

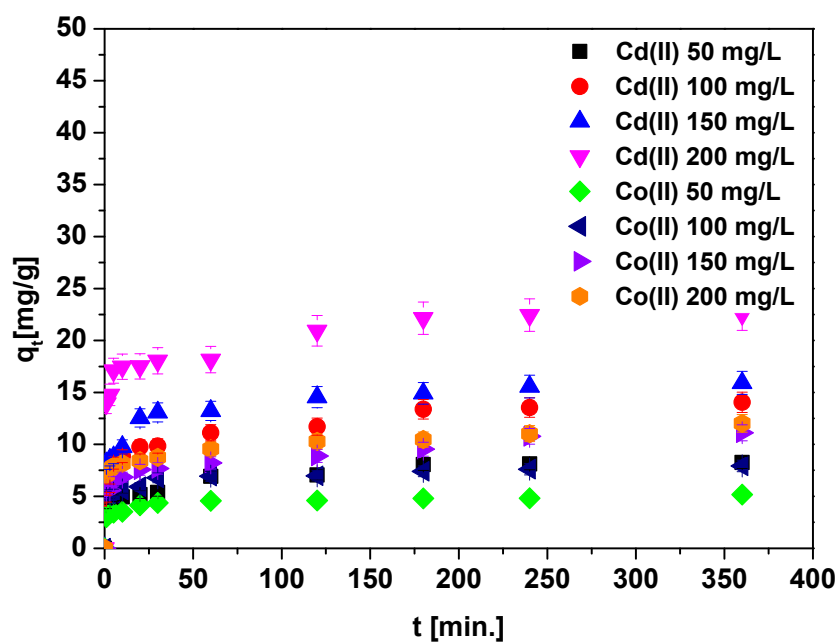
**Chitosan-Modified Biochars to Advance Research on Heavy
Metal Ion Removal: Roles, Mechanism and Perspectives**

Justyna Bąk¹, Peter Thomas², Dorota Kołodyńska¹

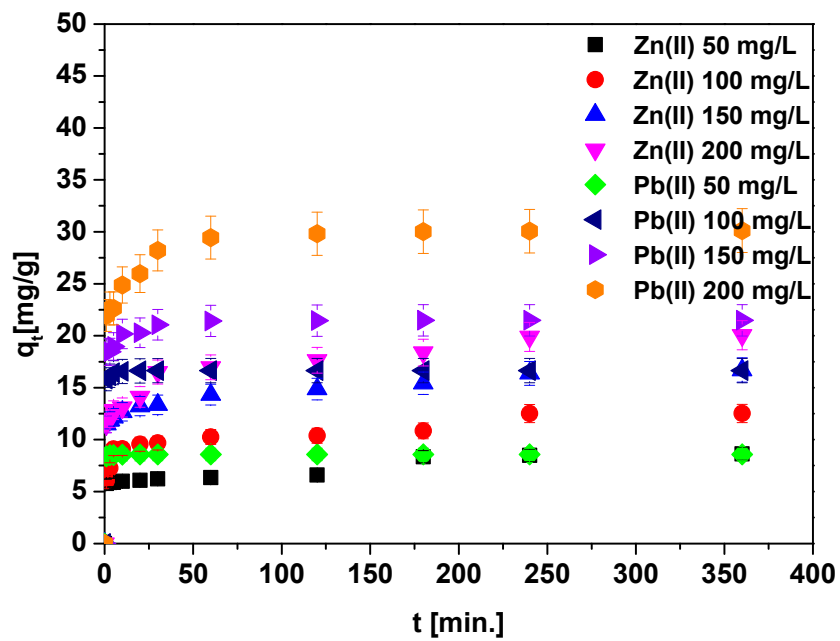
¹Department of Inorganic Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria
Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 2, 20-031, Lublin, Poland,

