Modified ZSM-5 zeolite/Fe_2O_3 composite as sorbent for magnetic dispersive solid-phase microextraction of cadmium, mercury and lead from urine samples prior to inductively coupled plasma optical emission spectrometry

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Appendix A. Supplementary data

Table S1. Instrumental conditions of ICP OES.

Operational parameters	
RF applied power (kW)	1.2
Outer gas flow rate (L min^{-1})	15
Auxiliar gas flow rate (L min^{-1})	1.5
Nebulizer	OneNeb®
Spray chamber	Cyclonic-type
Nebulizer gas flow rate (L min^{-1})	0.75
Sample uptake rate (mL min^{-1})	0.5
Number of replicates	5
Viewing mode	Axial
Read time (s)	1
Analytical emission line (nm)	Cd II (226.502)[a]
	Cd II (228.802)[b]
	Hg II (194.164)
	Pb II (220.253)

[a] Measured in the MDSPME optimization (Section 3.3).

[b] Measured in the validation of the method (Section 3.5) and the analysis of real urine samples (Section 3.6).

Table S2. Experimental factors and levels of the Plackett-Burman design.

Factors	Level	
	Low (-1)	High (+1)
Amount of sorbent (mg)	20	50
Sample pH	4	8
Extraction time (min)	3	6
Eluent solvent volume (mL)	0.5	1
Eluent solvent concentration (M)	5	10
Elution time (min)	2	5

Table S3. Matrix of experiments of Plackett-Burman design with 11 factors (N=12 experiments) used for screening step.

Run	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
1	50	8	3	1	10	5	-	-	-	+	-
2	20	8	6	0.5	10	5	+	-	-	-	+
3	50	4	6	1	5	5	+	+	-	-	-
4	20	8	3	1	10	2	+	+	+	-	-
5	20	4	6	0.5	10	5	-	+	+	+	-
6	20	4	3	1	5	5	+	-	+	+	+
7	50	4	3	0.5	10	2	+	+	-	+	+
8	50	8	3	0.5	5	5	-	+	+	-	+
9	50	8	6	0.5	5	2	+	-	+	+	-
10	20	8	6	1	5	2	-	+	-	+	+
11	50	4	6	1	10	2	-	-	+	-	+
12	20	4	3	0.5	5	2	-	-	-	-	-

F1: amount of sorbent (mg); F2: sample pH; F3: extraction time (min); F4: eluent solvent volume (mL); F5: eluent solvent concentration (M); F6: elution time (min); F7-F11: dummies.

Table S4. Factors, levels and star points of a CCCD.

Factors	Level			Star points (α = 1.68)	
	Low (-1)	Central (0)	High (+1)	- α	+ α
Eluent solvent volume (μL)	500	600	700	432	768
Eluent solvent concentration (M)	6.4	8.4	10.4	5.0	11.8
Sample pH	4.3	6.0	7.7	3.1	8.9

Table S5. Matrix of experiments of CCCD with 3 factors (N=20 experiments) used for optimization step.

Run	Sample pH	Eluent solvent volume (µL)	Eluent solvent concentration (M)
1	4.3	500	6.4
2	7.7	700	6.4
3	4.3	700	6.4
4	7.7	500	6.4
5	4.3	500	10.4
6	7.7	700	10.4
7	4.3	700	10.4
8	7.7	600	10.4
9	3.1	600	8.4
10	8.9	432	8.4
11	6.0	768	8.4
12	6.0	600	8.4
13	6.0	600	5.0
14	6.0	600	11.8
15	6.0	600	8.4
16	6.0	600	8.4
17	6.0	600	8.4
18	6.0	600	8.4
19	6.0	600	8.4
20	6.0	600	8.4

85

86 **Table S6.** Optimum extraction conditions for each analyte.

Emission Lines (nm)	Eluent solvent volume (µL)	Eluent solvent concentration (M)	Sample pH
Cd II (228.802)	432	7.3	6.2
Hg II (194.164)	432	11.8	4.0
Pb II (220.253)	432	8.4	3.1

