Enhancing Trace Metal Extraction from Wastewater: Magnetic Activated Carbon as a High-Performance Sorbent for Inductively Coupled Plasma Optical Emission Spectrometry Analysis

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Figures

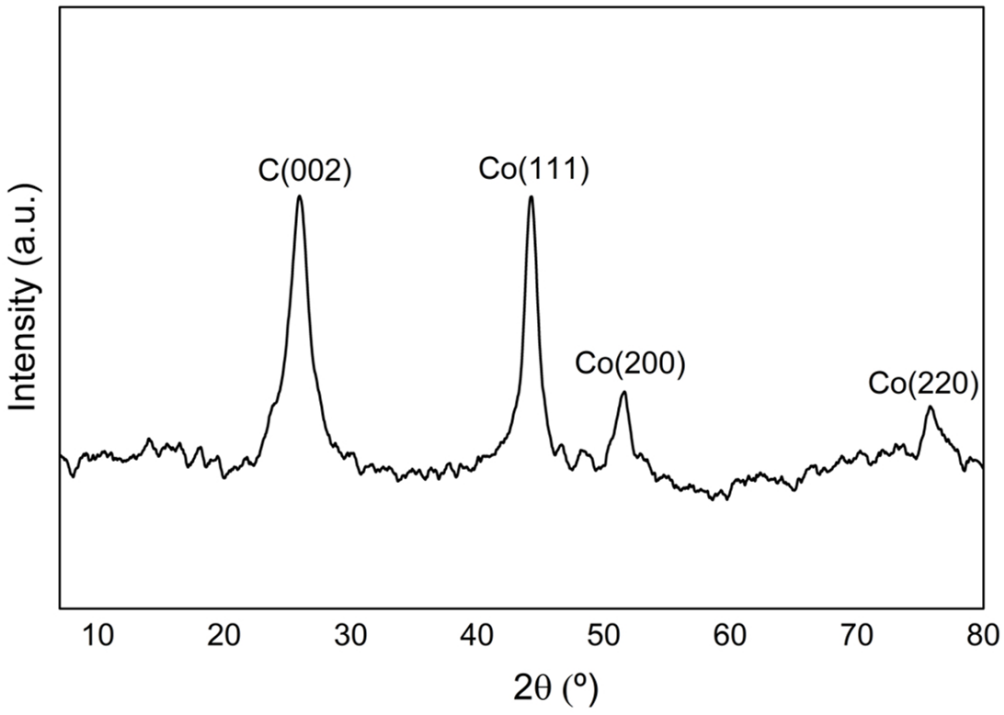


Figure S1. XRD pattern of ZIF67c_900_l registered between 5º and 80º with an angular step of 0.05º and a three second step time.

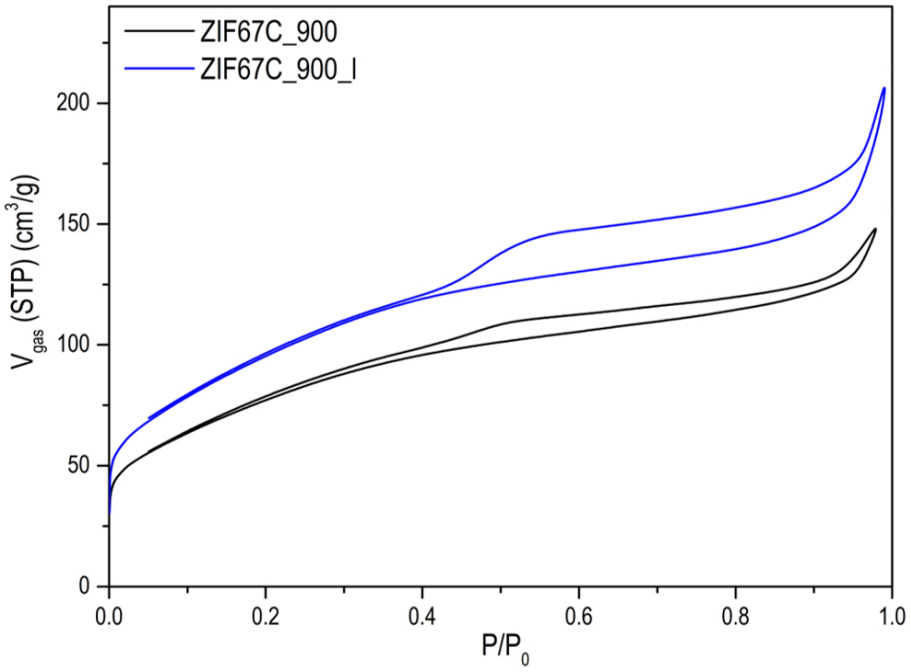


Figure S2. N_2 adsorption isotherm obtained at -196 ºC of the original carbon (i.e., ZIF67c_900) and the washed material ZIF67c_900_l after outgassing the sample at 150 ºC during 4 hours.

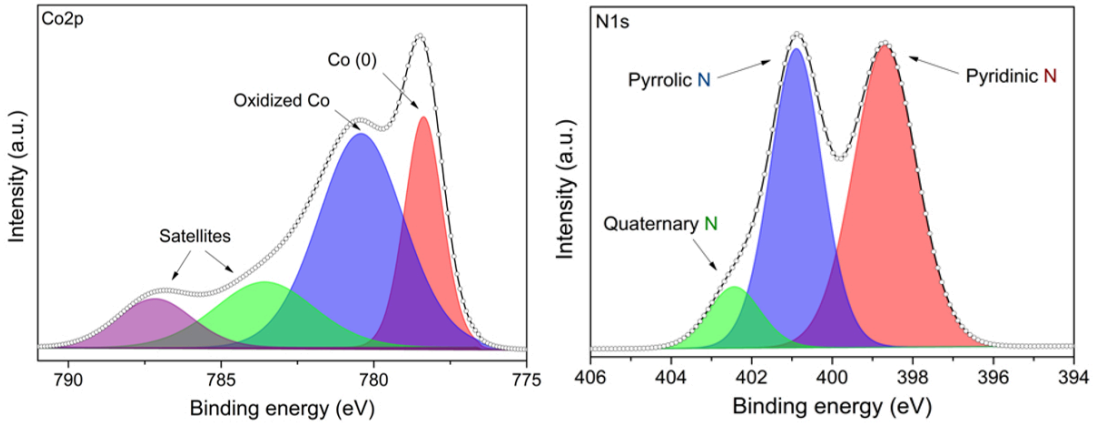


Figure S3. XPS spectra of cobalt and nitrogen in ZIF67c_900_l. Hv:1253.6 eV, pass energy of 50 eV and background pressure of $5 \cdot 10^{-7}$ Pa.

