



Determination and preconcentration of trace amounts of Cd(II), Cu(II), Ni(II), Zn(II), and Pb(II) ions by functionalized magnetic nanosorbent and optimization using a Box-Behnken design and detection of them by a flame atomic absorption spectrometer

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 Lead(II);
 Box-Behnken design.

Abstract. In this work, Fe₃O₄@SiO₂ core-shell nanoparticles functionalized with 2-mercaptobenzothiazole as a magnetic nanosorbent were utilized to simultaneously extract trace amounts of cadmium(II), copper(II), nickel(II), zinc(II), and lead(II) ions. A Box-Behnken design was applied with several variables to optimize the extraction and elution steps. In the selected conditions, it was observed that limits of detection included 0.14 ng mL⁻¹ for Cd(II), 0.24 ng mL⁻¹ for Cu(II), 0.30 ng mL⁻¹ for Ni(II), 0.27 ng mL⁻¹ for Zn(II) and 0.53 ng mL⁻¹ for Pb(II); the maximum sorption capacity rates of this suggested magnetic nanosorbent were 168, 138, 104, 120, and 220 mg g⁻¹ for Cd(II), Cu(II), Ni(II), Zn(II), and Pb(II), respectively. Finally, the suggested procedure was applied to determine target metal ions at trace levels in different water samples, sugar, edible salts, and various vegetables (lettuce, broccoli, and tomato) samples with satisfactory results.

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1. Introduction

In recent years, the application of nanoparticle materials, especially magnetic nanoparticles as sorbents, has aroused a great deal of attention in analytical chemistry [1-3]. In contrast, iron oxide nano-particles are suitable particles due to their important properties, such as the high surface area to volume ratio, nano-size range, and super-magnetism; they are highly desirable

in water treatments due to the aforementioned properties [4]. Silica is one of the ideal compositions to be applied as shell because silica surface with silanol groups can react with silane coupling in order to combine a variety of different ligands. Silica shell protects Fe₃O₄ NPs in acidic medium, which is necessary for elution of most metal ions [5]. Determining heavy metal pollutants at trace levels for monitoring environmental pollution is very critical. Heavy metals at higher concentrations can be dangerous and accumulated in living tissues, causing various diseases and disorders [6-8].

Over the last few decades, the pollution of water resources has kindled global concern due to the indiscriminate disposal of heavy metals [9]. Among existing heavy metals in the environment, copper ions are essential trace elements with an important role in

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many body functions. A number of separation methods for determining trace metal have gained high attention, and these methods include homogeneous liquid-liquid extraction [10,11], liquid-liquid extraction [12], ion exchange [13], and Solid Phase Extraction (SPE) [14]. SPE procedure is superior to other procedures due to its rapidity, simplicity, low cost, flexibility, high preconcentration factor, its use in combination with different detection techniques in on- or off-line modes, consumption of low organic solvent volume, and short extraction time for sample preparation [15–20].

In this study, for the first time, 2-mercaptobenzothiazole functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanosorbent ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MBT}$) was utilized as a magnetic nanosorbent for separation and preconcentration of trace Cd(II) , Cu(II) , Ni(II) , Zn(II) , and Pb(II) ions from various samples. The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MBT}$ nanosorbent was characterized by several techniques such as Fourier transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-Ray Diffraction (XRD), and thermogravimetric analysis (TGA). Flame atomic absorption spectrometry (AAS) was chosen to monitor the concentration of these target ions. A Box-Behnken design was used to evaluate possible interactions of the method and to determine the optimal conditions for extraction of trace target metal ions.

2. Experimental

2.1. Reagents and materials

All the reagents used in this study (i.e., NaOH , HCl , HNO_3 , CH_3COOH , 2-mercaptobenzothiazole, 3-chloropropyltrimethoxysilane (CPTMS), $\text{Cd(NO}_3)_2$, $\text{Cu(NO}_3)_2$, $\text{Ni(NO}_3)_2$, $\text{Zn(NO}_3)_2$, $\text{Pb(NO}_3)_2$, toluene, and ethanol) were purchased from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland) or Sigma-Aldrich (Steinheim, Germany) without any further purification. Tetraethoxysilane (TEOS), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$,

and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used in magnetic nanoparticles preparation and purchased from Aldrich. All other chemicals were of analytical grade purchased from Aldrich or Fluka.

