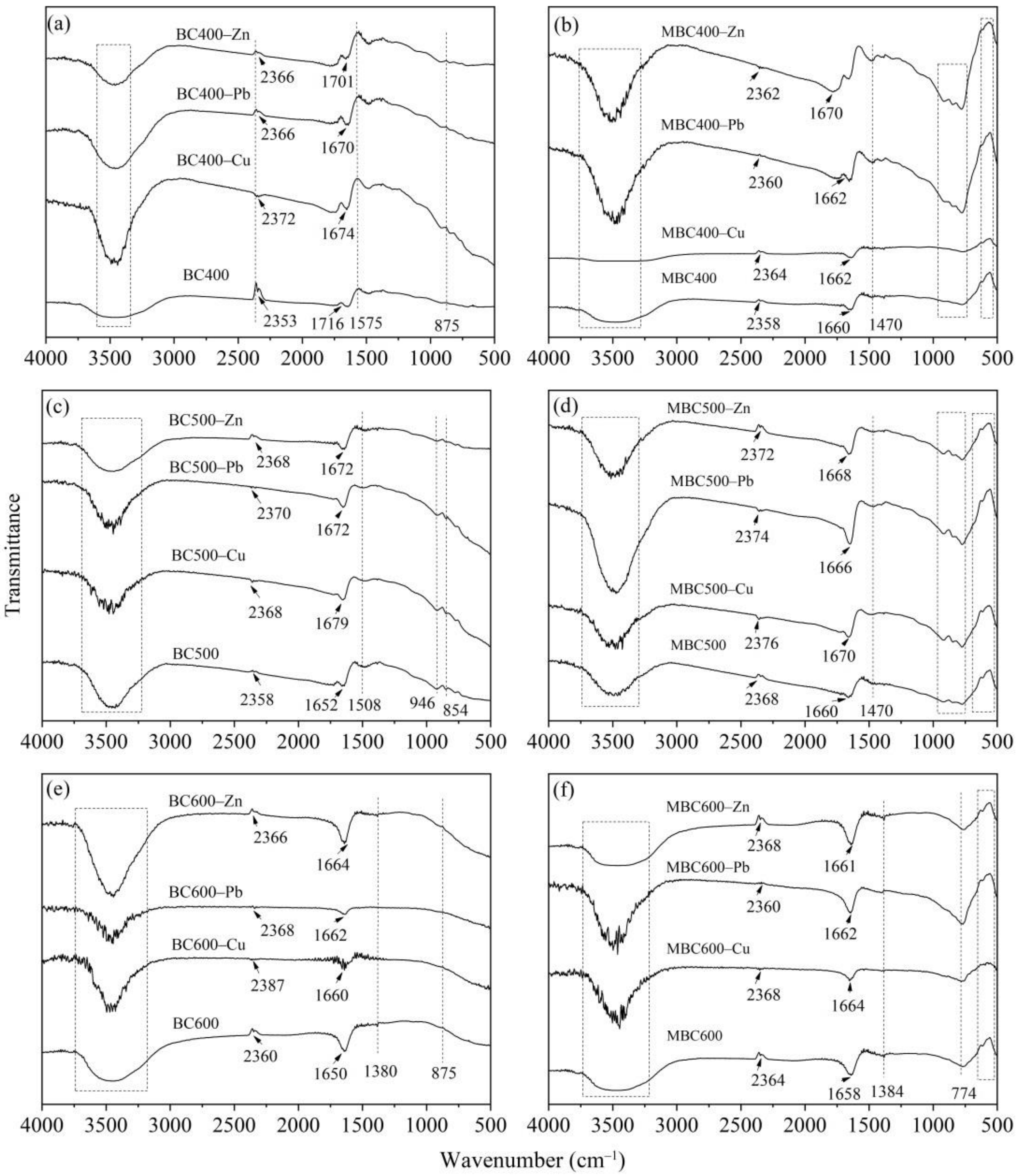

Figure S7. FTIR spectra of BCs (**a,c,e**) and MBCs (**b,d,f**) before and after adsorption of Cu^{2+}, Pb^{2+} and Zn^{2+}.