²Earthcare, LLC8524 Southport Drive, Evansville, IN 47711

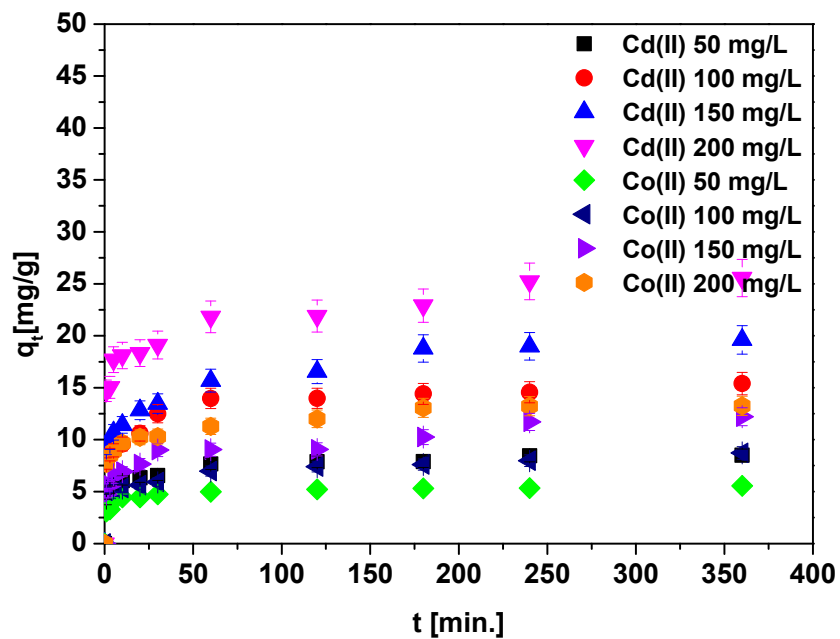
(a)



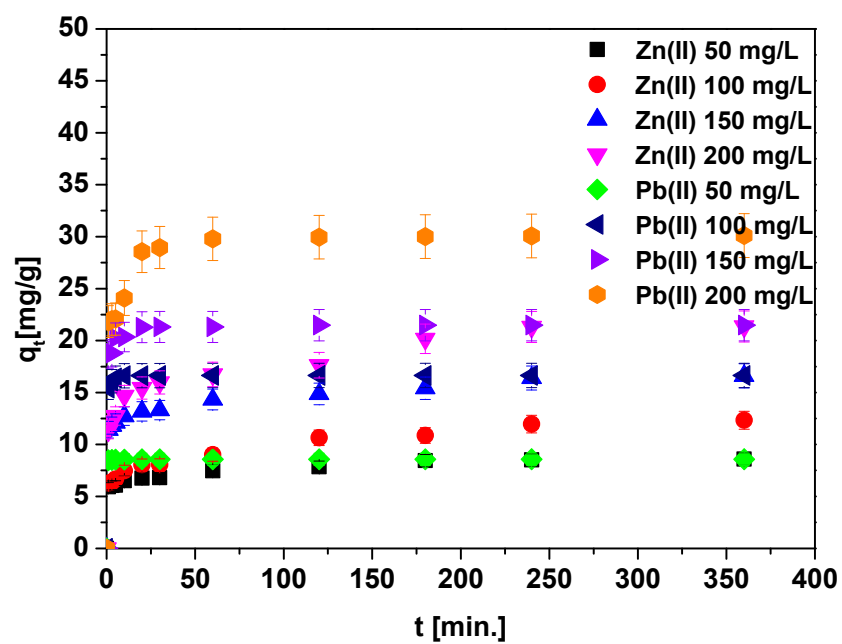
(b)



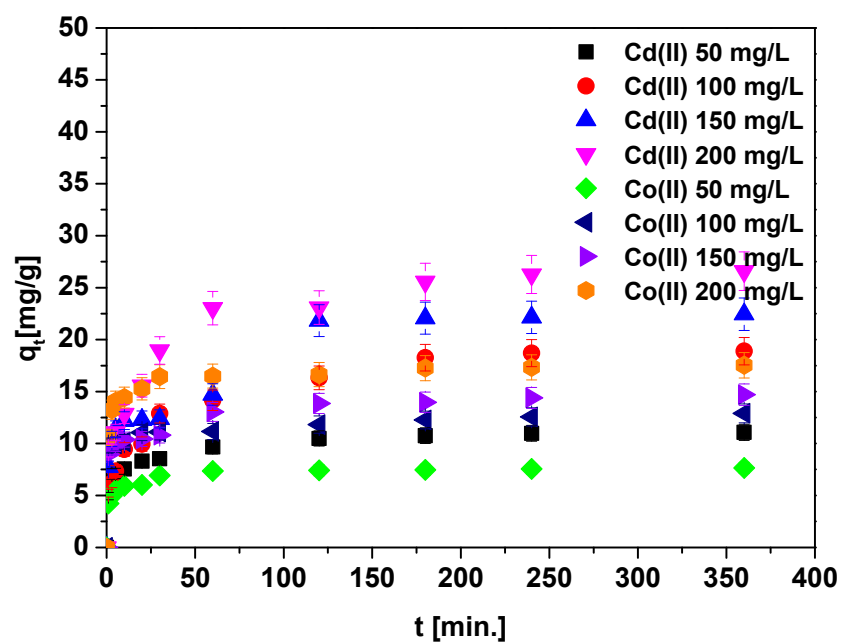
(c)



