Electronic Supplementary Information

Silanized magnetic amino-functionalized carbon nanotubes-based multi-ion imprinted polymer for the selective aqueous decontamination of heavy metal ions

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Section S1:

The surface functional groups of the prepared samples were investigated by the Fourier transform infrared spectra (FTIR, Thermo Nicolet, Avatar 360, USA) over the wavenumber range of 400−4000 cm^{-1}. The surface morphologies and elemental composition of the samples were studied by the field emission scanning electronic microscopy (FESEM, Zeiss, SIGMA VP-500, Germany) equipped with energy dispersive X-ray spectroscopy (EDX), respectively. The specific surface area ($m^2 g^{-1}$), total pore volume ($cm^3 g^{-1}$), and mean pore diameter (nm) were measured using nitrogen adsorption/desorption isotherm with a Brunauer–Emmett–Teller (BET) analysis (BEL, Belsorp- mini II. Japan) at 77 K. The magnetic properties of samples were analyzed by a vibrating sample magnetizer (VSM, Lake Shore, 735 VSM, Model 7304, USA) at 300 K in a field of +5000 to -5000 Oe. The concentration of heavy metal ions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Varian, Palo Alto, CA, USA).

Section S2:

The adsorption capacity at equilibrium (qe), and each time (qt), and also the removal efficiency percentage (R%) were evaluated through equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$(R\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (3)$$

where q_e and q_t (mg g^{-1}) shows the amount of adsorption at equilibrium and at time t, respectively while C_0, C_e, and Ct (mg L^{-1}) refer to the initial, equilibrium, and ion concentration at any time (t), respectively. Also, V (L) presents the volume of the contaminated solution, and m (g) denotes the mass of dry adsorbent.

Table S1. Experimental independent variables of central composite design (CCD) with coded levels and actual responses (removal %).

Independent variable			Variable levels				
Factors	**Coded**	**Units**	**-α (-2)**	**Low (-1)**	**Center (0)**	**High(+1)**	**+α (+2)**
pH	X_1	-	4.0	5.0	6.0	7.0	8.0
Adsorbent mass	X_2	mg	6.0	12	18	24	30
Contact time	X_3	min	7.0	14	21	28	35
Hg^{2+} concentration	X_4	mg L^{-1}	10	20	30	40	50
Cd^{2+} concentration	X_5	mg L^{-1}	8.0	16	24	32	40
Cu^{2+} concentration	X_6	mg L^{-1}	6.0	12	18	24	30
Ni^{2+} concentration	X_7	mg L^{-1}	4.0	8.0	12.0	16	20