2.2. Instrumentation

The information about instrumentation was obtained based on the earlier report [22].

2.3. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanosorbent

Magnetic Fe_3O_4 nanoparticles (MNPs) were obtained based on simple chemical coprecipitation of Fe^{2+} and Fe^{3+} ions, as reported elsewhere [21]. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanosorbent was synthesized according to the earlier report [22].

2.4. Functionalization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell NPs

The procedure for functionalizing $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell NPs was performed in two steps as follows. In the first step, 1 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was dispersed in dry toluene (50 mL); then, 2 mL of 3-chloropropyltrimethoxysilane was added to the mixture in one portion and was kept under constant stirring and refluxing at 80°C for 12 h under the nitrogen atmosphere. Afterwards, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$ core-shell NPs were isolated by the strong magnet and washed with water and ethanol several times until any impurities were discarded. The nanoparticles were used in the next step of the experiment after drying under vacuum at 40°C overnight.

In the second step, about 1.0 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$ core-shell NPs were dispersed in 50 mL toluene containing 1.0 g of 2-mercaptobenzothiazole, and the reaction mixture was stirred and refluxed for 24 h in an oil bath at 80°C in the presence of nitrogen. Hereafter, the black solid was successively collected by a strong magnet, washed several times with ethanol to remove excess unreacted materials, and dried under vacuum at 40°C overnight (Figure 1).

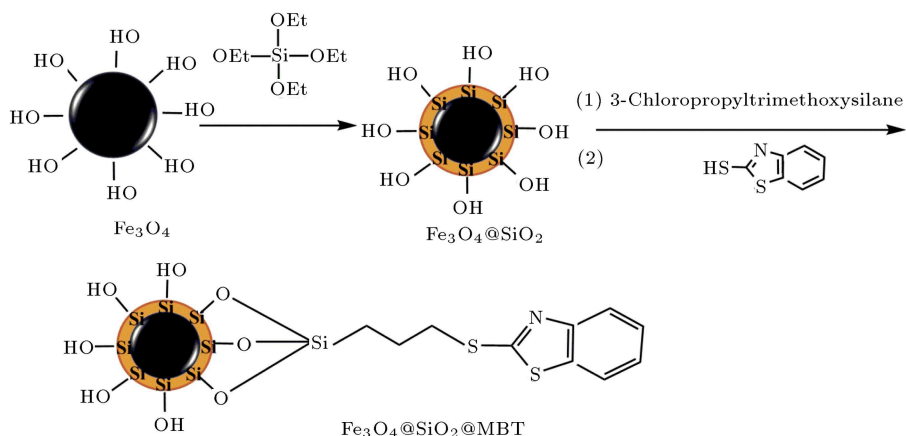


Figure 1. A schematic diagram of the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ modified with 2-mercaptobenzothiazole.

2.5. Determining the point of zero charge

In this work, the degassed 0.01 mol L^{-1} NaNO_3 solution at 20°C was used for determining the pHPZC of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$. In several beakers, 10 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanosorbent was dispersed in 10 mL of 0.01 mol L^{-1} NaNO_3 aqueous solution. The pH of the solutions was adjusted at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 using HNO_3 and/or NaOH solutions as proper. The initial pH values of the solutions were recorded, and the beakers were covered with a piece of Parafilm and shaken for 24 h. The final pH values were measured by pH meter, and the differences between the initial and final pHs (ΔpH) of the solutions were plotted against their initial pH values. The pHPZC corresponds to the pH, where $\Delta\text{pH} = 0$.

2.6. Extraction procedure

For the extraction procedure in the batch mode analysis, 8.7 mg of the suggested magnetic nanosorbent was added to 10 mL of solution containing 0.5 mg L^{-1} of target ions under controlled pH (The solution pH was adjusted by dilute NaOH or HCl (0.1 mol L^{-1}) to desired value). The mixture was stirred by a magnetic stirrer for about 6 min to ensure sufficient interaction between $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ NPs nanocomposites and heavy metals. After removing $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ NPs containing target ions from the solution rapidly using an external magnetic field, the concentrations of the metal ions in supernatant were directly determined by FAAS. In the elution step, 4.3 mL of 0.62 mol L^{-1} HCl solution was used to elute the metal ions adsorbed on the magnetic nanosorbent. Extraction percentage of each ion was calculated through the following equation:

$$\% \text{Extraction} = (C_A - C_B) / C_A \times 100,$$

where C_A and C_B are the initial and final concentrations (mg L^{-1}) of each ion in the solution, respectively.