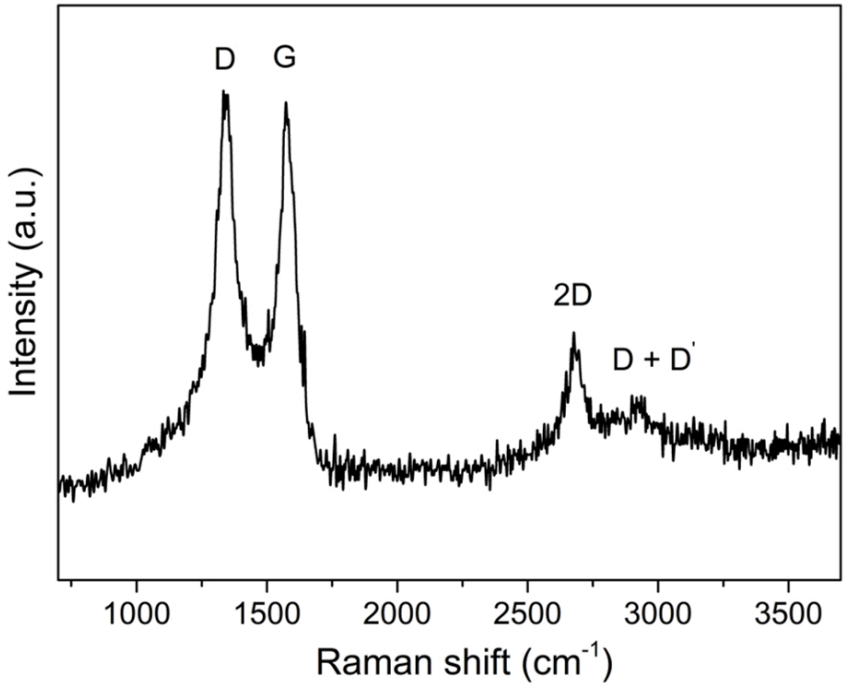


Figure S4. Raman spectrum of ZIF67c_900_l obtained using a 633 nm He laser.

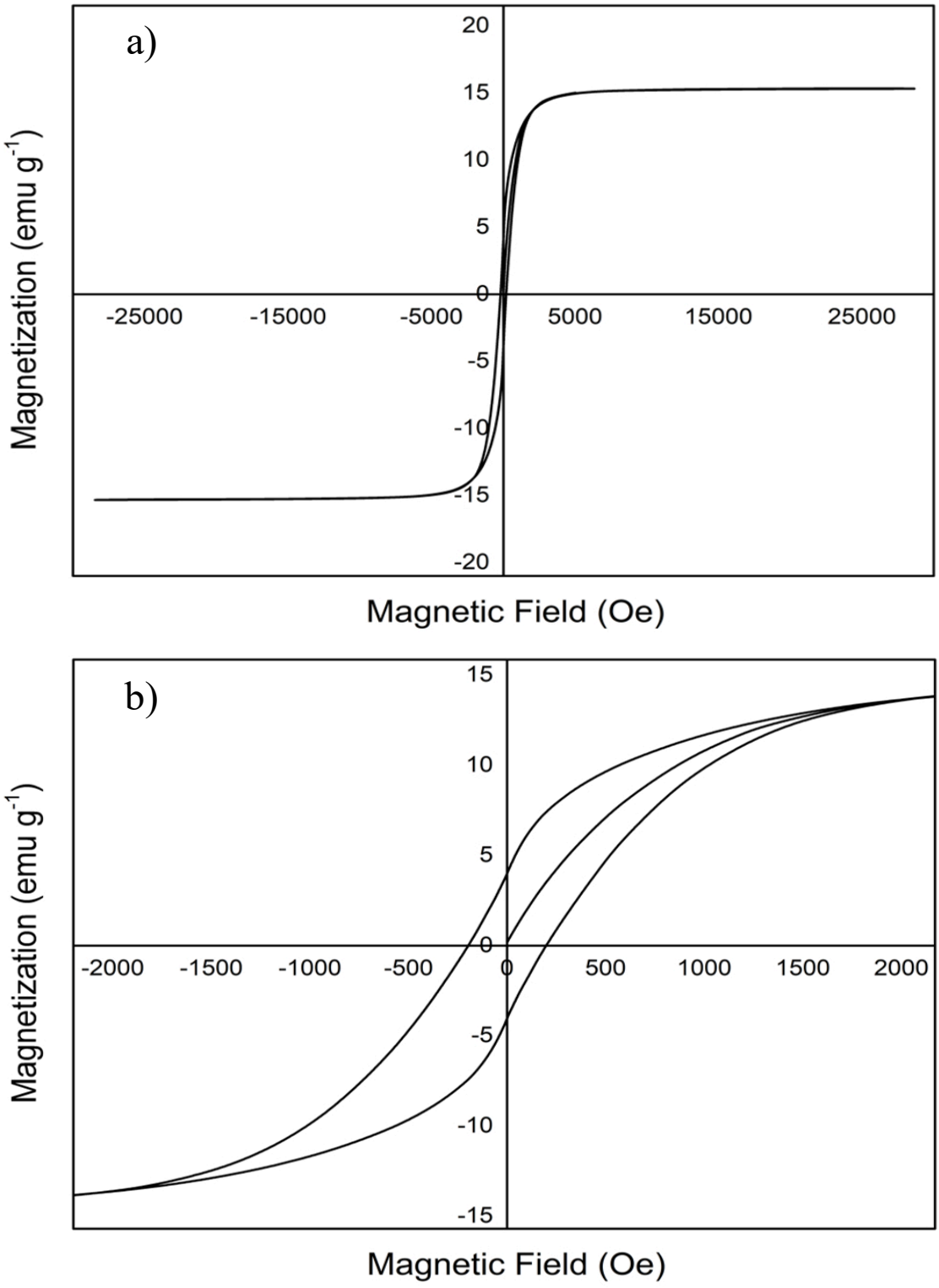


Figure S5. Magnetization curve of ZIF67c_900_l at 300K in a magnetic field from -30 to 30 kOe. a) representation of the magnetization curve (i.e., X axis from

-30 to 30 kOe) b) amplified representation of the magnetization curve (i.e., X axis from -2 to 2 kOe).