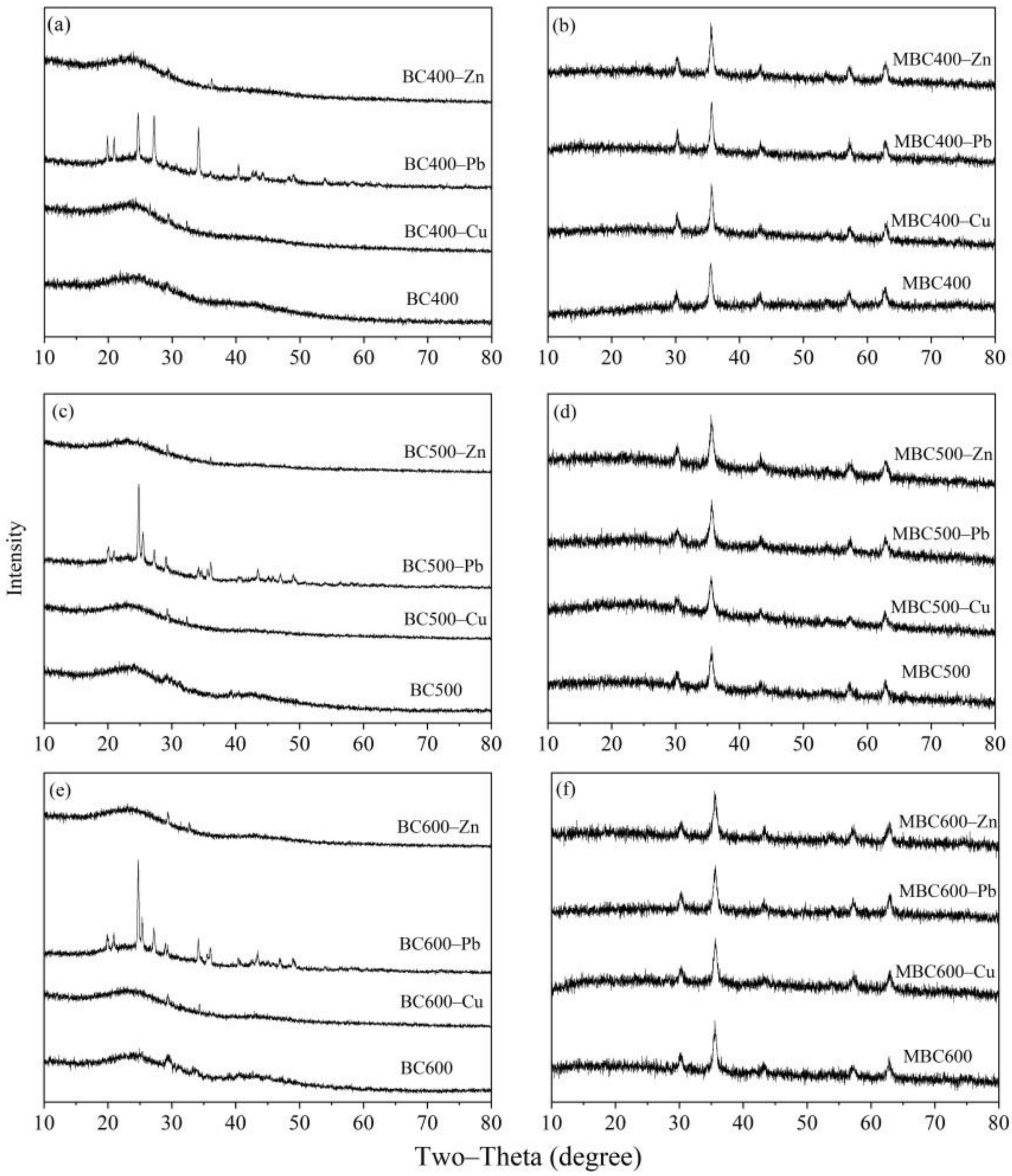

Figure S8. XRD patterns of BCs (**a,c,e**) and MBCs (**b,d,f**) before and after adsorption of Cu^{2+}, Pb^{2+} and Zn^{2+}.

Table S1. Kinetic parameters of the pseudo-second-order model for metal ions adsorption on BCs and MBCs.