Variables								Response (%)			
Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	Hg^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}
1	5.0	24	28	40	16	12	16	93.89	84.87	80.97	90.87
2	6.0	18	21	30	24	18	12	80.63	85.11	76.45	74.23
3	6.0	18	21	50	24	18	12	44.01	50.87	43.87	23.98
4	5.0	24	14	40	16	12	8	82.58	85.98	90.76	97.89
5	6.0	18	21	30	24	18	12	82.87	85.21	78.35	73.54
6	7.0	12	14	40	16	12	8	34.69	42.56	25.76	41.98
7	6.0	18	21	30	24	18	12	84.11	84.54	74.76	72.67
8	7.0	12	14	20	32	12	8	49.36	49.69	33.76	54.76
9	5.0	24	14	20	32	24	16	58.36	69.87	74.98	73.25
10	5.0	12	28	40	32	24	8	67.36	17.89	68.76	65.87
11	5.0	24	28	20	16	24	8	95.69	90.87	99.81	99.05
12	7.0	24	28	20	32	12	8	60.48	70.98	59.34	69.31
13	7.0	24	14	40	32	12	16	46.91	51.98	40.31	46.76
14	6.0	18	21	30	24	6	12	95.42	98.76	94.34	91.23
15	6.0	18	21	30	24	18	12	82.67	86.65	78.67	75.34
16	6.0	18	21	30	24	30	12	77.42	60.54	58.76	62.34
17	6.0	18	7	30	24	18	12	31.74	41.76	38.96	45.61
18	7.0	12	14	40	32	24	16	18.32	28.54	12.87	25.43
19	6.0	18	21	10	24	18	12	99.63	96.76	87.76	83.23
20	5.0	12	28	20	16	12	16	28.74	56.89	70.76	69.65
21	7.0	12	14	20	16	24	16	40.47	29.45	20.86	27.98
22	7.0	24	28	20	32	24	16	55.11	60.32	78.87	55.44
23	5.0	12	28	40	32	12	16	73.59	27.87	79.98	48.87
24	5.0	12	14	20	32	24	8	59.36	40.65	73.56	84.65
25	7.0	12	28	20	16	12	16	68.99	39.81	49.68	41.98
26	7.0	24	28	40	16	24	8	67.10	78.76	61.76	71.52
27	5.0	24	14	40	32	12	16	68.69	76.98	70.98	65.69
28	7.0	24	14	40	16	24	8	54.43	68.76	37.65	65.96
29	4.0	18	21	30	24	18	12	45.11	38.56	54.65	48.95
30	5.0	24	14	20	16	24	16	69.36	87.74	78.87	80.76
31	6.0	18	21	30	24	18	20	66.64	78.76	45.76	70.45
32	7.0	12	28	40	16	24	16	47.93	56.98	25.64	63.54
33	6.0	6	21	30	24	18	12	21.64	46.65	39.35	41.49
34	6.0	18	21	30	8	18	12	94.74	90.98	83.65	91.23
35	6.0	18	21	30	24	18	4	86.64	90.87	97.87	99.45
36	5.0	12	14	20	16	12	8	65.69	45.98	57.65	70.87
37	6.0	30	21	30	24	18	12	91.33	95.65	94.35	97.36
38	6.0	18	21	30	40	18	12	61.53	45.65	64.54	58.56
39	6.0	18	35	30	24	18	12	94.44	90.76	95.76	93.06
40	8.0	18	21	30	24	18	12	58.44	49.78	40.56	39.98

Table S2. Analysis of variance (ANOVA) results of the quadratic model to removal of Hg^{2+} and Cd^{2+} from contaminated water.

Source of variation	DF	R% Hg^{2+}				R% Cd^{2+}			