(d)



(e)



(f)

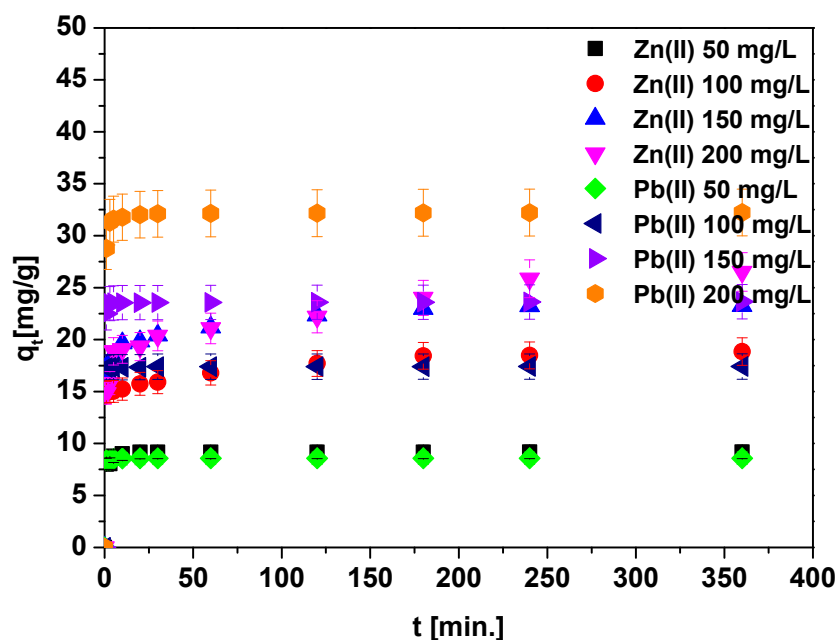
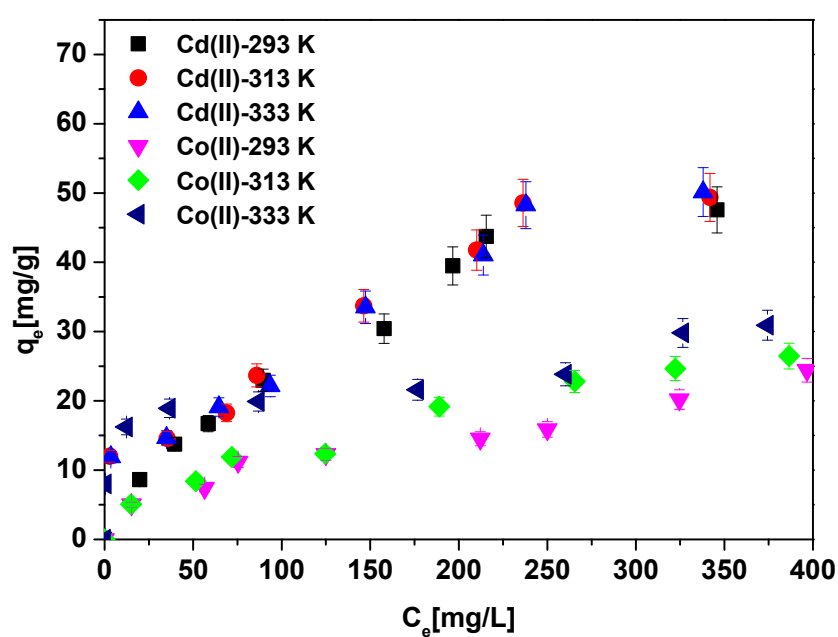
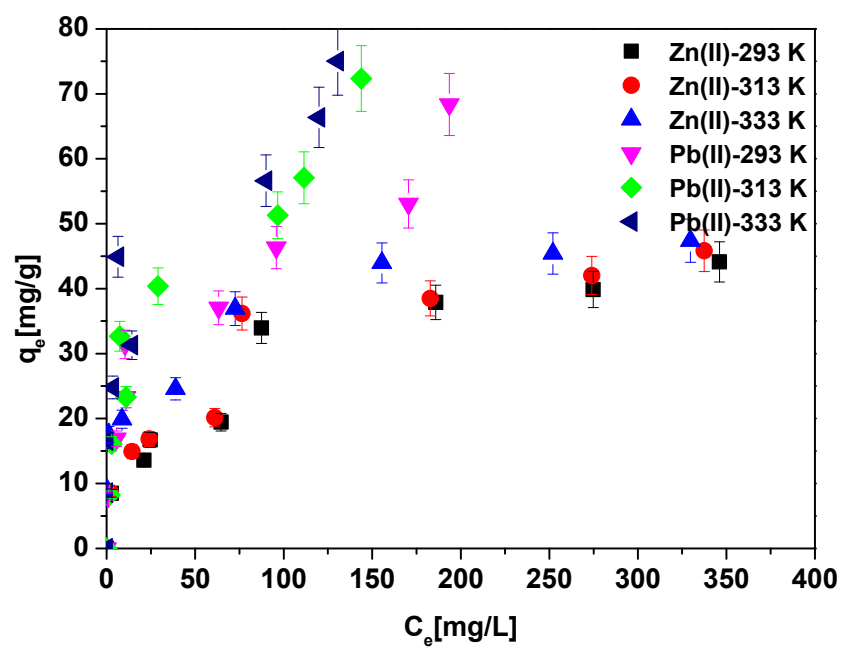