Metal Ions	Biochar	Pseudo-Second-Order Model			
		$Q_{e,exp}$ (mmol g^{-1})	$Q_{e,cal}$ (mmol g^{-1})	K_2 (g mmol^{-1} min^{-1})	R^2
Cu^{2+}	BC400	97.72	110.00	0.002	0.9995
	BC500	107.32	124.48	0.002	0.9936
	BC600	111.10	129.67	0.003	0.9973
	MBC400	89.38	91.90	0.004	0.9961
	MBC500	89.38	98.67	0.005	0.9997
	MBC600	105.91	113.15	0.003	0.9973
Pb^{2+}	BC400	91.22	95.75	0.001	0.9979
	BC500	93.48	96.91	0.001	0.9980
	BC600	95.32	101.83	0.011	0.9999
	MBC400	82.05	89.53	0.004	0.9962
	MBC500	89.58	93.19	0.011	0.9999
	MBC600	96.53	96.53	0.224	0.9999
Zn^{2+}	BC400	57.81	60.25	0.016	0.9991
	BC500	58.42	64.69	0.012	0.9930
	BC600	60.87	67.44	0.013	0.9963
	MBC400	58.42	60.71	0.015	0.9997
	MBC500	59.64	61.32	0.016	0.9999
	MBC600	60.25	61.17	0.016	0.9999

Table S2. Kinetic parameters of the intraparticle diffusion model for metal ions adsorption on BCs and MBCs.

Metal Ions	Biochar	Intraparticle Diffusion Model					
		K_{i1} mmol g^{-1} min$^{0.5}$	C	R^2	K_{i2} mmol g^{-1} min$^{0.5}$	C	R^2
Cu^{2+}	BC400	6.94	29.61	0.7540	1.99	89.30	1.0000
	BC500	7.92	24.71	0.9547	1.53	90.51	1.0000
	BC600	5.89	37.93	0.8482	1.02	86.64	1.0000
	MBC400	6.51	29.86	0.8384	0.86	79.97	1.0000
	MBC500	2.37	73.21	1.0000	0.86	79.75	0.9939
	MBC600	3.55	65.84	0.7314	1.15	93.28	1.0000
Pb^{2+}	BC400	10.66	11.38	0.8223	1.74	71.81	0.9931
	BC500	7.21	50.82	0.8078	0.42	88.88	0.9608
	BC600	6.10	57.15	0.9975	0.55	88.43	0.8218
	MBC400	4.00	42.39	0.6696	2.51	55.02	0.9798
	MBC500	4.65	49.38	0.9305	0.81	76.55	0.9972
	MBC600	2.60	74.16	0.8100	0.32	91.11	0.7903
Zn^{2+}	BC400	4.21	27.47	0.9717	0.38	54.05	0.8240
	BC500	3.87	14.92	0.9605	1.35	42.43	0.8635
	BC600	4.53	8.75	0.9794	2.29	27.29	0.9714
	MBC400	3.91	28.52	0.9894	0.32	55.04	0.9451
	MBC500	1.26	48.73	0.9171	0.17	57.66	0.9790
	MBC600	2.05	45.27	0.9418	0.09	59.28	0.9812

K_{i1} is the intraparticle diffusion rate constant of the first stage, K_{i2} is the intraparticle diffusion rate constant of the second stage.

Table S3. Fitting results of adsorption thermodynamics of Cu^{2+} on BCs and MBCs.

Biochar	Temperature (°C)	Langmuir			Freundlich		
		Q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2	K_f (mmol g^{-1})(mmol L^{-1})$^{1/n}$	1/n	R^2
BC400	25	43.90	0.119	0.9938	28.01	0.472	0.7945
	35	52.42	0.121	0.9615	31.79	0.407	0.9476
	45	62.84	0.081	0.9994	39.18	0.602	0.9432
BC500	25	69.71	0.317	0.9958	39.66	0.282	0.9217
	35	91.34	0.236	0.9769	49.41	0.373	0.9196
	45	91.92	0.334	0.9988	73.49	0.359	0.8951
BC600	25	93.03	0.192	0.9370	43.43	0.218	0.9056
	35	103.39	0.081	0.9994	89.38	0.112	0.9094
	45	133.76	0.360	0.9928	104.96	0.112	0.9028
MBC400	25	100.15	0.466	0.9966	97.25	1.603	0.9651
	35	118.54	0.079	0.8337	63.42	0.310	0.8326
	45	136.98	0.087	0.9133	96.78	0.436	0.9023
MBC500	25	116.19	0.054	0.8545	63.42	0.478	0.8536
	35	119.86	0.048	0.8807	76.79	0.428	0.8802
	45	140.44	0.038	0.9610	79.94	0.435	0.7579
MBC600	25	116.86	0.143	0.8779	82.15	0.357	0.8554
	35	118.49	0.099	0.8299	87.81	0.430	0.8117
	45	119.96	0.069	0.8647	79.47	0.423	0.8128

Table S4. Fitting results of adsorption thermodynamics of Pb^{2+} on BCs and MBCs.