2.6.1. Effect of metal ion concentration

Batch adsorption experiments were carried out by contacting 8.7 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ with 10 mL of metal ions solution of different initial concentrations (0.2 to 1 mg/L) at a pH value of 6.7 at temperature room. For all the metals, the extraction efficiency was found to be higher at the initial concentration of 0.5 mg/L ; in addition, the reduction of adsorption was observed when concentration increased from 0.5 to 1 mg/L . This is the reason why, at higher concentrations, as more ions are competing for the available binding sites, the rate of adsorption decreases, resulting in lower adsorption percentage.

2.7. Real sample preparation

2.7.1. Water samples

To analyze water samples, the laboratory water and distilled water samples were selected; pH of 50 mL of

each sample was adjusted to 6.7, and their target ions content was determined by the suggested extraction method.

2.7.2. Samples of sugar and edible salts

Samples of sugar and edible salts were prepared and, then, ground and sieved; then, 0.2 g of each sample was dissolved in 10.0 mL $\text{HNO}_3/\text{HClO}_4$ solution (4:1 v/v) and transferred to a volumetric flask; their volume reached 50 mL with distilled water. Then, pH of samples was adjusted to the desired amount; then, the suggested procedure was applied to analyze cadmium(II), copper(II), nickel(II), zinc(II), and lead(II) ions content of samples of the sugar and edible salts [23].

2.7.3. Vegetable samples

Three vegetable samples, including lettuce, broccoli, and tomato, were chosen as real samples from Tehran's growing areas (Shahriyar); then, 0.5 g of every sample was dried at 80°C and powdered. After sieving, sizes less than $20 \mu\text{m}$ were dissolved in 10 mL of 3 mol L^{-1} HNO_3 solution, and their volume reached 50 mL by adding distilled water [24]. After adjusting the pH at 6.7, the procedure was done in optimal conditions.

3. Results and discussion

3.1. Magnetic nanosorbents' characterization

3.1.1. Characterization by FT-IR

FT-IR spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites were recorded using the KBr pellet method. In the FT-IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, the peaks at 1089 and 798 cm^{-1} attributed to Si-O-Si and Fe-O-Si stretching vibrations. These results showed the Silica was coated on the surfaces of Fe_3O_4 nanoparticles.

For $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$, the stretching vibration peak in the area of 1398 represents a Si-C group in the magnetic nanocomposite structure, and the adsorption peak at 700 cm^{-1} (C-Cl) confirms the existence of CPTMS on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs. In FT-IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposite, $\text{CH}_2\text{-S}$ bond vibration at 1404 cm^{-1} and C=N bond vibration at 1647 cm^{-1} confirmed the modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with 2-mercaptobenzothiazole (Figure 2).

3.1.2. SEM and EDS characterization

To show the microstructure and morphology of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ NPs, SEM image was used. As depicted in Figure 3, these nanoparticles have a well-dispersed spherical structure and nanometer size. The average size of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanoparticles is about 45 nm . EDS spectra taken from $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites are presented in Figure 4(a) and (b). Results of EDX analysis also confirmed the presence of S and N atoms in the structure of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$.

