Extraction and preconcentration of Ni(II), Pb(II), and Cd(II) ions using a nanocomposite of the type Fe_3O_4@SiO_2@polypyrrole-polyaniline

Ali Akbar Asgharinezhad[*,a], Mohsen Esmaeilpour[a], Asal Yousefi Siavoshani[b]

[a] *Chemistry and Process Research Department, Niroo Research Institute, Tehran, Iran*

[b] *School of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH, USA*

* Corresponding author. Fax: +98 21 88078296; Tel: +98 21 88079400

E-mail: aasgharinezhad@nri.ac.ir (A.A. Asgharinezhad)

Instrumentation

An AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer with a deuterium background corrector was used for the determination of Cd(II), Pb(II) and Ni(II) ions. Cadmium, lead and nickel hollow cathode lamps (HCL) were used as the radiation sources with wavelengths of 228.8, 283.3 and 232.0 nm, respectively. All measurements were carried out in an air/acetylene flame. The pH of the solutions were measured at 25 ± 1 ℃ with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. CHN analysis was performed by a Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK, www.thermoscientific.com). IR spectra were recorded by a Bruker IFS-66 FT-IR Spectrophotometer (Karlsruhe, Germany, www.brukeroptics.com). Transmission electron microscopy (TEM) analyses were performed by a ZEISS EM90 electron microscope (ZEISS, Jena, Germany, www.zeiss.com) operating at 80 kV. Thermogravimetry analysis (TGA) was accomplished on a Bahr STA-503 instrument under air atmosphere. Magnetic properties of nanocomposites were measured by a vibrating sample magnetometer (VSM) (AGFM/VSM 117 3886 Kashan, Iran) at room temperature in a magnetic field strength of 1 Tesla. Dynamic light scattering (DLS) measurements were carried out with a Malvern Zetasizer Nano ZS using Dispersion Technology (United Kingdom, www.malvern.com).

Real sample pretreatment

Fish and shrimp samples

Fish samples were collected from Caspian Sea, Siahroud River (Gilan Province in the North of Iran) and two different sites in the Northwest of the Persian Gulf (in the south of Iran), The

shrimps and canned tuna were purchased from local supermarkets in Tehran, Iran. The river fish was collected from Siahroud River The fish and shrimp samples were placed in ice, transferred to the laboratory and stored at -20 °C prior to analysis. The fish samples and shrimp were dissected with a clean plastic knife and a part of the muscle was taken out quickly. The fish (platycephalus indicus) and shrimp samples were dissected with a clean plastic knife and a part of the muscle was taken out quickly. Then it was dried in an oven at 70 °C for 48 h. Analysis were accomplished according to the procedure reported by Yilmaz (2003) [35]. A porcelain mortar was used to grind dried tissues. 0.5 g of each sample was digested with 5 mL of concentrated HNO_3 in Teflon beakers for 4 h at 100°C. The content was filtered into a 25 mL standard volumetric flask and was diluted up to 25 mL with double distillated water. Sediment samples were collected using a Peterson grab sampler, stored in a plastic bag in ice, transferred to the laboratory and kept at -20 °C before analysis. One gram of these samples was digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then venting for 8 min. The residue resulted from the digestion was then diluted to 100 mL with double distilled water.

Agricultural Products

The agricultural products including broccoli, apple, lettuce, and mushroom were collected from Tehran growing areas (Shahriyar-Tehran). To supply the samples according to their type, cleaned polyethylene bags were applied. After washing samples with distilled water, they were dried at 100 °C for 2 days. For spiked samples preparation, 1.0 mL of the standard working solution was used to 1.0 g of each sample. For the evaporation of the solvent they were stand at room

temperature; therefore, the equilibration between the analytes and the agricultural products was achieved. After grinding the dry samples (spiked or non-spiked), microwave-assisted acid digestion was carried out by adding 2 mL of distilled water, 4 mL of nitric acid 65%, and 2 mL of hydrogen peroxide 33% (w/v) to 0.5 g of each sample. The reactors were then subjected to the microwave program (2.5 min at room temperature, 6 min at 140 °C, 5 min at 200 °C in power of 550 W) [35]. After acid digestion was completed, the acid digests were diluted up to 25 mL with distilled water and kept in a refrigerator before magnetic solid phase extraction.