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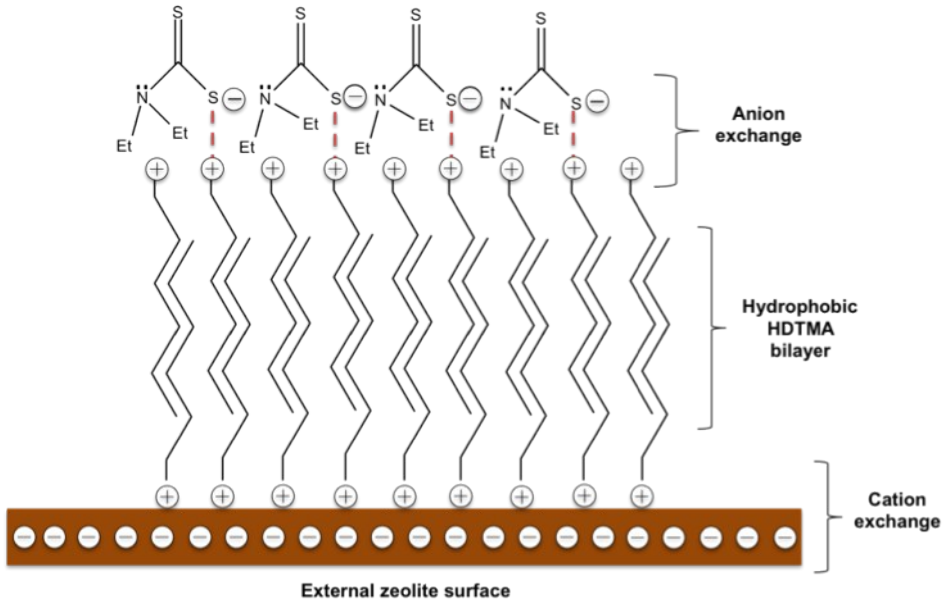
(a)



(b)

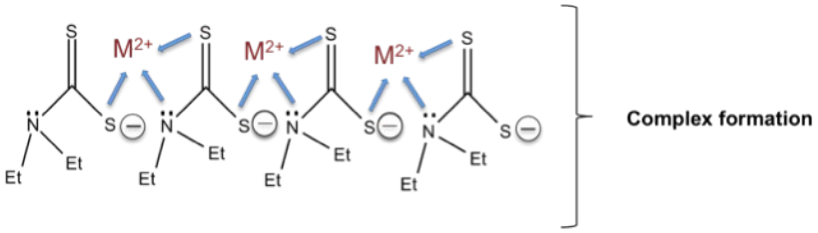


Fig. S1. Scheme of zeolite surface modified by HDTMABr surfactant and DDTC chelating agent (a) adapted from [29] and complex formation of DDTC with M^{2+} cations (b).

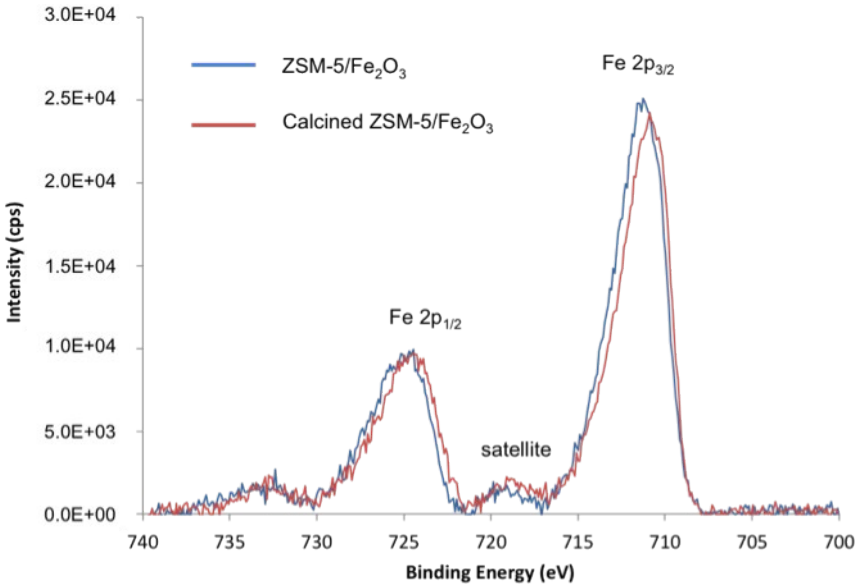
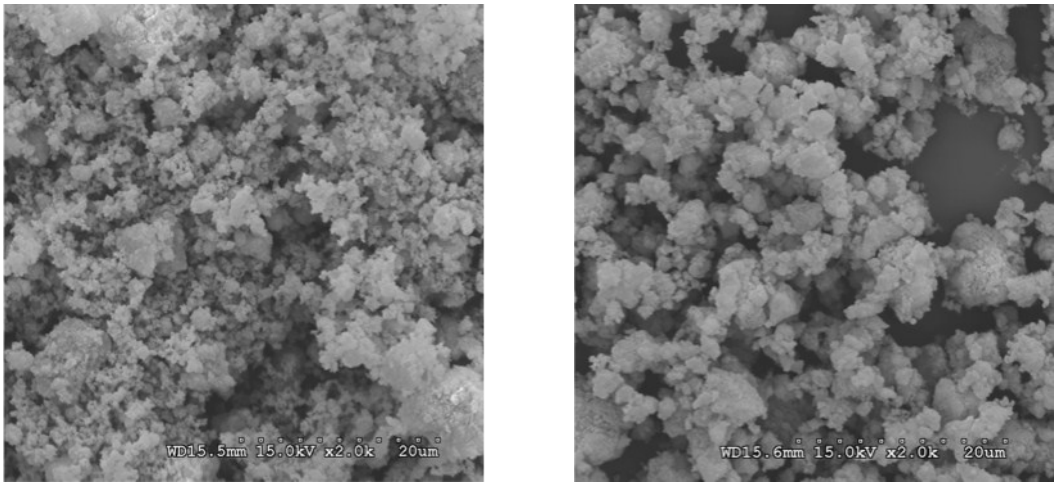