Figure S1. Effect of the phase contact time on (a) Cd(II) and Co(II) ions adsorption on BC-CS 1-1, (b) Zn(II) and Pb(II) ions adsorption on BC-CS 1-1, (c) Cd(II) and Co(II) ions adsorption on BC-CS 2-1, (d) Zn(II) and Pb(II) ions adsorption on BC-CS 2-1, (e) Cd(II) and Co(II) ions adsorption on BC-CS 4-1, (f) Zn(II) and Pb(II) ions adsorption on BC-CS 4-1 (pH 5, sorbent mass 0.1 g, shaking speed 180 rpm, temperature 293 K).

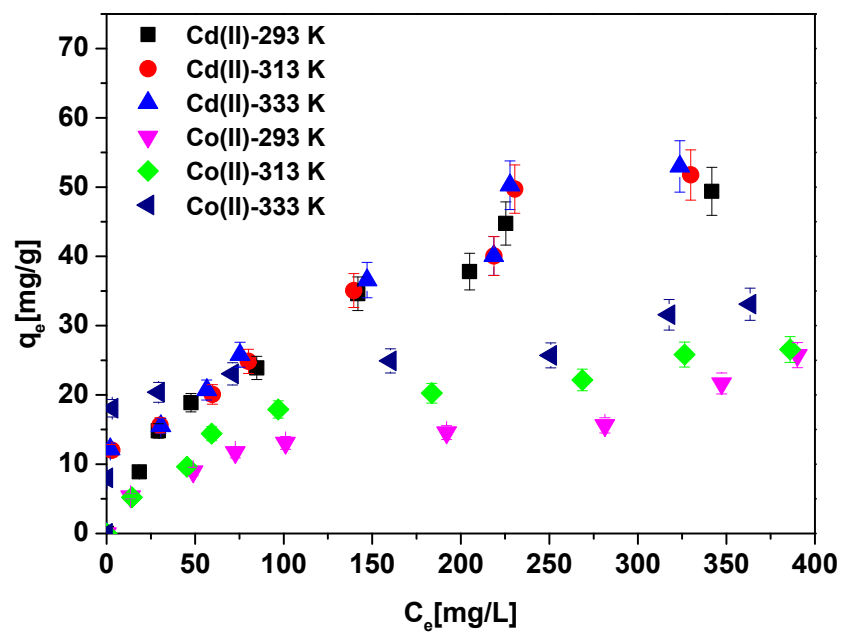
(a)