Reference material

The concentration of Cd(II), Pb(II) and Ni(II) ions was determined at optimum conditions in a standard reference material (Sea food mix 02-2932). The standard material was digested according to the mentioned procedure for fish and blank digestion. The pH of the solution was adjusted to 6.2 for the separation and preconcentration of Cd(II), Pb(II) and Ni(II) ions form the solution. Ultimately, the preconcentration procedure mentioned above was applied to the resulted solutions.

Sorption step

The optimization step for the uptake of metal ions on the magnetic nanosorbent was carried out using Box-Behnken design (BBD). Variables affecting the extraction efficiency were chosen to be: pH, amount of the magnetic nanosorbent, and extraction time. Other parameters involved in the extraction were kept constant, particularly the concentration of heavy metal ions (0.5 mg L^{-1}). This design permitted the responses to be modeled by a second-order polynomial, which can be expressed as the following equation:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3$$

$$+ \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_{13}^2$$

where, x_1, x_2, and x_3 are the independent variables, β_0 is an intercept, β_1- β_{33} are the regression coefficients, and Y is the response (removal% or recovery%). The number of experiments (N) is then defined by the expression below:

$$N = 2K\,(K-1) + C_o$$

where K is the number of variables and C_o is the number of center points [32]. In this study, K and C_o were both set at 3, which meant that 15 experiments had to be done. The levels of each factor are listed in Table 1. The results of the analysis of variance (ANOVA) produced the Pareto chart of main and interaction effects which is shown in Fig. 3a. The standard effect was estimated for computing the t-statistic for each effect. The vertical line on the plot shows statistically significant effects. The bar extracting beyond the line corresponds to the effects that are statistically significant at 95% confidence level [30, 32]. Furthermore, the positive or negative sign (corresponding to a colored or colorless response) can enhance or reduce the extraction efficiency, respectively, while increasing from the lowest to the highest level set for that specific factor. According to the Pareto chart the pH of the solution causes the most significant positive effect on the extraction efficiency. The uptake of heavy metal ions increases as the pH value increases. In less acidic solutions, the uptake is quite low. This observation is due to the protonation of the magnetic nanosorbent active sites, especially the N atoms of PPy-PANI copolymer. As the pH increases, the protonation of these active sites decreases and the condition becomes more favorable for complex formation and sorption of the heavy metal ions to

the magnetic nanosorbent. At pH > 6.2 the extraction efficiencies of heavy metal ions decreased due to the formation of insoluble hydroxide forms of metals. To avoid the precipitation of metal ions at higher pH values, pH 6.4 was selected as optimum. The response surface methodology (RSM) (Fig. 3b) was applied to analysis simultaneous effects of the uptake time and pH value on the response plot that displayed the interaction between these independent variables. The sorption efficiency of target metal ions increased along with the increase in pH. Moreover, the extraction time and the sorbent amount both showed positive effect on the extraction efficiency and were the second and third important factors, respectively. According to the overall results of the optimization study, the following experimental conditions were chosen: pH, 6.2; extraction time, 9.0 min; amount of the magnetic sorbent, 10 mg.

Selection of eluent

In this work several acidic eluents including HCl, HNO_3, H_2SO_4 and $HClO_4$ solutions were examined as the elution solvent. Other factors were kept constant during the optimization (pH, 6.2; extraction time, 9.0 min; the magnetic sorbent amount, 10 mg; eluent volume, 5 mL; elution time, 15 min). Results showed that HNO_3 can recover the target metal ions. In the next step the effect of HNO_3 volume and concentration were optimized.

Elution step

Three factors were studied in the elution step using experimental design: eluent volume (mL), elution time (min), and eluent concentration (mol L^{-1}). In this condition, a response surface design is accomplished without previously performing a screening design. The BBD was chosen because it requires the least number of experiments (15 run). The data obtained were evaluated

by ANOVA. The results of the experimental design were evaluated at 5% of significance and analyzed by standardized Pareto chart (Fig. 4a). Based on BBD, both the concentration and volume of the eluent showed positive and significant effect on the recovery of the target metal ions while elution time has a positive but non-significant effect. These observations are most possibly due to increased protonation of the hetero atoms of the sorbent as the concentration of the eluent increases and also fast kinetics of elution process is of great importance. As Fig. 4a shows, eluent volume has the greatest influence on the extraction recovery. The RSM (Fig. 4b) was applied to analyze simultaneous effects of the elution time and eluent concentration on the responses. The extraction efficiency of target ions increased along with an increase in the eluent concentration and also elution time. According to the overall results of the optimization study, the following experimental conditions were chosen as the optimized ones: eluent volume, 5.4 mL; elution time, 11.5 min; and eluent concentration, 1.7 mol L^{-1} HNO$_3$ solution.