Fig. S2. High resolution XPS spectra in the Fe 2p region for ZSM-5/ Fe_2O_3 and calcined ZSM-5/ Fe_2O_3.

(a) (b)



(c) (d)

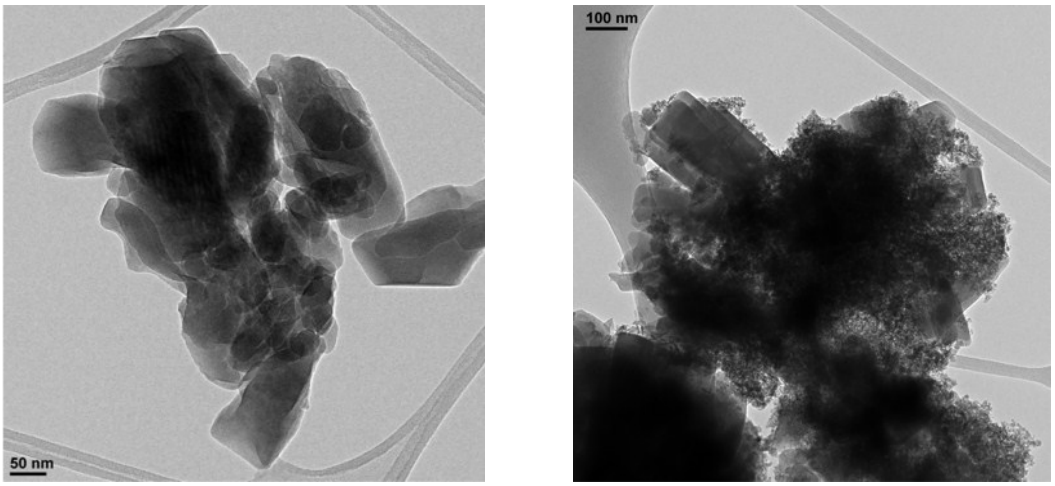
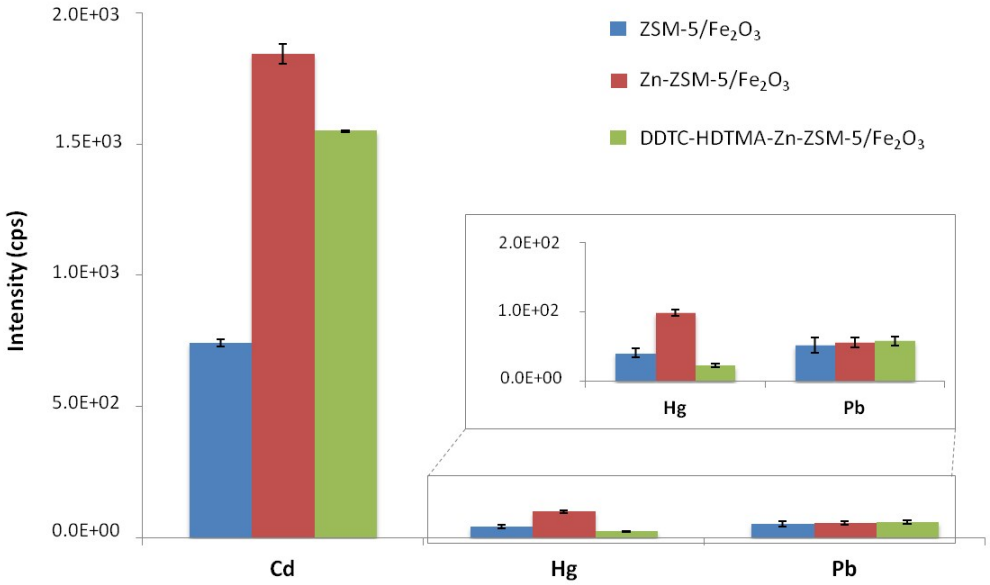


Fig. S3. SEM images of ZSM-5 (a) and DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 (b) composites and TEM images of ZSM-5 (c) and DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 (d) composites.