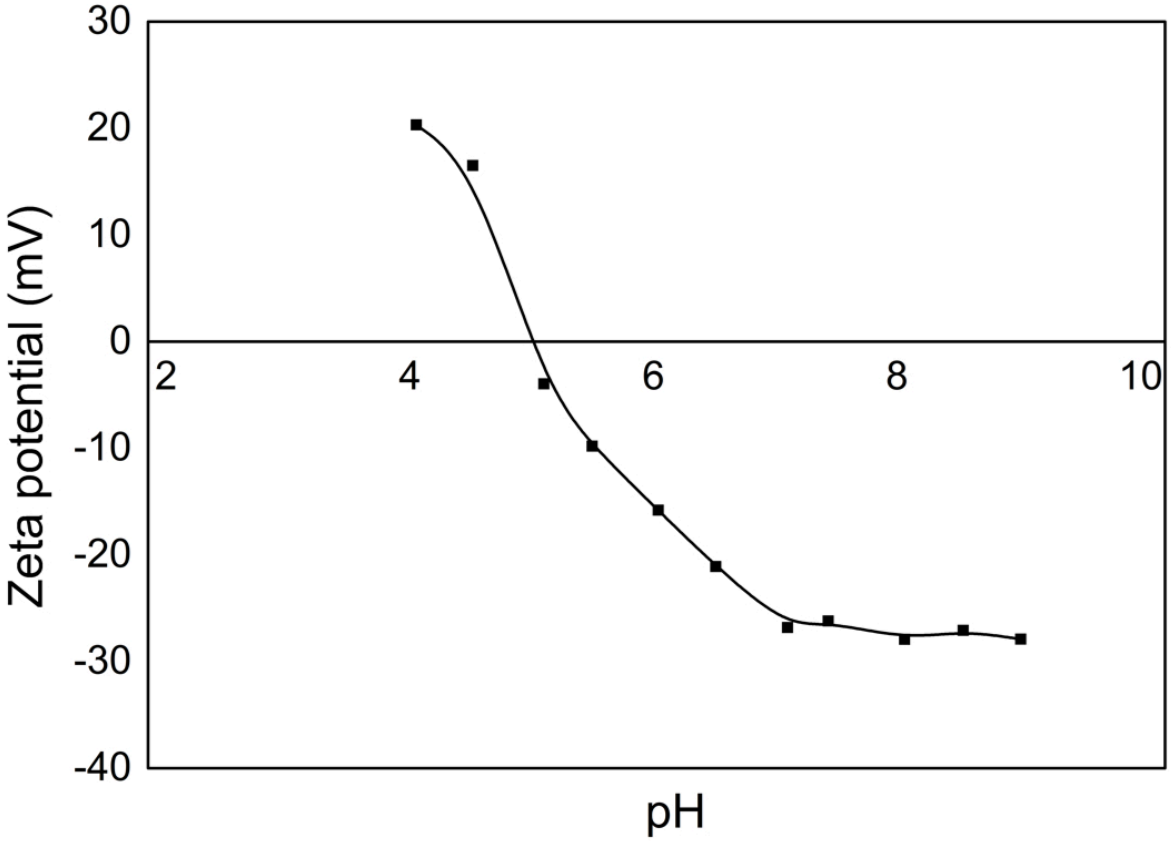
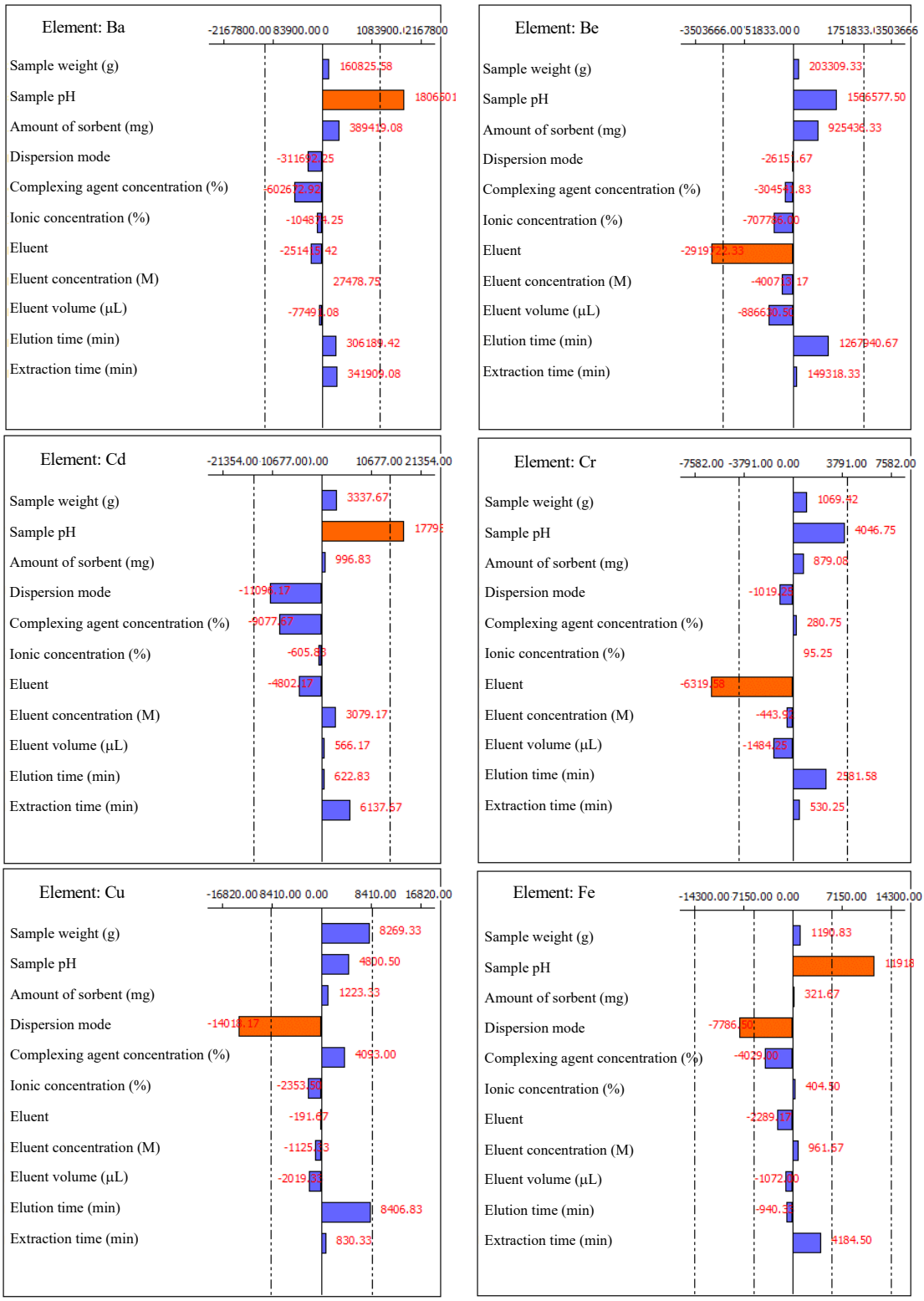


Figure S6. Zeta potential of ZIF67c_900_l/DDTC complex as function of the pH value. Complexing agent concentration: 0.5 %.