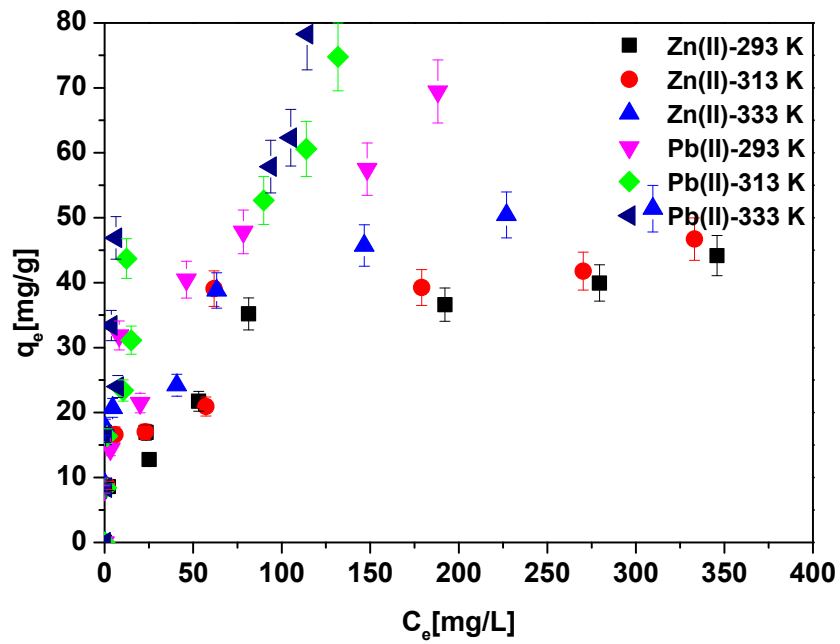
(b)



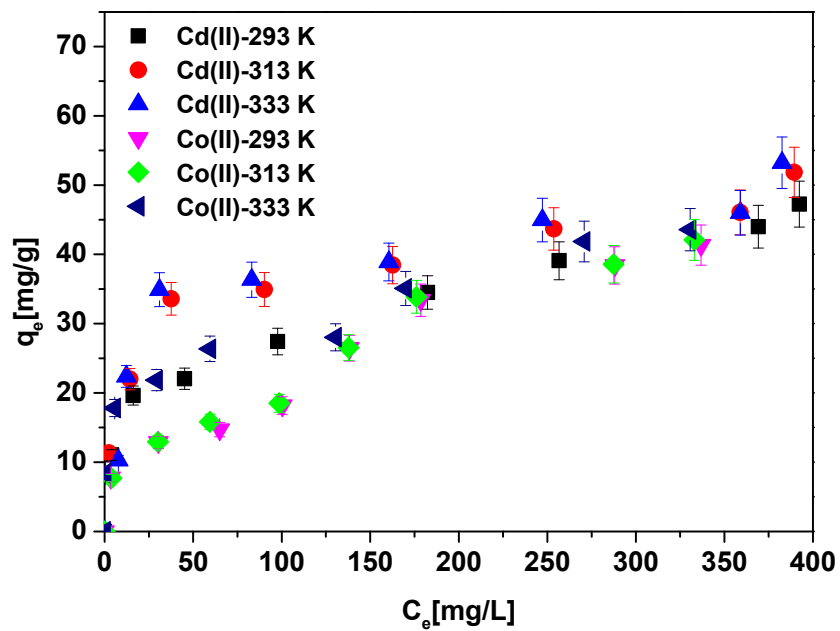
(c)



(d)



(e)



(f)