131 (a)



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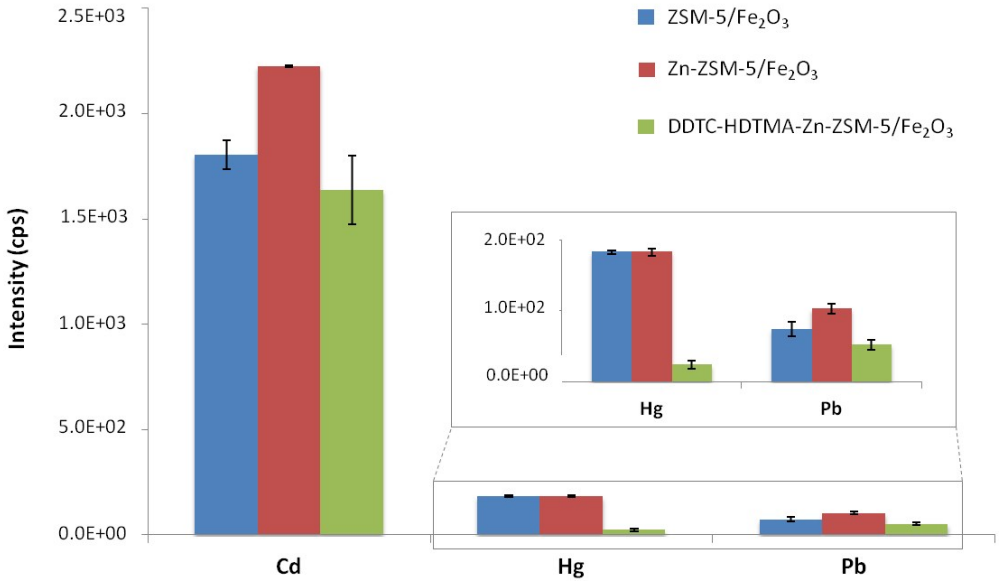
133 (b)



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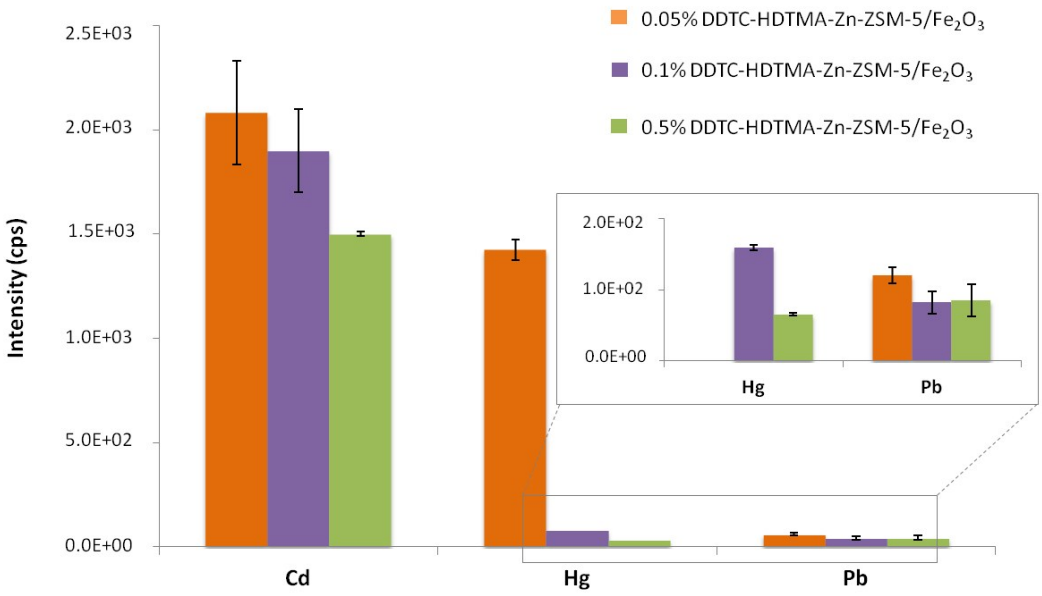
135 **Fig. S4.** Supernatant signal of different modified ZSM-5/Fe_2O_3 composites in
136 aqueous standard (a) and in a urine sample (b) spiked with 50 μg L^{-1} of Cd, Hg
137 and Pb, respectively. The error bars are the standard deviation of three
138 replicates.