Table1S
Experimental variables and levels of the Box Behnken design (BBD).

		Level		
		Lower	Central	Upper
	A: pH	3.5	5.5	7.5
Sorption step	B: Uptake time (min)	5.0	10	15
	C: Nanosorbent amount (mg)	5.0	10	15
	A: Eluent concentration (mol L^{-1})	0.5	1.25	2.0
Elution step	B: Eluent volume (mL)	2.0	4.5	7.0
	C: Elution time (min)	2.0	8.5	15

Table 2S
The tolerance limit of various ions on the determination of Cd(II), Pb(II) and Ni(II) ions.

Potentially interfering ion	Tolerable Concentration Ratio X/ Cd, Pb, Ni	R^a (%) $\pm$ S^b		
		Pb(II)	Cd(II)	Ni(II)
K^+	10000	98.5 ± 1.5	99.0 ± 1.5	97.4 ± 2.4
Na^+	10000	99.0 ± 2.9	98.0 ± 2.2	99.6 ± 3.6
Ca^{2+}	1000	97.8 ± 1.4	96.3 ± 1.8	98.6 ± 2.0
Mg^{+2}	1000	98.6 ± 3.5	95.9 ± 1.6	97.1 ± 3.1
Al^{3+}	1000	96.6 ± 2.8	97.6 ± 2.5	98.3 ± 1.8
Co^{2+}	500	95.4 ± 1.8	96.7 ± 3.6	98.5 ± 2.0
Fe^{3+}	500	94.8 ± 2.7	95.5 ± 2.6	97.5 ± 2.8
Cr^{3+}	500	97.5 ± 3.1	95.3 ± 2.8	95.0 ± 1.9
Sn^{2+}	500	95.5 ± 2.4	93.2 ± 1.5	97.3 ± 1.4
Zn^{2+}	500	94.6 ± 1.6	95.9 ± 3.1	94.8 ± 2.5
Mn^{2+}	400	96.9 ± 2.0	95.1 ± 2.4	96.6 ± 2.1
Cu^{2+}	250	95.3 ± 2.3	96.7 ± 2.6	95.4 ± 2.8
Hg^{2+}	150	96.3 ± 1.9	98.3 ± 3.5	94.8 ± 1.7
CrO_4^{2-}	1000	97.2 ± 2.6	99.0 ± 2.6	99.2 ± 1.6
PO_4^{3-}	1000	98.0 ± 3.1	97.5 ± 2.7	98.7 ± 3.0

[a] Recovery
[b] Relative standard deviation (n = 3)
Conditions: sample pH = 6.2, sample volume = 100 mL, 0.01 mg of Cd(II), Pb(II) and Ni(II) ions, sorption time = 9.0 min; eluent = 5.4 mL, 1.7 mol L^{-1} HNO$_3$ solution, elution time = 11.5 min.
X: Concentration of potentially interfering ions.

Table 3S

Comparison the performance of $Fe_3O_4@SiO_2@$polypyrrole-polyaniline with the other sorbents.

Method	Instrument	LOD (ng mL^{-1})	Sorption capacity (mg g^{-1})	PF[a]	RSD (%)	Ref.
$Fe_3O_4@SiO_2@$polypyrrole-polyaniline	FAAS	0.09-1.1	75-98	185	< 7.5	This work
Decanoic acid-coated Fe_3O_4 nanoparticles	ICP-OES	0.3-0.8	-	118-136	< 8.2	[1]
$Fe_3O_4@$2-aminibenzothiazole nanosorbent	FAAS	0.009-0.1	49-78	277	< 8.4	[2]
Magnetic multiwalled carbon nanotube composite	FAAS	0.09-1.0	150-201	181	< 5.1	[3]
$Fe_3O_4@$ 4-(2-pyridylazo) resorcinol	FAAS	0.07-0.7	78-92	250	< 7.0	[4]

[a] Preconcentration factor.