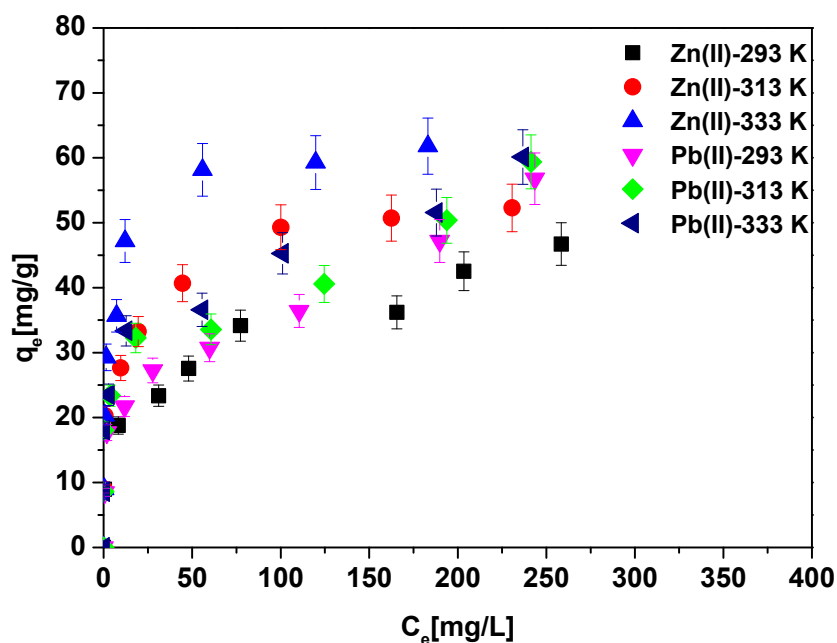


Figure S2. Effect of temperature on (a) Cd(II) and Co(II) ions adsorption on BC-CS 1-1, (b) Zn(II) and Pb(II) ions adsorption on BC-CS 1-1, (c) Cd(II) and Co(II) ions adsorption on BC-CS 2-1, (d) Zn(II) and Pb(II) ions adsorption on BC-CS 2-1, (e) Cd(II) and Co(II) ions adsorption on BC-CS 4-1, (f) Zn(II) and Pb(II) ions adsorption on BC-CS 4-1 (C_0 50-600 mg/L, sorbent mass 0.1 g, pH 5, shaking speed 180 rpm).

Table S1. Parameters for various adsorption kinetic models for Cu(II), Cd(II), Zn(II) Co(II) and Pb(II) sorption on BC-CS 2-1.

		Parameters									
C ₀ [mg/L]	q _{exp}	PFO			PSO				IPD		
		log(q ₁ -q _t)=log(q ₁)- $\frac{k_1t}{2.303}$			$\frac{t}{q_t} = \frac{1}{k_2q_2^2} + \frac{t}{q_2}$				q _t = k _i t ^{1/2} + C		
		q ₁	k ₁	R ²	q ₂	k ₂	h	R ²	k _i	C	R ²
Cu(II)											
50	7.95	0.78	0.018	0.821	7.96	0.146	9.229	1.000	0.010	7.761	0.753
100	14.01	5.86	0.010	0.875	13.93	0.009	1.814	0.996	0.217	9.881	0.915
150	18.22	10.00	0.013	0.930	18.36	0.005	1.748	0.996	0.339	12.029	0.719
200	24.53	13.40	0.011	0.972	24.68	0.003	2.102	0.995	0.328	18.347	0.987
Cd(II)											
50	8.50	3.28	0.015	0.887	8.53	0.021	1.541	0.999	0.101	6.674	0.684
100	15.40	5.45	0.009	0.826	15.30	0.011	2.548	0.999	0.128	12.762	0.967
150	19.61	9.39	0.012	0.973	19.76	0.006	2.147	0.997	0.151	16.711	0.981
200	25.56	9.69	0.011	0.865	25.49	0.006	3.581	0.996	0.438	17.576	0.724
Zn(II)											
50	8.59	2.71	0.015	0.978	8.65	0.024	1.804	0.999	0.026	8.098	0.962