		SS	MS	F-value	P-value	SS	MS	F-value	P-value
Model	35	18700	534.5	297.2	< 0.0001	20600	588.6	255.4	< 0.0001
X_1	1	88.84	88.84	49.4	0.0022	62.94	62.94	27.32	0.0064
X_2	1	2428	2428	1350	< 0.0001	1201	1201	521	< 0.0001
X_3	1	1966	1966	1093	< 0.0001	1201	1201	521	< 0.0001
X_4	1	1547	1547	860.1	< 0.0001	1053	1053	457	< 0.0001
X_5	1	551.5	551.5	306.6	< 0.0001	1027	1027	445.9	< 0.0001
X_6	1	162	162	90.08	0.0007	730.4	730.4	317	< 0.0001
X_7	1	200	200	111.2	0.0005	73.33	73.33	31.82	0.0049
X_1X_2	1	5.983	5.983	3.326	0.1422	22.02	22.02	9.559	0.0365
X_1X_3	1	8.638	8.638	4.803	0.0935	29.14	29.14	12.65	0.0237
X_1X_4	1	18.72	18.72	10.41	0.0321	250.5	250.5	108.7	0.0005
X_1X_5	1	199.4	199.4	110.9	0.0005	235.6	235.6	102.3	0.0005
X_1X_6	1	11.16	11.16	6.205	0.0674	299.3	299.3	129.9	0.0003
X_1X_7	1	6.509	6.509	3.619	0.1299	9.608	9.608	4.17	0.1107
X_2X_3	1	48.52	48.52	26.98	0.0065	274.9	274.9	119.3	0.0004
X_2X_4	1	15.4	15.4	8.564	0.0430	69.53	69.53	30.18	0.0051
X_2X_5	1	446.4	446.4	248.2	< 0.0001	793.8	793.8	344.5	< 0.0001
X_2X_6	1	25.92	25.92	14.41	0.01916	35.04	35.04	15.21	0.0176
X_2X_7	1	106.4	106.4	59.18	0.0015	308.3	308.3	133.8	0.0003
X_3X_4	1	22.6	22.6	12.56	0.0239	295.5	295.5	128.2	0.0004
X_3X_5	1	0.070	0.070	0.039	0.8536	3.265	3.265	1.417	0.2997
X_3X_6	1	1.378	1.378	0.7663	0.4308	20.2	20.2	8.766	0.0415
X_3X_7	1	11.54	11.54	6.419	0.0644	117.1	117.1	50.83	0.0021
X_4X_5	1	105.8	105.8	58.81	0.0016	83.02	83.02	36.03	0.0039
X_4X_6	1	2.84	2.84	1.579	0.2773	137.7	137.7	59.77	0.0015
X_4X_7	1	18.93	18.93	10.52	0.0316	93.26	93.26	40.48	0.0031
X_5X_6	1	11.57	11.57	6.435	0.0642	27.16	27.16	11.79	0.02646
X_5X_7	1	34.1	34.1	18.96	0.0121	54.69	54.69	23.73	0.0082
X_6X_7	1	67.07	67.07	37.29	0.0036	284	284	123.3	0.0004
X_1^2	1	1800	1800	1001	< 0.0001	3534	3534	1534	< 0.0001
X_2^2	1	1284	1284	713.9	< 0.0001	470.7	470.7	204.3	0.0001
X_3^2	1	707	707	393.1	< 0.0001	814.4	814.4	353.4	< 0.0001
X_4^2	1	206.6	206.6	114.9	0.0004	322.8	322.8	140.1	0.0003
X_5^2	1	30.65	30.65	17.04	0.0145	658.6	658.6	285.8	< 0.0001
X_6^2	1	36.7	36.7	20.41	0.0107	96.04	96.04	41.68	0.0030
X_7^2	1	58.19	58.19	32.35	0.0047	6.616	6.616	2.871	0.1654
Residual	4	7.194	1.798			9.217	2.304		
Lack of Fit	1	0.9587	0.9587	0.4613	0.5457	6.797	6.797	8.425	0.0624
Pure Error	3	6.235	2.078			2.42	0.8068		
Corr. Total	39	18700				20600			