Biochar	Temperature (°C)	Langmuir			Freundlich		
		Q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2	K_f (mmol g^{-1})(mmol L^{-1})$^{1/n}$	1/n	R^2
BC400	25	79.57	0.007	0.9337	79.49	0.38	0.9325
	35	93.38	0.077	0.9879	91.80	0.33	0.9823
	45	119.06	0.015	0.9933	109.11	1.11	0.9140
BC500	25	120.82	0.010	0.9841	95.46	1.23	0.9305
	35	128.06	0.019	0.9924	92.81	1.19	0.8770
	45	135.08	0.022	0.9832	108.06	6.83	0.7985
BC600	25	96.66	0.158	0.9960	95.00	0.77	0.6985
	35	101.58	0.065	0.9215	95.91	1.60	0.7667
	45	108.98	0.027	0.9934	96.37	3.13	0.8803
MBC400	25	117.87	0.023	0.9993	38.80	0.82	0.7512
	35	121.55	0.020	0.9891	42.86	2.13	0.6670
	45	124.69	0.003	0.9856	39.24	1.40	0.5884
MBC500	25	125.77	0.007	0.9751	39.00	1.14	0.4012
	35	138.41	0.008	0.9435	40.88	1.12	0.8750
	45	155.35	0.010	0.9909	59.36	0.56	0.8036
MBC600	25	119.32	0.016	0.9367	38.37	1.68	0.7806
	35	127.55	0.012	0.9618	31.37	1.81	0.6285
	45	133.46	0.020	0.9701	30.79	1.54	0.6826

Table S5. Fitting results of adsorption thermodynamics of Zn^{2+} on BCs and MBCs.

Biochar	Temperature (°C)	Langmuir			Freundlich		
		Q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2	K_f (mmol g^{-1})(mmol L^{-1})$^{1/n}$	1/n	R^2
BC400	25	32.68	0.167	0.9862	24.01	0.26	0.7747
	35	37.35	0.093	0.9308	24.16	0.31	0.9176
	45	64.62	0.084	0.9937	30.43	0.45	0.9008
BC500	25	61.07	0.063	0.9895	11.32	0.40	0.9573
	35	71.80	0.033	0.9550	13.30	0.55	0.9484
	45	83.72	0.013	0.9901	17.13	0.93	0.9739
BC600	25	57.14	0.094	0.8995	20.03	0.44	0.8727
	35	72.12	0.061	0.9842	27.07	0.53	0.9217
	45	86.44	0.005	0.9153	42.51	0.62	0.9061
MBC400	25	12.23	0.377	0.9962	71.72	0.16	0.9742
	35	14.99	0.079	0.9850	77.53	0.18	0.9520
	45	15.14	0.058	0.9926	89.31	0.19	0.9750
MBC500	25	25.89	0.116	0.9894	17.43	0.05	0.9745
	35	39.85	0.081	0.9864	22.63	0.09	0.9693
	45	41.66	0.085	0.9836	24.01	0.13	0.9182
MBC600	25	31.36	0.188	0.9973	11.62	0.76	0.9793
	35	36.59	0.104	0.9733	13.61	0.45	0.9344
	45	47.76	0.109	0.9956	18.66	0.42	0.9056

Table S6. Fitting results of Langmuir model for competitive adsorption of Cu^{2+} with Pb^{2+}/Zn^{2+}.

Biochar	Ion System	Q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2
BC500	Cu^{2+}	48.24	0.0079	0.9933
	Cu^{2+}–Zn^{2+}	41.27	0.0014	0.9885
	Cu^{2+}–Pb^{2+}	28.67	0.0013	0.9938
MBC500	Cu^{2+}	105.48	0.0616	0.9619
	Cu^{2+}–Zn^{2+}	28.74	0.0179	0.9567
	Cu^{2+}–Pb^{2+}	16.21	0.0219	0.9558

Table S7. Fitting results of Langmuir model for competitive adsorption of Pb^{2+} with Cu^{2+}/Zn^{2+}.