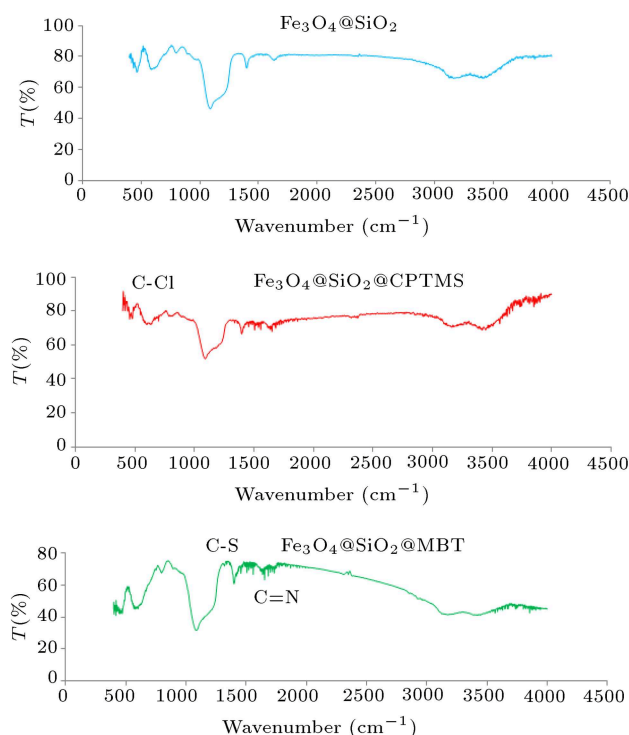


Figure 2. The FT-IR of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$.

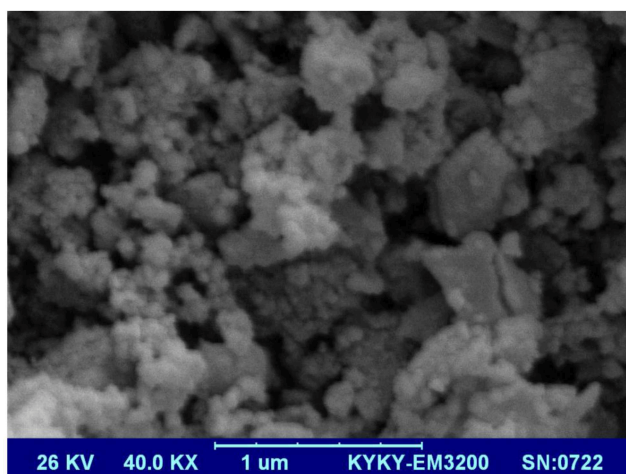


Figure 3. The SEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites.

MBT that confirmed the successful functionalization of this magnetic nanosorbent.

3.1.3. X-ray characterization

Figure 5 shows XRD patterns of nanocomposite after the reaction of magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with 2-mercaptobenzothiazole. Seven diffraction peaks in the region of $2\theta = 30.1, 35.5, 43.2, 53.8, 57.1, 62.7$, and 74.7 and the broad peak at $2\theta = 20\text{-}30$ (SiO_2 group) in Figure 5 showed that the structure of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles remained intact after coating with 2-mercaptobenzothiazole.

3.1.4. Thermogravimetric analysis

The percentage weight loss process of nanocomposites, which demonstrated the difference between $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$, was evaluated by TGA analysis (Figure 6). The results exhibited that $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was stable up to 300°C . By comparing $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ curves, the weight loss of 15% from 150°C up to 570°C in curve $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ could result from decomposition of the 2-MBT coating. This observation suggested that 2-MBT was coated successfully on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

3.2. Optimization procedure

3.2.1. Sorption Step

To study the interaction between effective factors and obtain a proper quantity of each parameter, the Box-Behnken design method was used. The interaction between the main parameters cannot be studied with a one-parameter-at-a-time procedure; however, it is possible using experimental design methodology. In addition, the one-parameter-at-a-time procedure is required to spend much time and carry out abundant tests to determine optimum levels. The Statgraphics plus 5.1 Software was used for experimental design methodology.

The process variables, such as pH, extraction time, and amount of magnetic nanocomposite parameters, were optimized by the multi-variable optimization method to study the effect of parameters on target metal ions sorption. At this point, the number of analysis is given by the following equation:

$$N = 2K(K - 1) + C_0,$$

where K is the number of variants, and C_0 is the repeat number of tests at the center point. In this study, $K = 3$ and $N = 3$; as a result, the number of analysis is 15. Table 1 gives the initial factors and their studied level in this work. The levels of all factors are used without any change in all steps.