Fig. 1S: Particle size distribution curve of (a) Fe_3O_4 nanoparticles, and (b) $Fe_3O_4@SiO_2@PANI$-PPy NPs.
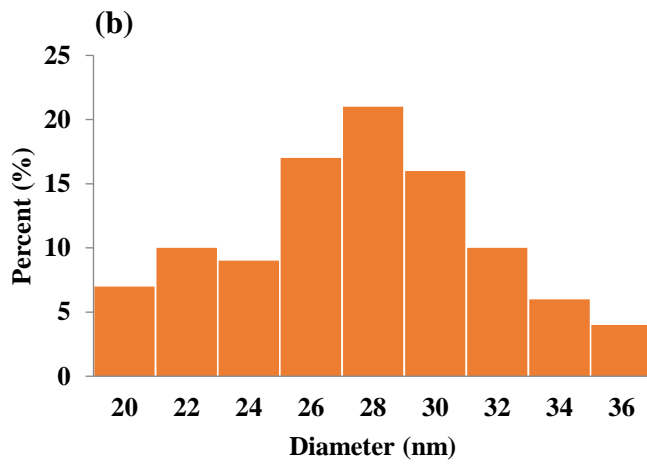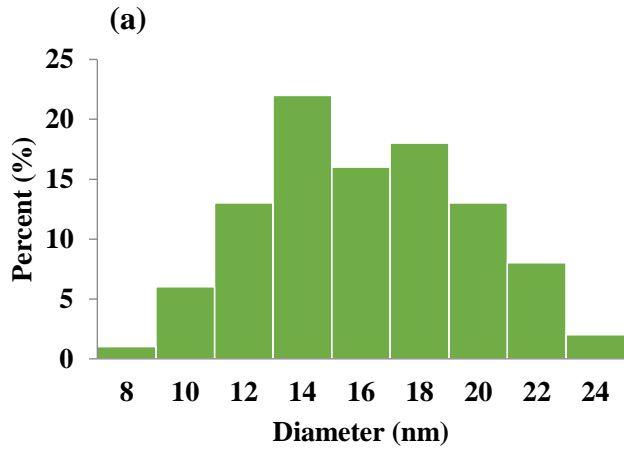
Fig. 2S: DLS profile of size distributions of $Fe_3O_4@SiO_2@PANI-PPy$ NPs.
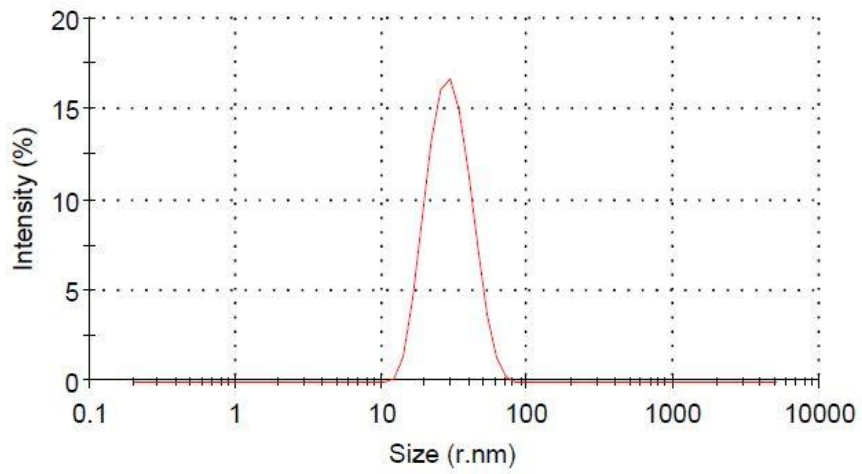
Fig. 2S: (a) Pareto chart of the main effects in the BBD (sorption step). AA, BB and CC are the quadratic effects of pH, the uptake time and the amount of the magnetic sorbent, respectively. AB, AC and BC are the interaction effects between pH and the uptake time; pH and the amount of sorbent and the uptake time and the amount of magnetic sorbent, respectively. (b) RSM obtained by plotting pH *vs.* uptake time using the BBD.