Quadratic model summary statistics

Response	R^2	Adj- R^2	Pre- R^2	CV (%)	SD	AP
R% Hg^{2+}	0.999	0.9996	0.956	2.058	1.341	64.11
R% Cd^{2+}	0.999	0.996	0.934	2.352	1.518	55.57

Table S3. Analysis of variance (ANOVA) results of the quadratic model to removal of Cu^{2+} and Ni^{2+} from contaminated water.

Source of variation	DF	R% Cu^{2+}				R% Ni^{2+}			
		SS	MS	F-value	P-value	SS	MS	F-value	P-value
Model	35	21420	612.1	232.9	< 0.0001	171060	487.5	198.9	< 0.0001
X_1	1	99.26	99.26	37.77	0.0036	40.23	40.23	16.41	0.0155
X_2	1	1513	1513	575.5	< 0.0001	1561	1561	636.8	< 0.0001
X_3	1	1613	1613	613.7	< 0.0001	1126	1126	459.3	< 0.0001
X_4	1	963.2	963.2	366.5	< 0.0001	1755	1755	716.1	< 0.0001
X_5	1	182.6	182.6	69.47	0.0011	533.7	533.7	217.7	0.0001
X_6	1	633	633	240.8	0.0001	417.3	417.3	170.3	0.0002
X_7	1	1358	1358	516.6	< 0.0001	420.5	420.5	171.6	0.0002
X_1X_2	1	333.7	333.7	127	0.0004	87.01	87.01	35.5	0.0040
X_1X_3	1	4.508	4.508	1.715	0.2605	115.5	115.5	47.11	0.0024
X_1X_4	1	17.02	17.02	6.475	0.0637	299.6	299.6	122.2	0.0004
X_1X_5	1	215.5	215.5	82	0.0008	304.3	304.3	124.1	0.0004
X_1X_6	1	189	189	71.92	0.0011	134.4	134.4	54.85	0.0018
X_1X_7	1	18.01	18.01	6.852	0.0590	1.834	1.834	0.748	0.4358
X_2X_3	1	184.7	184.7	70.28	0.0011	260.3	260.3	106.2	0.0005
X_2X_4	1	2.128	2.128	0.8097	0.4191	35.66	35.66	14.55	0.0189
X_2X_5	1	634.4	634.4	241.4	0.0001	769.5	769.5	314	< 0.0001
X_2X_6	1	11.18	11.18	4.252	0.1082	2.201	2.201	0.898	0.3970
X_2X_7	1	155.3	155.3	59.08	0.0015	84.96	84.96	34.66	0.0042
X_3X_4	1	63.68	63.68	24.23	0.0080	83.77	83.77	34.18	0.0043
X_3X_5	1	177.4	177.4	67.5	0.0012	3.279	3.279	1.338	0.3118
X_3X_6	1	0.336	0.336	0.128	0.7389	92.69	92.69	37.82	0.0036
X_3X_7	1	10.87	10.87	4.134	0.1118	29.2	29.2	11.91	0.0260
X_4X_5	1	44.21	44.21	16.82	0.0148	10.86	10.86	4.43	0.1031
X_4X_6	1	377	377	143.4	0.0003	98.32	98.32	40.11	0.0032
X_4X_7	1	13.31	13.31	5.064	0.0876	78.5	78.5	32.03	0.0048
X_5X_6	1	36.86	36.86	14.02	0.0200	77.73	77.73	31.71	0.0049
X_5X_7	1	21.28	21.28	8.096	0.0466	43.12	43.12	17.59	0.0138
X_6X_7	1	300.8	300.8	114.4	0.0004	243.4	243.4	99.3	0.0006
X_1^2	1	1743	1743	663	< 0.0001	1567	1567	639.1	< 0.0001
X_2^2	1	219.4	219.4	83.48	0.0008	21.62	21.62	8.822	0.0411
X_3^2	1	198.8	198.8	75.63	0.0010	22.81	22.81	9.306	0.0380
X_4^2	1	264.4	264.4	100.6	0.0006	717.6	717.6	292.8	< 0.0001
X_5^2	1	21.84	21.84	8.311	0.0450	9.028	9.028	3.683	0.1274
X_6^2	1	1.533	1.533	0.5834	0.4875	31.92	31.92	13.02	0.0226
X_7^2	1	61.85	61.85	23.53	0.0083	291.6	291.6	119	0.0004
Residual	4	10.51	2.628			9.804	2.451		
Lack of Fit	1	0.595	0.595	0.18	0.7000	5.987	5.987	4.706	0.1185
Pure Error	3	9.918	3.306			3.817	1.272		
Corr. Total	39	21420				17060			

Quadratic model summary statistics						
Response	R^2	Adj- R^2	Pre- R^2	CV (%)	SD	AP
R% Cu^{2+}	0.999	0.995	0.955	2.551	2.621	56.43
R% Ni^{2+}	0.999	0.994	0.928	2.36	1.566	50.81

Table S4. Isotherm parameters for the adsorption of target heavy metal ions by SMACNT-MIIP.

Isotherm	Plot	Parameters	Hg^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}
Langmuir $\frac{C_e}{q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m}$	C_e/q_e vs. C_e	Q_m (mg g^{-1})	105.34	91.79	75.03	63.54
		K_L (L mg^{-1})	2.779	3.614	4.188	4.088
		R^2	0.998	0.992	0.999	0.996
		$R_L=1/(1+(K_L \times C_0))$	0.007-0.067	0.007-0.065	0.006-0.056	0.008-0.075
Freundlich $ln q_e = ln K_F + \frac{1}{n} ln C_e$	$ln\ q_e$ vs. $ln\ C_e$	1/n	0.337	0.303	0.235	0.269
		K_F (L mg^{-1})	6.009	5.957	5.426	5.117
		R^2	0.962	0.979	0.972	0.967
Temkin $q_e = B_1 \ln K_T + B_1 \ln C_e$	q_e vs. $ln\ C_e$	B_1	15.53	11.10	7.94	7.06
		K_T (L mg^{-1})	1.000	1.000	1.000	1.000
		R^2	0.953	0.885	0.913	0.861
Dubinin-Radushkevich $ln\ q_e = ln Q_S - k\varepsilon^2$	$ln\ q_e$ vs. ε^2	Q_s (mg g^{-1})	74.83	59.44	53.77	41.97
		β	-1.6E-08	-7.9E-09	-5.9E-09	-6.1E-09
		E (kJ mol^{-1})	5.651	7.952	9.183	9.056
		R^2	0.830	0.772	0.758	0.735

Table S5. Adsorption kinetic parameters for the adsorption of target heavy metal ions by SMACNT-MIIP.