100	12.34	5.91	0.010	0.955	12.35	0.008	1.183	0.995	0.293	7.064	0.900
150	16.60	4.86	0.011	0.913	16.57	0.007	3.167	0.998	0.198	12.978	0.764
200	21.36	10.70	0.018	0.839	21.52	0.006	2.622	0.996	0.193	17.873	0.649
Co(II)											
50	5.56	1.48	0.009	0.855	5.53	0.045	1.371	0.999	0.047	4.659	0.933
100	8.72	3.39	0.007	0.959	8.55	0.013	0.941	0.994	0.151	5.724	0.963
150	12.21	6.08	0.009	0.866	12.06	0.007	1.004	0.988	0.331	6.101	0.831
200	13.26	5.40	0.019	0.957	13.39	0.014	2.439	0.999	0.033	12.653	0.763
Pb(II)											
50	8.57	0.04	0.016	0.829	8.57	2.583	189.909	1.000	0.001	8.557	0.701
100	16.64	0.10	0.028	0.673	16.65	1.231	341.215	1.000	0.001	16.641	0.960
150	21.49	1.22	0.042	0.910	21.51	0.142	65.564	1.000	0.001	21.486	0.979
200	30.10	4.45	0.022	0.858	30.22	0.025	23.151	1.000	0.017	29.791	0.959

Table S2. Parameters for various adsorption kinetic models for Cu(II), Cd(II), Zn(II) Co(II) and Pb(II) sorption on BC-CS 4-1.

C ₀ [mg/L]	q _{exp}	Parameters									
		PFO				PSO				IPD	
		$\log(q_i - q_e) = \log(q_i) - \frac{k_1 t}{2.303}$				$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2}$				$q_t = k_i t^{1/2} + C$	
		q ₁	k ₁	R ²	q ₂	k ₂	h	R ²	k _i	C	R ²
Cu(II)											
50	9.18	0.21	0.031	0.774	9.19	0.651	54.979	1.000	0.001	9.177	0.647
100	16.90	3.50	0.023	0.981	16.99	0.037	10.693	1.000	0.026	16.471	0.682
150	17.79	5.30	0.014	0.876	17.87	0.015	4.896	1.000	0.071	16.429	0.999
200	25.51	13.45	0.023	0.970	26.01	0.005	3.386	0.998	0.040	24.785	0.757
Cd(II)											
50	11.07	4.32	0.016	0.984	11.18	0.017	2.098	0.999	0.053	10.088	0.852
100	18.89	12.70	0.017	0.984	19.41	0.004	1.555	0.997	0.434	11.487	0.738
150	22.45	13.46	0.018	0.928	23.19	0.003	1.842	0.993	0.070	21.100	0.961
200	26.58	15.25	0.016	0.966	27.09	0.002	2.729	0.998	0.174	23.355	0.874
Zn(II)											
50	9.18	0.21	0.031	0.774	9.19	0.651	54.979	1.000	0.026	8.098	0.962
100	18.85	3.35	0.011	0.980	18.86	0.015	5.408	0.999	0.293	7.064	0.900
150	23.25	5.94	0.020	0.953	23.38	0.015	8.333	1.000	0.198	12.978	0.764
200	26.51	9.67	0.010	0.912	26.37	0.005	3.489	0.996	0.193	17.873	0.649
Co(II)											
50	7.65	1.87	0.014	0.841	7.67	0.044	2.618	1.000	0.032	7.047	0.991
100	12.90	2.84	0.009	0.970	12.84	0.019	3.181	0.999	0.156	10.064	0.976
150	14.70	4.97	0.012	0.961	14.76	0.012	2.637	0.999	0.127	12.329	0.945
200	17.53	3.44	0.013	0.878	17.54	0.004	7.263	1.000	0.051	16.559	0.988
Pb(II)											
50	8.58	0.06	0.017	0.715	8.58	2.257	166.230	1.000	0.001	8.517	0.956
100	17.41	0.06	0.010	0.685	17.41	1.406	426.102	1.000	0.001	17.388	0.874
150	23.65	0.18	0.008	0.479	23.64	0.399	222.724	1.000	0.004	23.463	0.972
200	32.23	0.61	0.018	0.782	32.24	0.220	229.119	1.000	0.004	32.152	0.982

Table S3. Adsorption isotherm parameters and correlation coefficients for the adsorption of Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) on BC-CS 2-1.