Element: Ba
-2167800.00 83900.00 0 1083900.00 2167800
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
160825.58
1806501
389419.08
-311692.25
-602672.92
-1048574.25
-2514153.42
27478.75
-774911.08
306189.42
341909.08
Element: Be
-3503666.00 51833.00 0 1751833.00 3503666
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
203309.33
1566577.50
925436.33
-261511.67
-707736.00
-2919122.33
-8866530.50
1267940.67
149318.33
Element: Cd
-21354.00 10677.00 0.00 10677.00 21354.00
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
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-907767
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-4802.17
3079.17
566.17
622.83
6137.67
Element: Cr
-7582.00 -3791.00 0.00 3791.00 7582.00
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
1069.42
4046.75
879.08
-1019.25
280.75
95.25
-6319.58
-443.92
-1484.25
2581.58
530.25
Element: Cu
-16820.00 8410.00 0.00 8410.00 16820.00
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
8269.33
4800.50
1223.33
-14018.17
4093.00
-2353.50
-191.67
-1125.83
-2019.83
8406.83
830.33
Element: Fe
-14300.00 7150.00 0.00 7150.00 14300.00
Sample weight (g)
Sample pH
Amount of sorbent (mg)
Dispersion mode
Complexing agent concentration (%)
Ionic concentration (%)
Eluent
Eluent concentration (M)
Eluent volume (µL)
Elution time (min)
Extraction time (min)
1190.83
11918
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-4029.00
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961.67
-1072.00
-940.33
4184.50

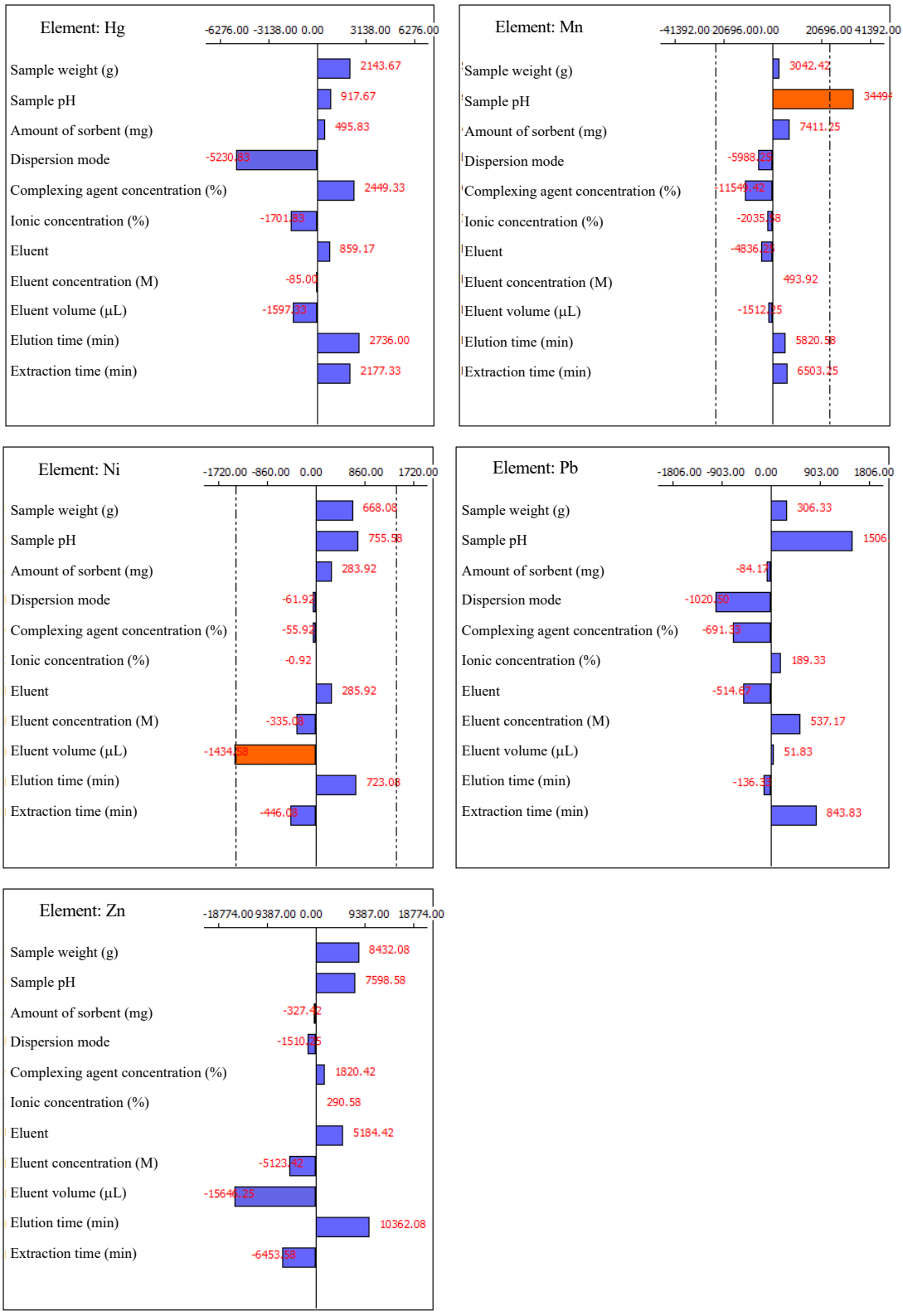
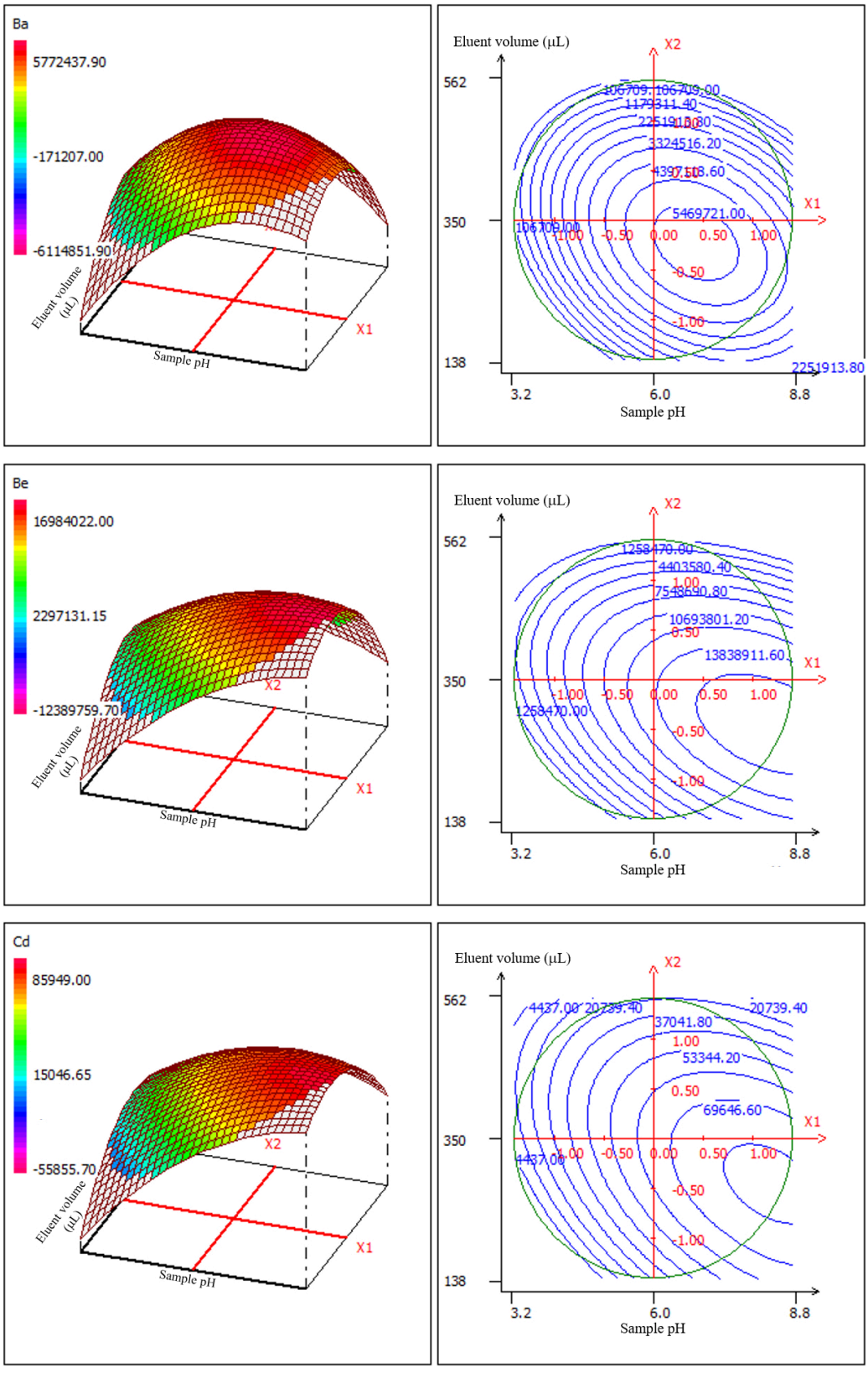