Model	Plot	Parameters	Hg^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}
First-order- kinetic $\ln(q_e - q_t) = \ln q_e - k_1 t$	$ln\ (q_e - q_t)$ vs. t	k_1 (min^{-1})	0.1910	0.2065	0.1352	0.1799
		$q_{e\ (calc)}$ (mg g^{-1})	233.42	162.75	69.30	64.61
		R^2	0.8874	0.8312	0.9369	0.8739
Pseudo-second-order-kinetic $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	t/q_t vs. t	k_2 (min^{-1})	0.0008	0.0022	0.0020	0.0045
		$q_{e\ (calc)}$ (mg g^{-1})	100.57	60.08	57.92	34.67
		R^2	0.9906	0.9942	0.9880	0.9987
		h (mg $g^{-1}min^{-1}$)	8.36	7.96	6.66	5.43
Intraparticle diffusion $q_t = k_{diff} t^{1/2} + C$	q_t vs. $t^{1/2}$	K_{diff} (mg g^{-1} $min^{-1/2}$)	11.94	6.43	6.32	3.57
		C (mg g^{-1})	6.40	12.63	10.04	8.96
		R^2	0.9274	0.9495	0.9500	0.9420
Elovich $q_t = \frac{1}{\beta}\ln(t) + \frac{1}{\beta}\ln(\alpha\beta)$	q_t vs. $ln\ t$	β (g mg^{-1})	16.47	18.82	15.61	13.38
		α (mg g^{-1} min^{-1})	0.0422	0.0795	0.0817	0.1413
		R^2	0.9797	0.9737	0.9543	0.9904
Experimental data		$q_{e\ (exp)}$ (mg g^{-1})	74.71	49.78	47.00	29.53

Table S6. The thermodynamic parameters for the adsorption of target heavy metal ions.

	Hg^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}
T(k)	**ΔG°(kJ mol^{-1})**			
278.15	-0.76	-0.20	-0.44	-0.73
288.15	-2.70	-1.30	-1.05	-1.37
298.15	-3.89	-2.61	-2.36	-2.12
308.15	-5.95	-3.82	-3.59	-3.49
318.15	-7.92	-4.99	-4.77	-4.37
R^2	0.992	0.999	0.986	0.979
ΔS°(J mol^{-1} k^{-1})	175.11	120.86	111.29	93.07
ΔH°(kJ mol^{-1})	47.97	33.45	30.74	25.33