Isotherm models	Parameters	Cu(II)	Cd(II)	Zn(II)	Co(II)	Pb(II)
Langmuir $q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$	$q_{e,exp}$	44.17	49.39	44.16	25.74	69.43
	q^0	46.99	71.44	47.67	27.13	70.35
	K_L	0.040	0.007	0.023	0.009	0.050
	R^2	0.984	0.976	0.976	0.961	0.949
	K_F	7.44	1.72	5.86	1.87	13.29
Freundlich $q_e = K_F C_e^{1/n}$	$1/n$	0.327	0.609	0.344	0.405	0.296
	R^2	0.971	0.973	0.918	0.951	0.928
	K_T	1.425	0.086	0.646	0.143	5.498
Temkin $q_e = \frac{RT}{b_T} \ln(k_T C_e)$	b_T	353.62	167.91	329.96	490.93	301.34
	R^2	0.900	0.939	0.858	0.835	0.809
	q_m	0.0012	0.0030	0.0012	0.0007	0.0015
Dubinin-Raduszkiewicz $\ln q_e = \ln q_m - \beta \epsilon^2$ $E_a = \frac{1}{\sqrt{2\beta}}$	β	0.0032	0.0073	0.0036	0.0049	0.0025
	E_a	16.486	8.292	11.812	10.059	14.010
	R^2	0.953	0.974	0.887	0.939	0.899

Table S4. Adsorption isotherm parameters and correlation coefficients for the adsorption of Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) on BC-CS 4-1.

Isotherm models	Parameters	Cu(II)	Cd(II)	Zn(II)	Co(II)	Pb(II)
Langmuir $q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$	$q_{e,exp}$	43.24	47.26	46.72	41.34	58.76
	q^0	41.67	51.63	47.07	51.51	59.02
	K_L	0.042	0.014	0.044	0.009	0.047
	R^2	0.968	0.968	0.972	0.905	0.969
	K_F	8.97	6.88	10.37	14.81	11.57
Freundlich $q_e = K_F C_e^{1/n}$	$1/n$	0.265	0.304	0.260	0.378	0.284
	R^2	0.962	0.954	0.970	0.902	0.960
	k_T	38.221	0.608	4.295	0.335	3.578
Temkin $q_e = \frac{RT}{b_T} \ln(k_T C_e)$	b_T	628.87	332.14	424.50	337.14	332.63
	R^2	0.740	0.854	0.904	0.761	0.909
	q_m	0.0007	0.0011	0.0010	0.0010	0.0013
Dubinin-Raduszkiewicz $\ln q_e = \ln q_m - \beta \epsilon^2$ $E_a = \frac{1}{\sqrt{2\beta}}$	β	0.0016	0.0033	0.0025	0.0039	0.0027
	E_a	17.774	12.263	14.271	11.259	16.612
	R^2	0.818	0.922	0.971	0.846	0.954

Table S5. Thermodynamic parameters for the sorption of Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) ions on: BC-CS 2-1.

Ions	K _d			ΔH° [kJ/mol]	ΔS° [J/molK]	ΔG°[kJ/mol]		
	Temperature [K]					Temperature [K]		
	293	313	333			293	313	333
Cu(II)	0.173	0.201	0.237	6.34	7.12	-12.56	-13.91	-15.13
Cd(II)	0.145	0.157	0.164	2.53	-7.40	-12.12	-13.16	-14.11
Zn(II)	0.128	0.140	0.166	5.29	0.79	-11.81	-12.86	-14.15
Co(II)	0.066	0.069	0.091	6.42	-1.02	-10.21	-11.01	-12.49
Pb(II)	0.369	0.567	0.684	12.60	34.99	-14.40	-16.50	-18.07

Table S6. Thermodynamic parameters for the sorption of Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) ions on: BC-CS 4-1.

Ions	K _d			ΔH° [kJ/mol]	ΔS° [J/molK]	ΔG°[kJ/mol]		
	Temperature [K]					Temperature [K]		
	293	313	333			293	313	333
Cu(II)	0.222	0.557	0.601	20.52	58.55	-13.16	-16.46	-17.71
Cd(II)	0.121	0.133	0.139	2.94	-7.50	-11.67	-12.73	-13.66
Zn(II)	0.180	0.227	0.337	12.57	28.39	-12.66	-14.11	-16.12
Co(II)	0.123	0.126	0.132	1.41	-12.63	-11.72	-12.59	-13.51
Pb(II)	0.233	0.246	0.254	1.74	6.15	-13.28	-14.33	-15.33