Figure S7. Pareto charts obtained in the screening study of the factors affecting the MDSPE. Orange means significant effect while blue means non-significant effect on MDSPE.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5772437.90
-171207.00
-6114851.90
Eluent volume (µL)
Sample pH
X1
X2
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
106709.00
1179311.40
2251913.80
3324516.20
5469721.00
-1.00
-0.50
0.00
0.50
1.00
Be
16984022.00
2297131.15
-12389759.70
1258470.00
4403580.40
7548690.80
10693801.20
13838911.60
Cd
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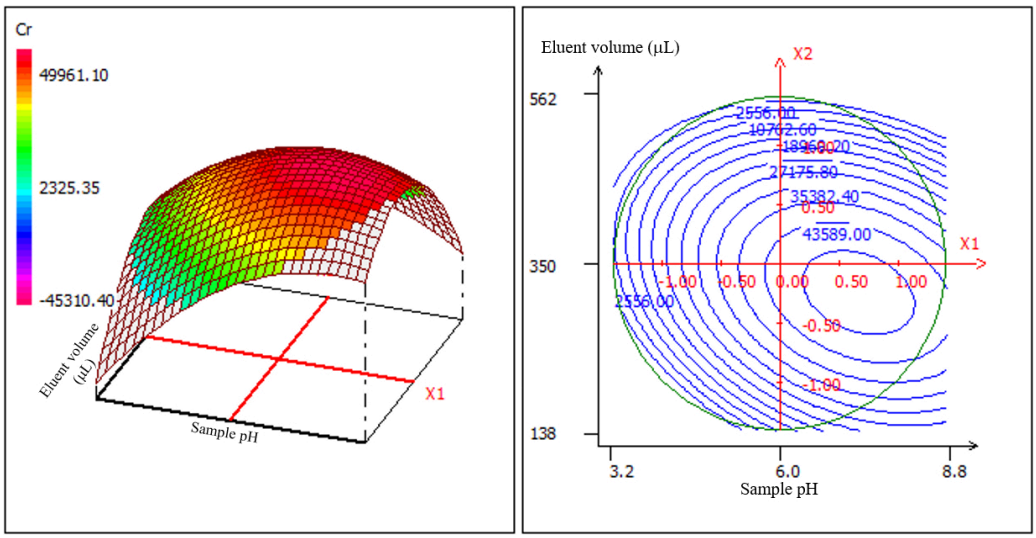
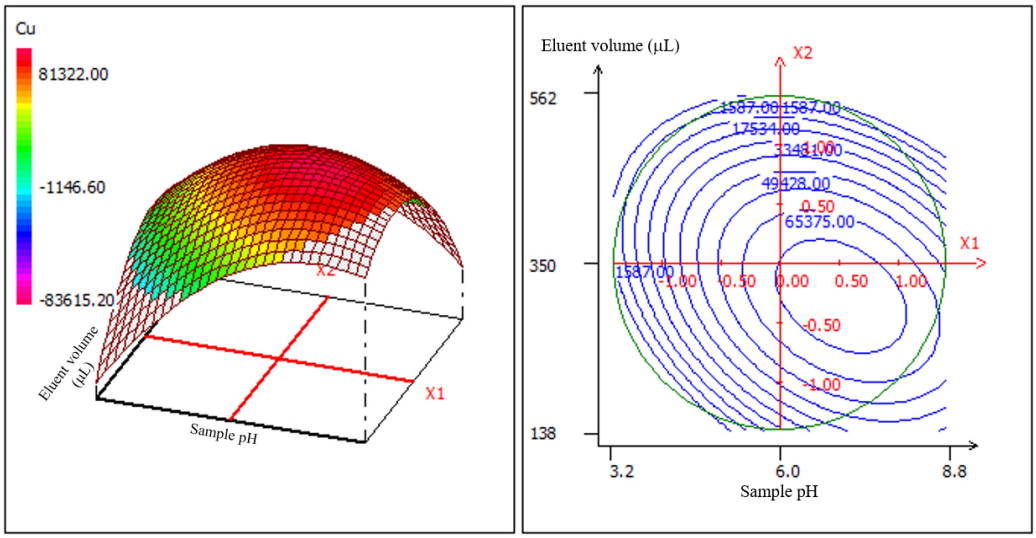
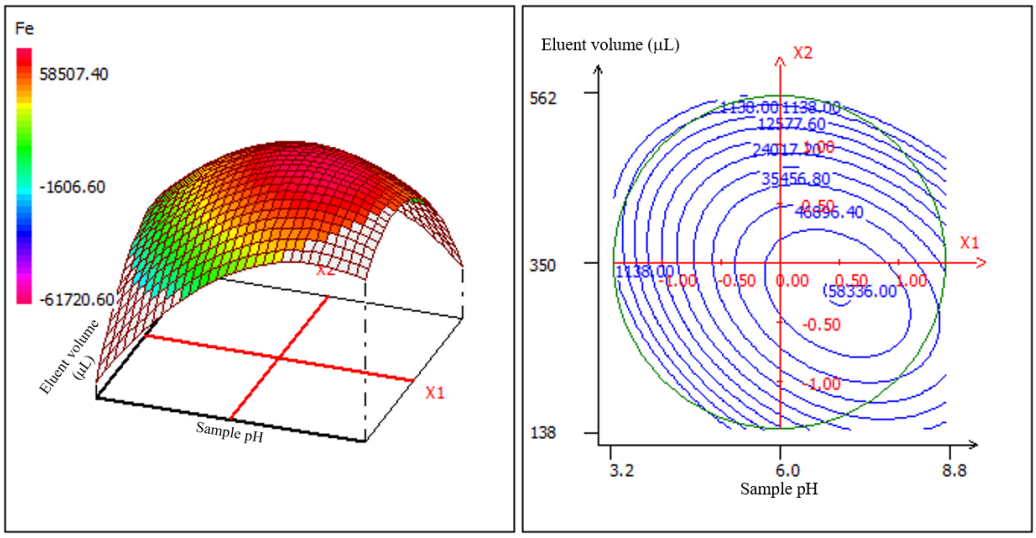
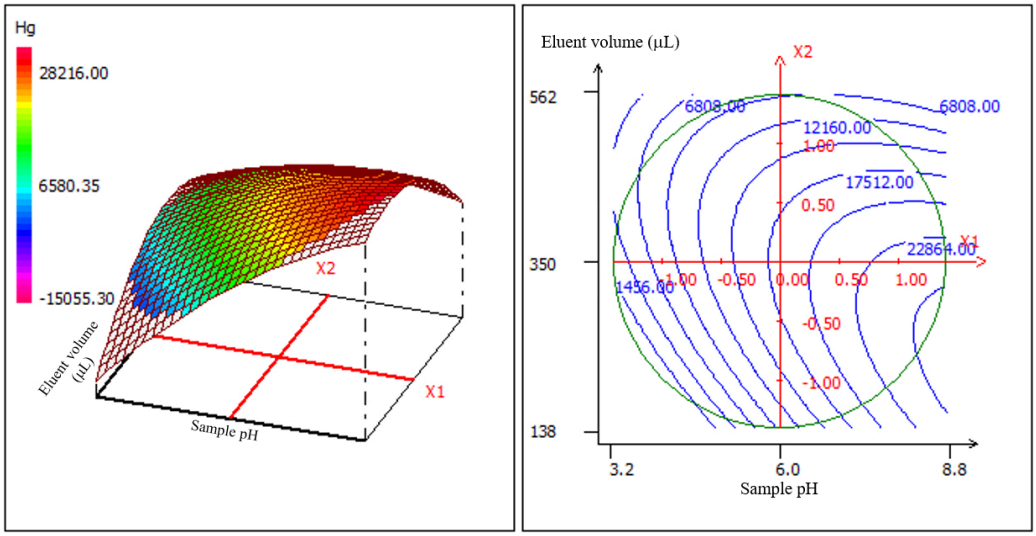
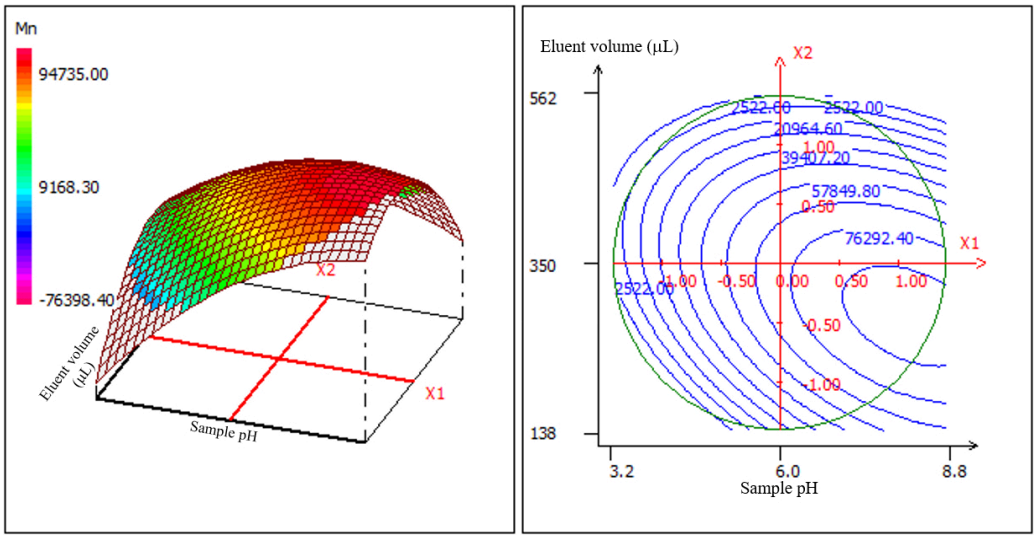
15046.65
-55855.70
4437.00
20739.40
37041.80
53344.20
69646.60