Biochar	Ion System	Q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2
BC500	Pb^{2+}	79.84	0.0121	0.9928
	Pb^{2+}–Cu^{2+}	38.01	0.0202	0.9239
	Pb^{2+}–Zn^{2+}	46.01	0.0013	0.9997
MBC500	Pb^{2+}	64.77	0.0111	0.9943
	Pb^{2+}–Cu^{2+}	30.01	0.2362	0.9963
	Pb^{2+}–Zn^{2+}	33.57	0.0135	0.9982

Table S8. Fitting results of Langmuir model for competitive adsorption of Zn^{2+} with Cu^{2+}/Pb^{2+}.

Biochar	Ion System	Q_m (mmol g^{-1})	K_L (L $mmol^{-1}$)	R^2
BC500	Zn^{2+}	45.94	0.0131	0.9652
	Zn^{2+}–Cu^{2+}	76.27	0.0047	0.9896
	Zn^{2+}–Pb^{2+}	27.64	0.0028	0.9792
MBC500	Zn^{2+}	66.99	0.0958	0.9929
	Zn^{2+}–Cu^{2+}	31.36	0.0014	0.9940
	Zn^{2+}–Pb^{2+}	42.70	0.0094	0.9700

Table S9. Fitting results of Langmuir model for competitive adsorption of Cu^{2+}, Pb^{2+} and Zn^{2+}.

Biochar	Adsorption System	Metal Ions	Q_m (mmol g^{-1})	K_L (L $mmol^{-1}$)	R^2
BC500	Single	Cu^{2+}	42.66	0.0178	0.9936
		Pb^{2+}	62.24	0.0093	0.9949
		Zn^{2+}	46.08	0.0139	0.9763
	Ternary	Cu^{2+}	21.85	0.0011	0.9881
		Pb^{2+}	44.30	0.0171	0.9374
		Zn^{2+}	18.20	0.0034	0.9680
MBC500	Single	Cu^{2+}	45.96	0.0080	0.9975
		Pb^{2+}	64.81	0.0011	0.9984
		Zn^{2+}	42.55	0.1119	0.9871
	Ternary	Cu^{2+}	31.53	0.0983	0.9879
		Pb^{2+}	48.74	0.0057	0.9201
		Zn^{2+}	10.26	0.0033	0.9858

Table S10. Maximum adsorption capacities of some adsorbents for Pb^{2+} in previous studies.

Adsorbents	Adsorption Systems	Maximum Adsorption Capacities (mg g^{-1})	References
Rice straw biochar	Binary	0.58	[1]
Chicken manure biochar	Binary	0.54	
Sewage sludge biohcar	Binary	0.11	
Egyptian Na-activated bentonite	Single	5.44	[2]
Chitosan-modified biochar	Single	9.24	[3]
Magnetic pomelo peel biochar	Ternary	10.10	In this study [a]

[a] The maximum adsorption capacity of MBC in ternary-metal system was small than that in single- and binary-system, only the maximum adsorption capacity of MBC in ternary-metal system compared in Table S10 is representative.

References

1. Zhao, M.; Dai, Y.; Zhang, M.; Feng, C.; Qin, B.; Zhang, W.; Zhao, N.; Li, Y.; Ni, Z.; Xu, Z.; Tsang, D.C.W.; Qiu, R. Mechanisms of Pb and/or Zn adsorption by different biochars: Biochar characteristics, stability, and binding energies. *Sci. Total Environ*. **2020,** *717*, 136894.
2. Taha, A.A.; Shreadah, M.A.; Ahmed, A.M.; Heiba, H.F. Multi-component adsorption of Pb(II), Cd(II), and Ni(II) onto Egyptian Na-activated bentonite; equilibrium, kinetics, thermodynamics, and application for seawater desalination. *J. Environ. Chem. Eng.* **2016**, *4*, 1166–1180.
3. Deng, J.; Liu, Y.; Liu, S.; Zeng, G.; Tan, X.; Huang, B.; Tang, X.; Wang, S.; Hua, Q.; Yan, Z. Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. *J. Colloid Interface Sci.* **2017**, *506*, 355–364.