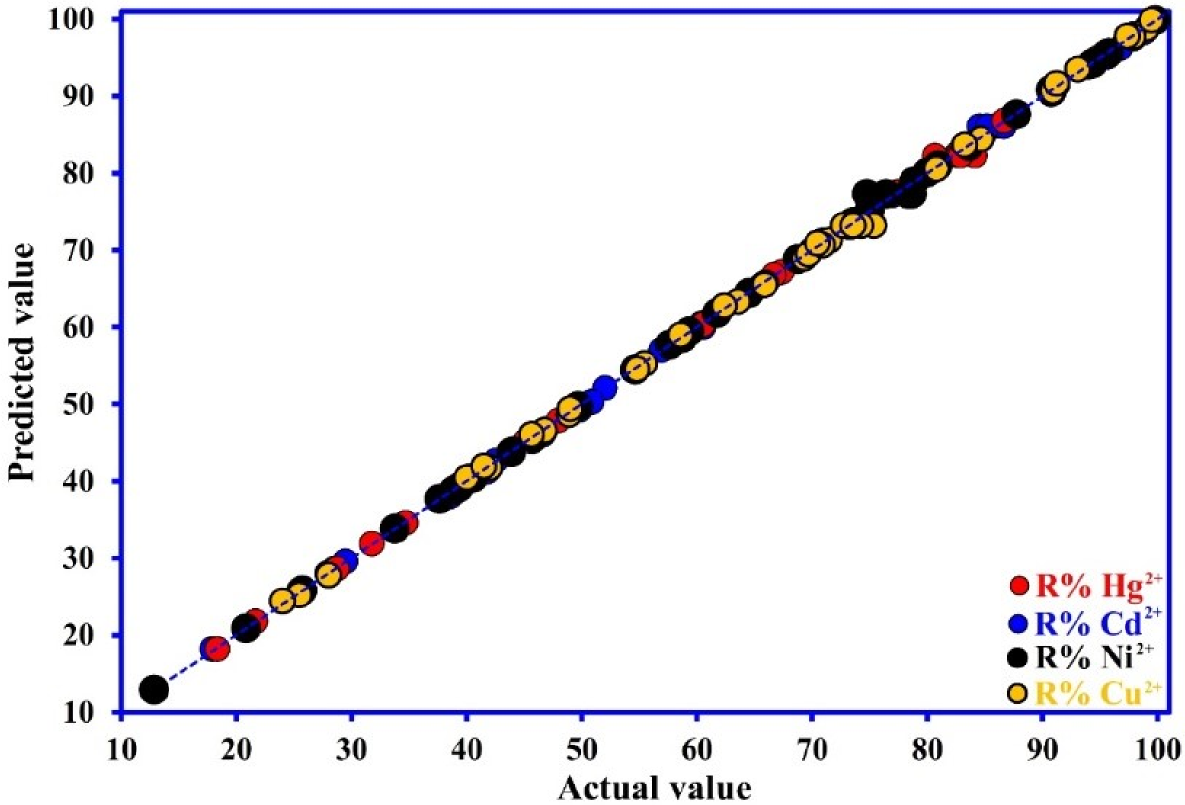

Fig. S1. Scatter plot of actual vs. predicted values of heavy metal ions removal by SMACNT-MIIP.