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140 **Fig. S5**. Supernatant signal of DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 composite
141 evaluated at three different DDTC concentrations (0.05, 0.1 and 0.5 % (w/v)) in
142 urine. The error bars are the standard deviation of three replicates.

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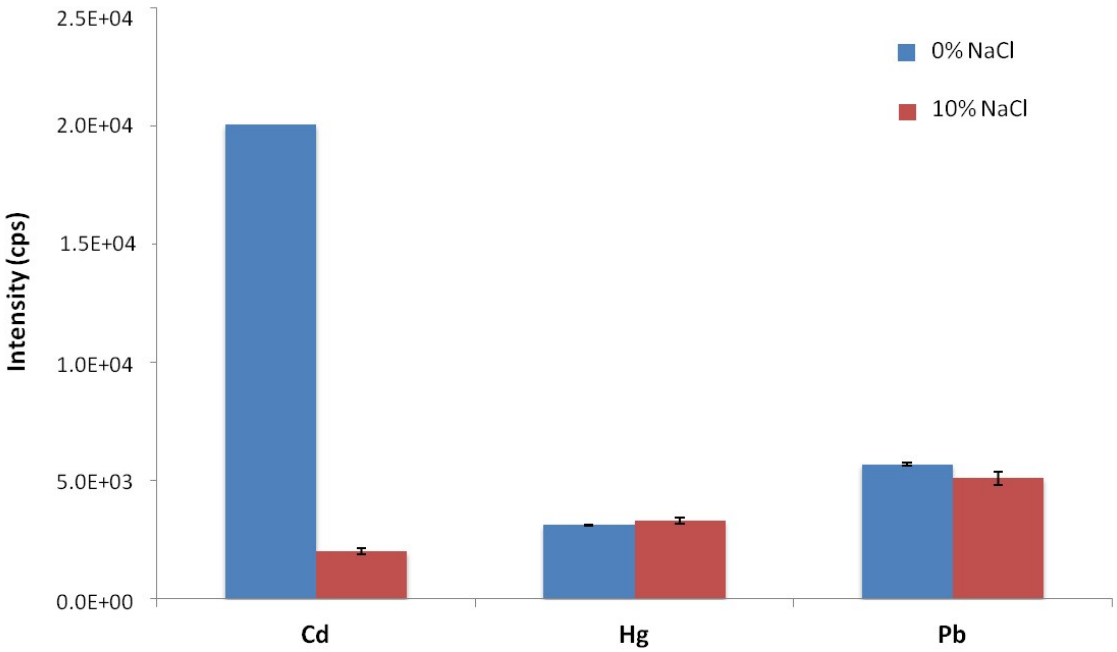


Fig. S6. Effect of ionic strength on the extraction efficiency of DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 composite in aqueous standard spiked with 50 µg L^{-1} of Cd, Hg and Pb, respectively. The error bars are the standard deviation of three replicates.