(a) Standardized Pareto Chart for Removal%

(b) Estimated Response Surface
Nanosorbent amount=10.0
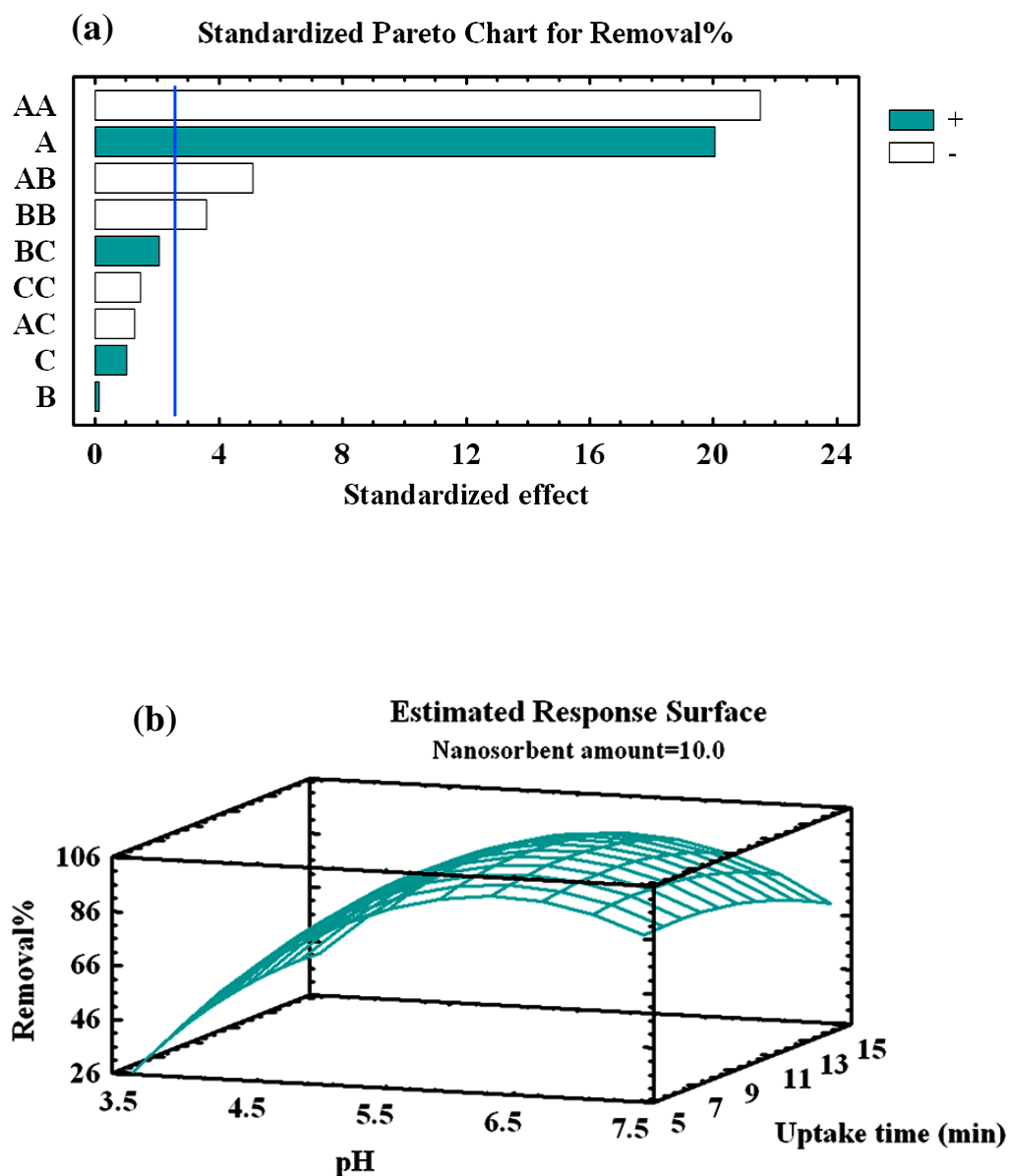
Fig. 3S: (a) Pareto chart of the main effects in the BBD (elution step). AA, BB and CC are the quadratic effects of the eluent concentration, eluent volume and elution time, respectively. AB, AC and BC are the interaction effects between eluent concentration and eluent volume; eluent concentration and elution time; and eluent volume and elution time, respectively. (b) RSM obtained by plotting eluent concentration *vs.* elution time.
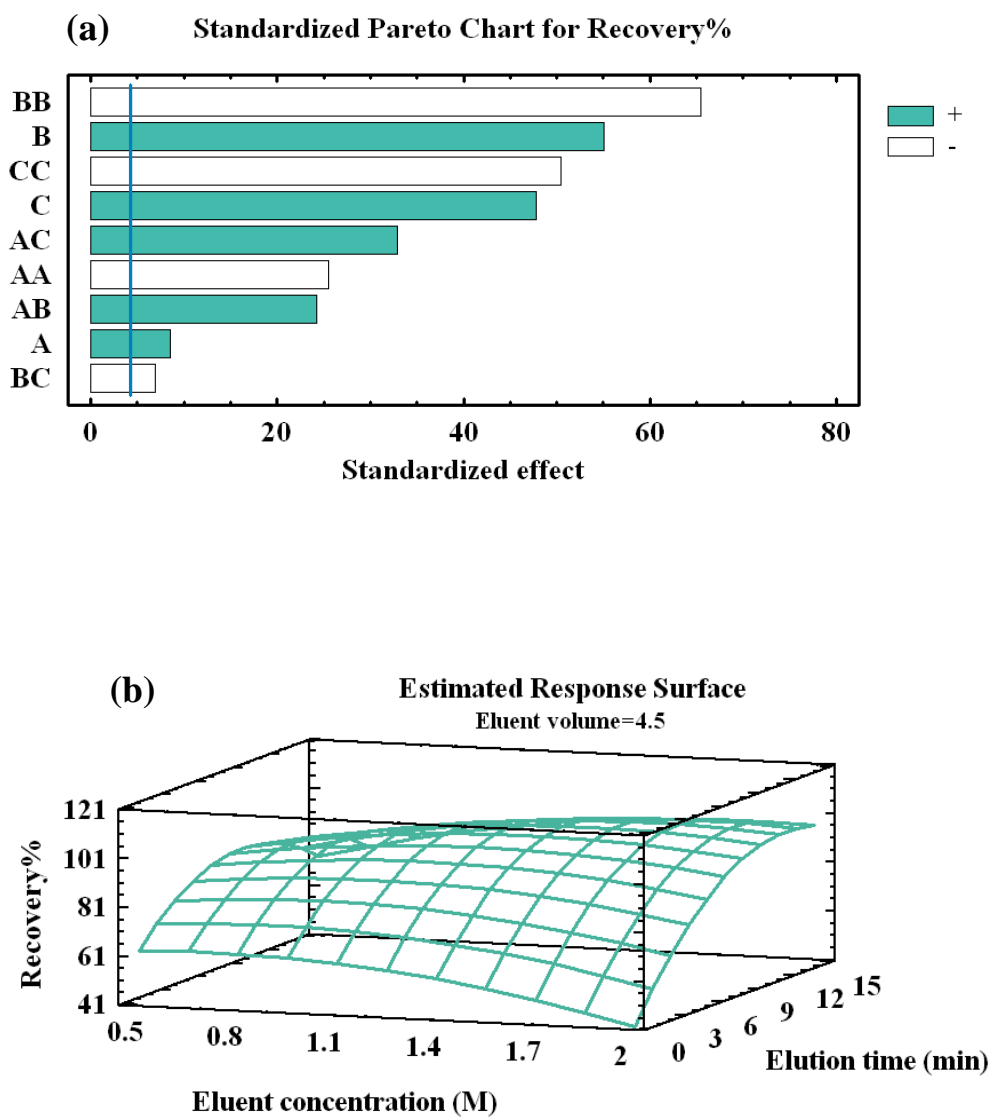
References:

[1] M. Faraji, Y. Yamini, A. Saleh, M. Rezaee, M. Ghambarian, R. Hassani, 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, Analytica Chimica Acta 659 (2010) 172-177.

[2] H. Bagheri, A.A. Asgharinezhad, H. Ebrahimzadeh, Determination of trace amounts of Cd(II), Cu(II), and Ni(II) in food samples using a novel functionalized magnetic nanosorbent, Food Analytical Methods 9 (2016) 876-888.

[3] M. Taghizadeh, A.A. Asgharinezhad, N. Samkhaniany, A. Tadjarodi, A. Abbaszadeh, M. Pooladi, Solid phase extraction of heavy metal ions based on a novel functionalized magnetic multi-walled carbon nanotube composite with the aid of experimental design methodology, Microchimica Acta 181 (2014) 597-605.

[4] A.A. Asgharinezhad, H. Ebrahimzadeh, M. Rezvani, N. Shekari, M. Loni, A novel 4-(2-pyridylazo) resorcinol functionalized magnetic nanosorbent for selective extraction of Cu(II) and Pb(II) ions from food and water samples, Food Additive Contaminants: Part A 31 (2014) 1196-1204.