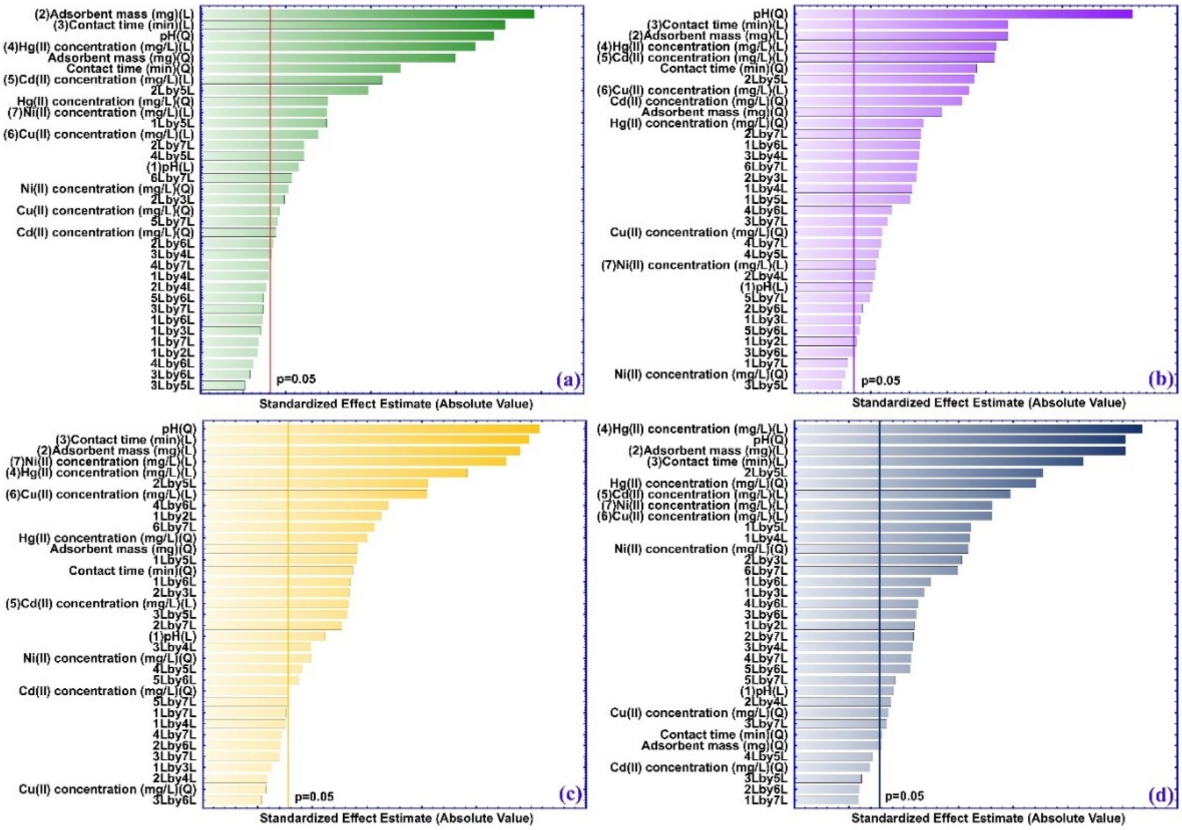

Fig. S2. Pareto charts of effective independent valuables for removal of (a) Hg^{2+}, (b) Cd^{2+}, (c) Ni^{2+}, and (d) Cu^{2+} metal ions by SMACNT-MIIP.

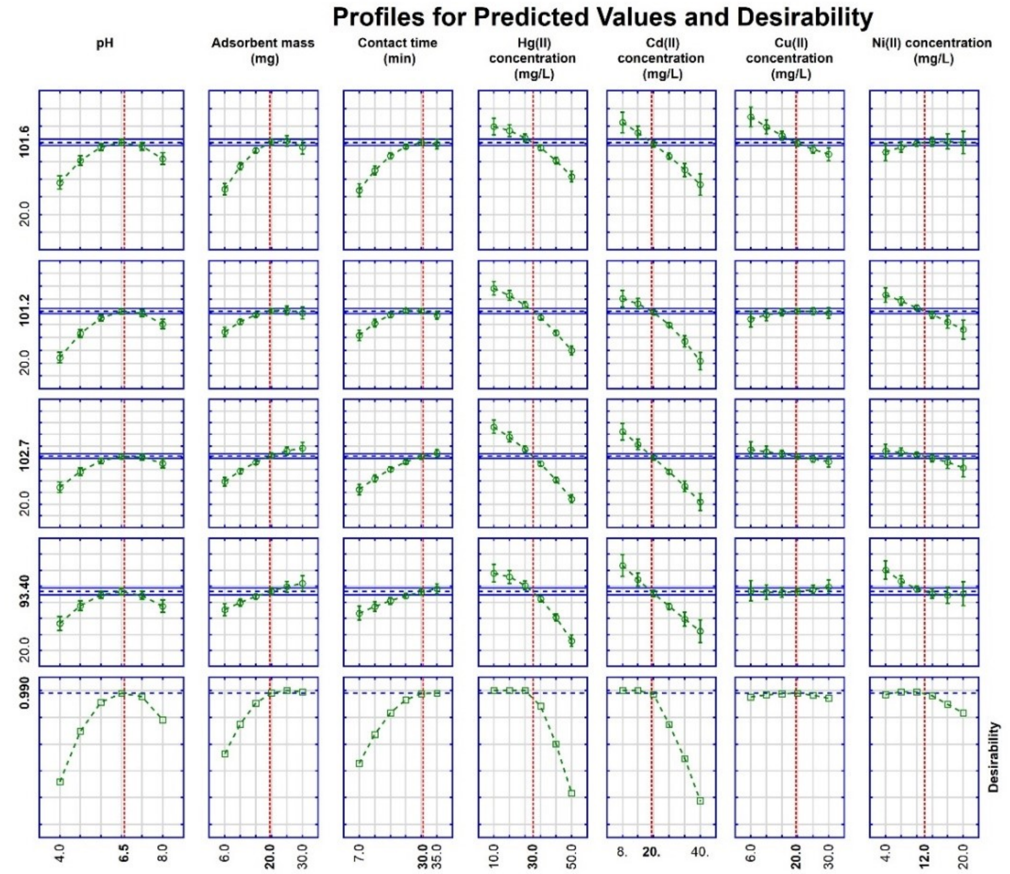

Fig. S3. Profiles for predicted values and desirability function for the removal of heavy metal ions by SMACNT-MIIP. Red lines indicate optimized values for each independent parameter.