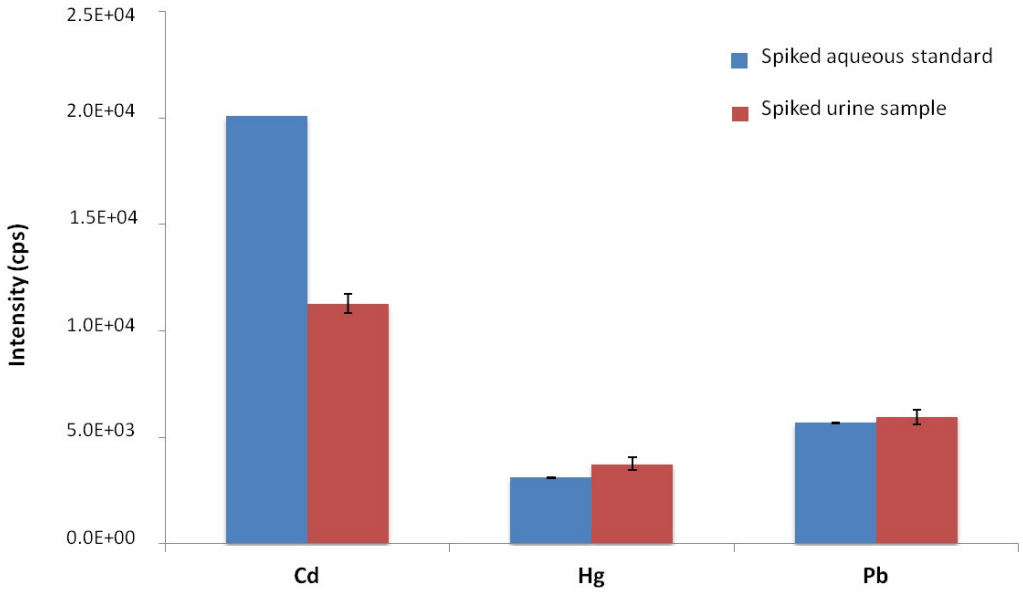
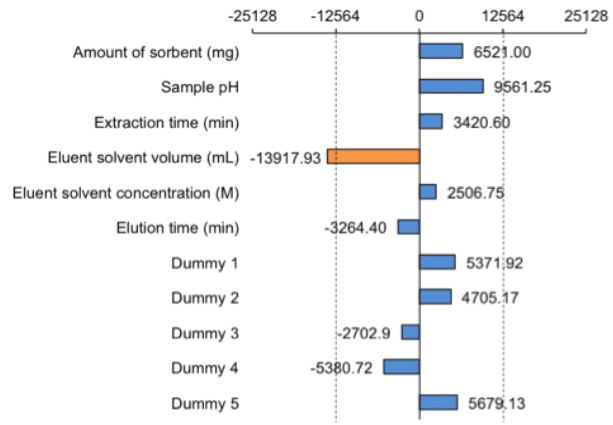
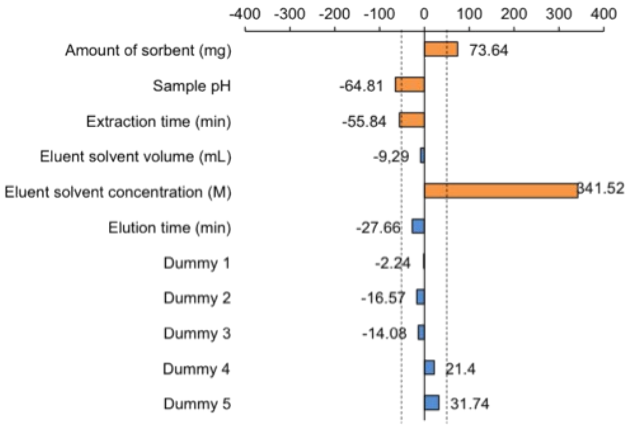


Fig. S7. Extraction efficiency of DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 composite both in aqueous standard (blue) and in urine sample (red) spiked with 50 µg L^{-1} of Cd, Hg and Pb. In aqueous standard, the error bars are the standard deviation of three replicates. In spiked urine sample the error bars are the standard deviation of three urine samples.

(a)



(b)



(c)

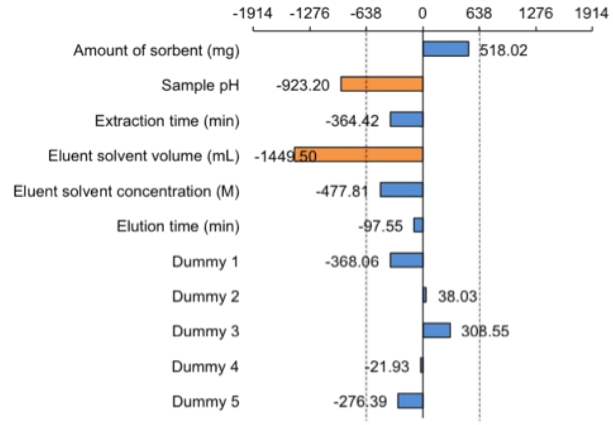
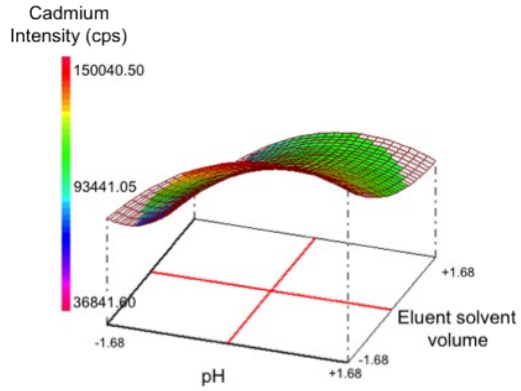
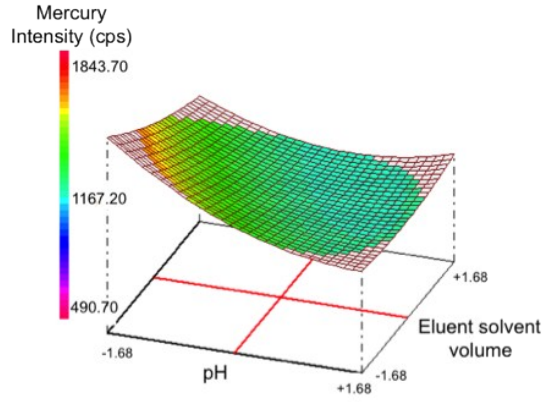


Fig. S8. Pareto charts of Plackett-Burman design for: (a) Cd; (b) Hg; and (c) Pb.