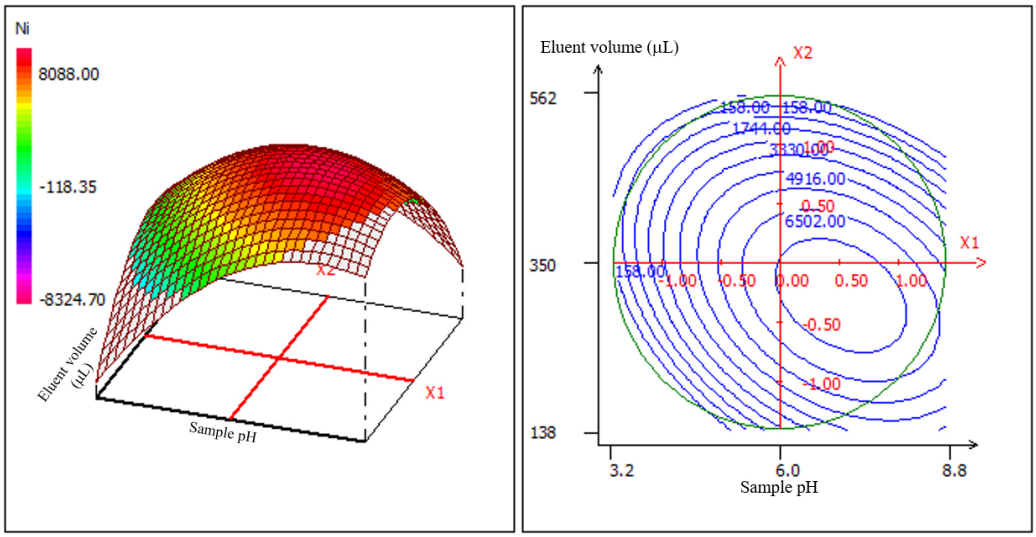

Cr
49961.10
2325.35
-45310.40
Eluent volume (µL)
Sample pH
X1
X2
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
2556.00
10762.60
18968.20
27175.80
35382.40
43589.00
0.50
-0.50
-1.00
1.00


Cu
81322.00
-1146.60
-83615.20
Eluent volume (µL)
Sample pH
X1
X2
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
1587.00
17534.00
33481.00
49428.00
65375.00
0.50
-0.50
-1.00
1.00


Fe
58507.40
-1606.60
-61720.60
Eluent volume (µL)
Sample pH
X1
X2
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
1138.00
12577.60
24017.20
35456.80
46896.40
(58336.00
0.50
-0.50
-1.00
1.00


Hg
28216.00
6580.35
-15055.30
Eluent volume (µL)
Sample pH
X2
X1
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
6808.00
12160.00
17512.00
22864.00
1456.00
1.00
0.50
-0.50
-1.00
-1.00
-0.50
0.00
0.50
1.00


Mn
94735.00
9168.30
-76398.40
Eluent volume (µL)
Sample pH
X2
X1
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
2522.00
20964.60
39407.20
57849.80
76292.40
1.00
0.50
-0.50
-1.00


Ni
8088.00
-118.35
-8324.70
Eluent volume (µL)
Sample pH
X2
X1
Eluent volume (µL)
562
350
138
3.2
6.0
8.8
Sample pH
158.00
1744.00
3330.00
4916.00
6502.00
1.00
0.50
-0.50
-1.00