(a)



(b)



(c)

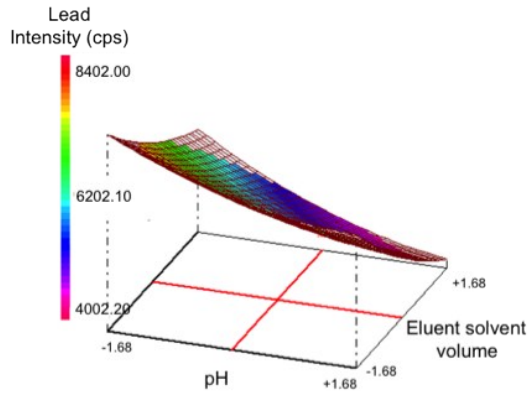
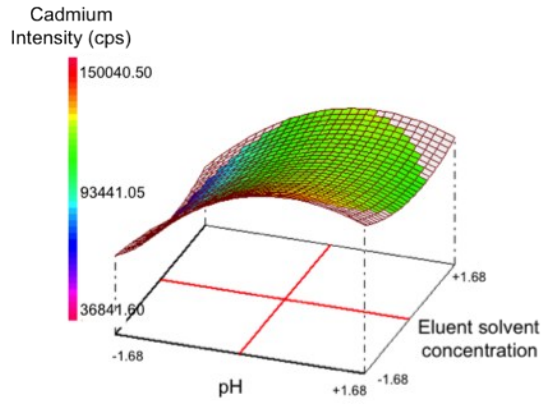


Fig. S9. Response surfaces of CCCD obtained by plotting the sample pH vs. eluent solvent volume, keeping the eluent solvent concentration at the optimum value for: (a) Cd (7.3 M), (b) Hg (11.8 M) and (c) Pb (8.4 M). The optimum value for the eluent solvent concentration for each analyte is in parenthesis.

198 (a)



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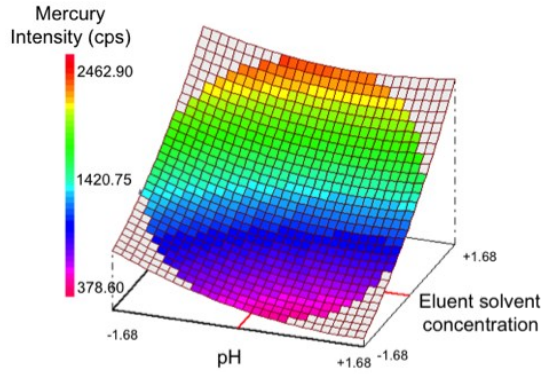
200 (b)



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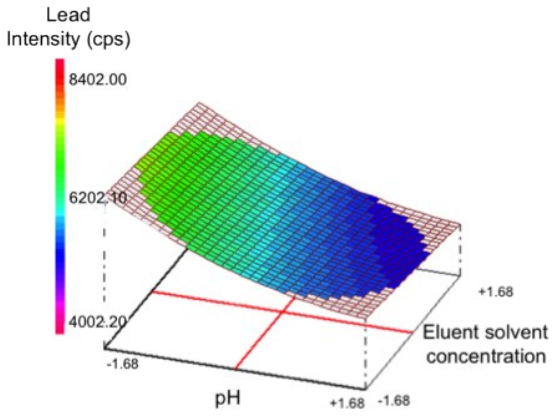
202 (c)



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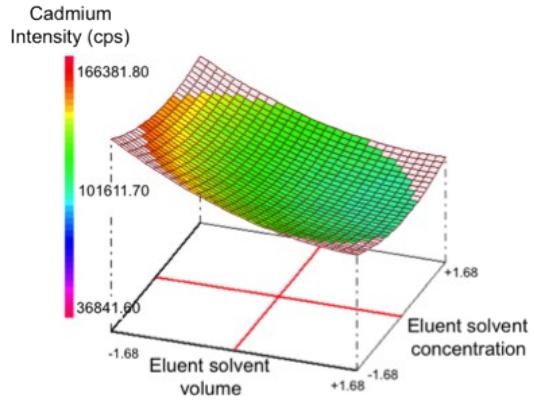
205 **Fig. S10.** Response surfaces of CCCD obtained by plotting sample pH vs.
206 eluent solvent concentration, keeping the eluent solvent volume at the optimum
207 value: 432 µL for: (a) Cd, (b) Hg and (c) Pb.

208 (a)



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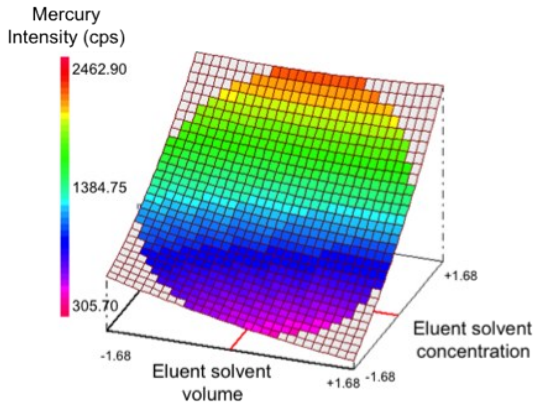
210 (b)



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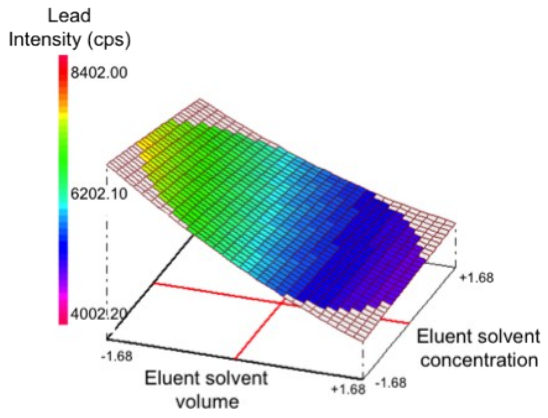
212 (c)



213

214 **Fig. S11.** Response surfaces of CCCD obtained by plotting eluent solvent
215 volume vs. eluent solvent concentration, keeping the sample pH at the optimum
216 value for: (a) Cd (6.2), (b) Hg (4.0) and (c) Pb (3.1). The optimum value for the
217 sample pH for each analyte is in parenthesis.

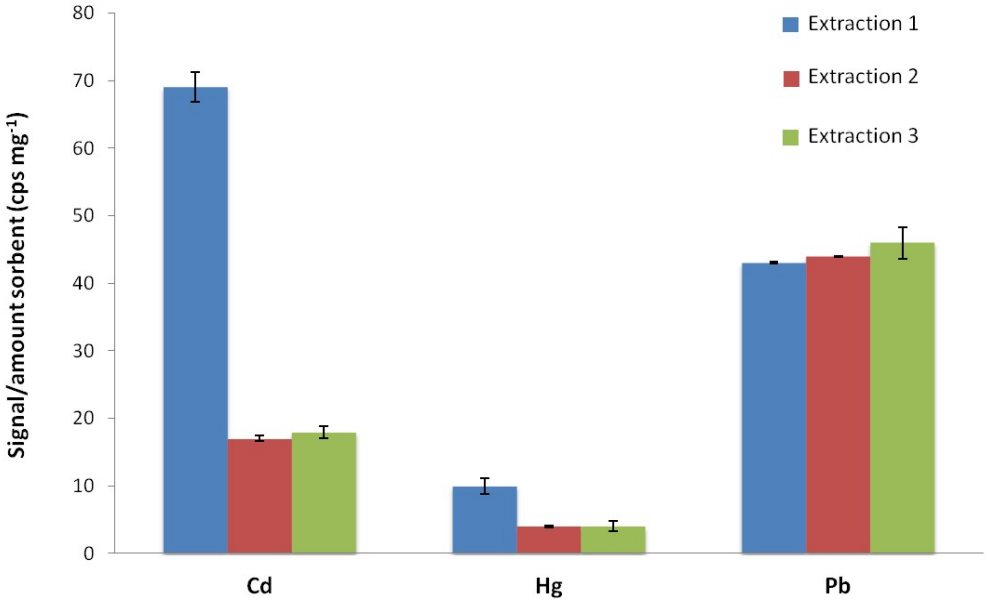


Fig. S12. Study of sorbent reutilization using the same DDTC-HDTMA-Zn-ZSM-5/Fe_2O_3 composite in three consecutives extractions. The error bars are the standard deviation of three replicates.