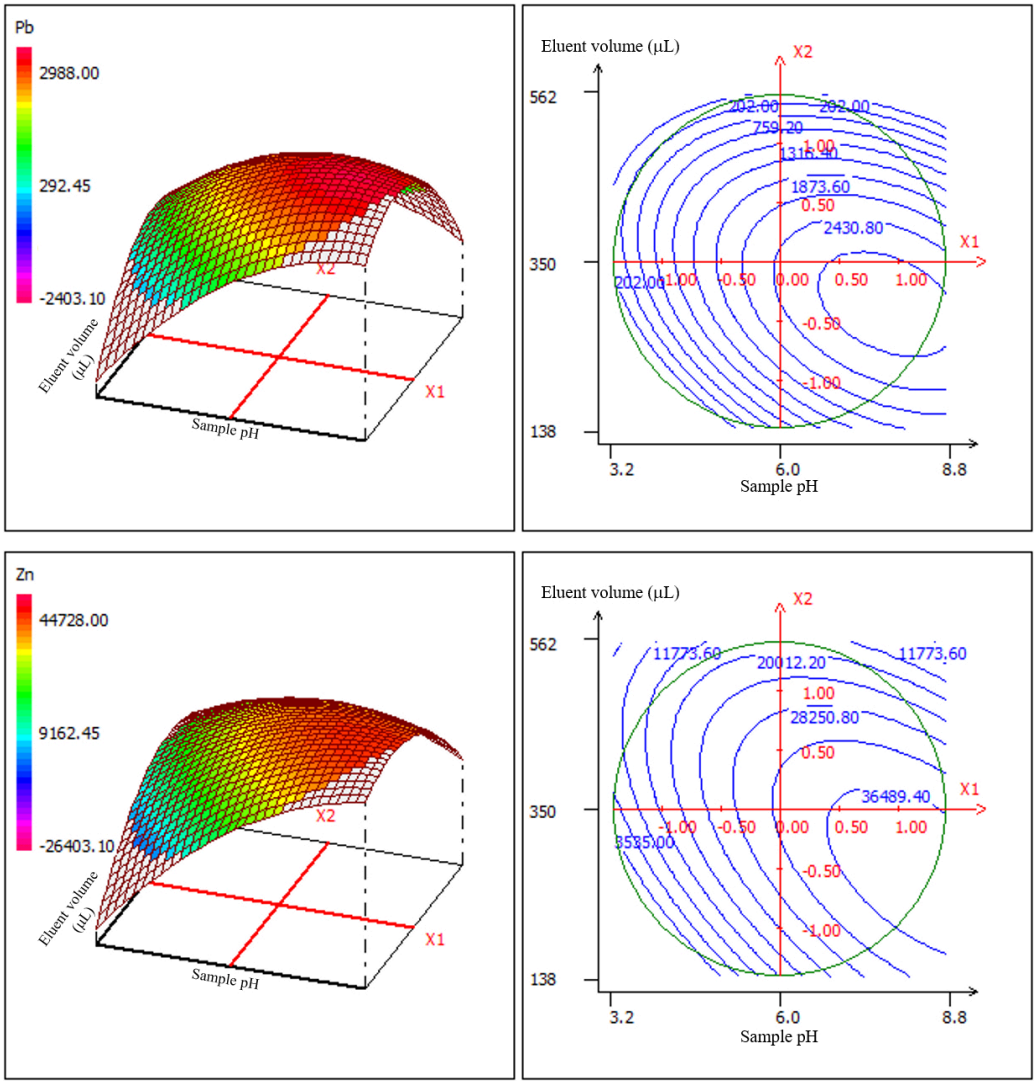


Figure S8. Response surface from CCD of sample pH and eluent volume for each analyte evaluated. Experimental fixed conditions: (i) sample weight, 10 g; (ii) amount of sorbent, 10 mg; (iii) dispersion mode, vortex; (iv) complexing agent concentration, 0.5 %; (v) ionic concentration, 0 %; (vi) eluent, HCl; (vii) eluent concentration, 0.5 M; (viii) extraction time, 3 min and (ix) elution time, 3 min.

Tables

Table S1. Operational parameters employed in Agilent 720 ICP OES.

Instrumental parameter	Value
RF applied power (kW)	1.4
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Nebulizer gas flow rate (L min^{-1})	0.75
Sample uptake rate (μL min^{-1})	100
Nebulizer	OneNeb®
Spray chamber	Cyclonic
Number of replicates	3
Viewing mode	Axial
Read time (s)	1
Element	**Emission line (nm)**
Ba	455.403
Be	313.042
Cd	214.439
Cr	267.716
Cu	327.395
Fe	238.204
Hg	184.887
Mn	257.610
Ni	231.604
Pb	220.353
Zn	213.857

Table S2. Considered experimental factors and levels in the Plackett-Burman design.

Factors	Level	
	Low (-1)	High (+1)
Sample weight (g)	8	10
Sample pH	4	8
Amount of sorbent (mg)	5	10
Dispersion mode	Vortex	Ultrasonication
Complexing agent concentration (%)	0.5	1
Ionic concentration (%)	0	2.5
Eluent	HCl	HNO_3
Eluent concentration (M)	0.5	1
Eluent volume (μL)	200	500
Extraction time (min)	1	3
Elution time (min)	1	3

Table S3. Considered experimental levels in CCD design.

Factors	Level				
	-α (-1.41)	-1	0	+1	+α (+1.41)
Sample pH	3.2	4	6	8	8.8
Eluent volume (μL)	138	200	350	500	562

Table S4. Optimum sample pH and eluent volume for each determined element.

Factor	Element										
	Ba	Be	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Sample pH	6.9	8.3	8.4	7.3	7.0	7.0	8.8	8.2	7.0	7.8	8.5
Eluent volume (μL)	316	282	281	314	308	311	138	283	308	296	269

Table S5. Optimum experimental conditions for MDSPE.

Factor	Value
Sample weight (g)	10
Sample pH	7.6
Amount of sorbent (mg)	10
Dispersion mode	Vortex
Complexing agent concentration (%)	0.5
Ionic concentration (%)	0
Eluent	HCl
Eluent concentration (M)	0.5
Eluent volume (μL)	300
Extraction time (min)	3
Elution time (min)	3

Table S6. Comparison of analytical figures of merit of the proposed method and other published methods.

Sample	Analytical technique	Sorbent	Sample amount (mL or g)	Sorbent Amount (mg)	Analytes	Extraction time (min)	LOD (μg L^{-1})	EF	Ref.
Water	SPE-FAAS	B. Subtilis - XAD-4	250	250	Cd and Cu	85	-	50	1
Water	MSPE-FAAS	$Fe_3O_4/SiO_2/L$	350	130	Cd, Cu and Pb	10	0.12-0.19	-	2
Water	SPE-FAAS	XAD-2000	50-500	250	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	3-25	0.15-0.45	100	3
Water	MSPE-ETAAS	Zeolite@Fe_3O_4@crown	25	250	Cd	5	0.0019	-	4
Water	MDSPE-GFAAS	Fe_3O_4@graphene oxide nanospheres	100	20	Cd and Pb	6	0.005-0.008	200	5
Environmental sample	MSPE-ICP-MS	γ-MPTMS-SCMNPs	250	50	Cd, Cu, Hg and Pb	10	$24\cdot10^{-6}$-$107\cdot10^{-6}$	-	6
Water	MSPE-ICP OES	Decanoic acid-Fe_3O_4	50	12	Cd, Co, Cr, Ni, Pb and Zn	5	0.3-0.8	116-150	7
Environmental sample	MSPE-ICP OES	BSCMNPs	200	100	Cr, Cu and Pb	10	0.043-0.085	87-96	8
Water	MSPE-ICP OES	AMT–TMSPT-MNPs	250	50	Ag, Cd, Cu and Zn	15	0.11-0.13	170-194	9
Water	UA-MSPE-ICP OES	Fe_3O_4@MnO_2, Al_2O_3@AAPTMS	-	10-100	Cr	5-15	0.02-0.05	94	10
Wastewater	MDSPE-ICP OES	ZIF67c_900_l	10	10	Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn	3	0.073-1.3	3.2-13	This work

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(7) Faraji, M.; Yamini, Y.; Saleh, A.; Rezaee, M.; Ghambarian, M.; Hassani, R. A Nanoparticle-Based Solid-Phase Extraction Procedure Followed by Flow Injection Inductively Coupled Plasma-Optical Emission Spectrometry to Determine Some Heavy Metal Ions in Water Samples. *Anal. Chim. Acta* **2010**, *659*, 172–177. https://doi.org/10.1016/j.aca.2009.11.053.

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Trace Amounts of Cr, Cu and Pb in Environmental Samples by Magnetic Solid-Phase Extraction with Bismuthiol-II-Immobilized Magnetic Nanoparticles and Their Determination by ICP-OES. *Talanta* **2009**, *77*, 1579–1583. https://doi.org/10.1016/j.talanta.2008.09.049.

(9) Mashhadizadeh, M. H.; Karami, Z. Solid Phase Extraction of Trace Amounts of Ag, Cd, Cu, and Zn in Environmental Samples Using Magnetic Nanoparticles Coated by 3-(Trimethoxysilyl)-1-Propantiol and Modified with 2-Amino-5-Mercapto-1,3,4-Thiadiazole and Their Determination by ICP-OES. *J. Hazard. Mater.* **2011**, *190*, 1023–1029. https://doi.org/10.1016/j.jhazmat.2011.04.051.

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