Table 2 gives experimental design by BBD method in order to optimize effective parameters for target ions sorption, and respective results were obtained from measurement. The predicted response value Y in each experiment of the quadratic model is expressed as follows:

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2,$$

where x_1 , x_2 , and x_3 are the independent variables, β_0 is the intercept, $\beta_1 - \beta_{33}$ are the regression coefficients, and Y is the response (recovery %). The results obtained were evaluated by analysis of variance (ANOVA) method. R-square and adjusted R-square

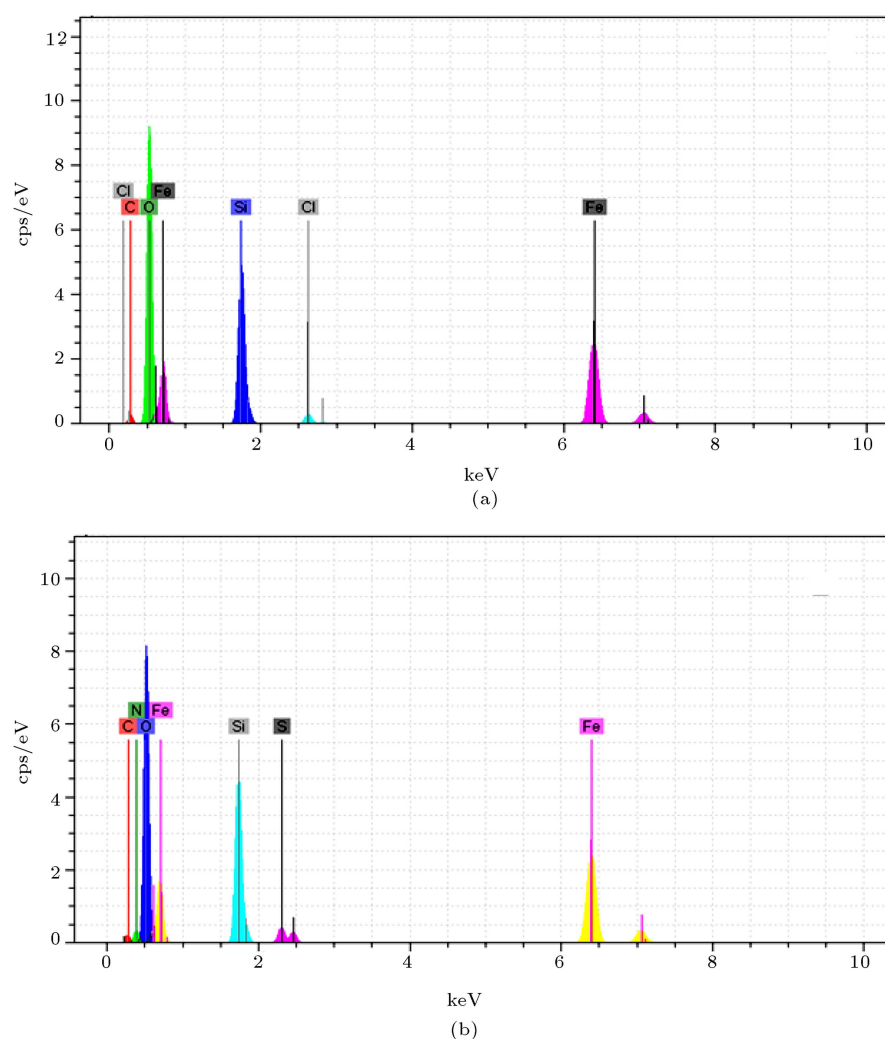


Figure 4. EDS spectrum of (a) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$ and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites.

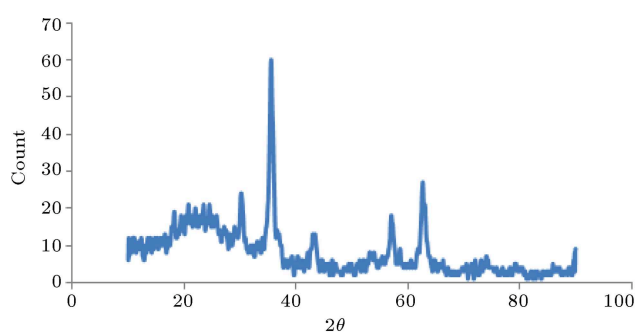


Figure 5. The XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites.

(with values 0.97196 and 0.92151, respectively) imply that the correlation between experimental and applied models is good.

The Pareto chart obtained by the three-level test at 95% significance is given in Figure 7. The vertical line in the figure shows significant effects. Figure 7 shows that pH of solution is the main factor in the extraction efficiency.

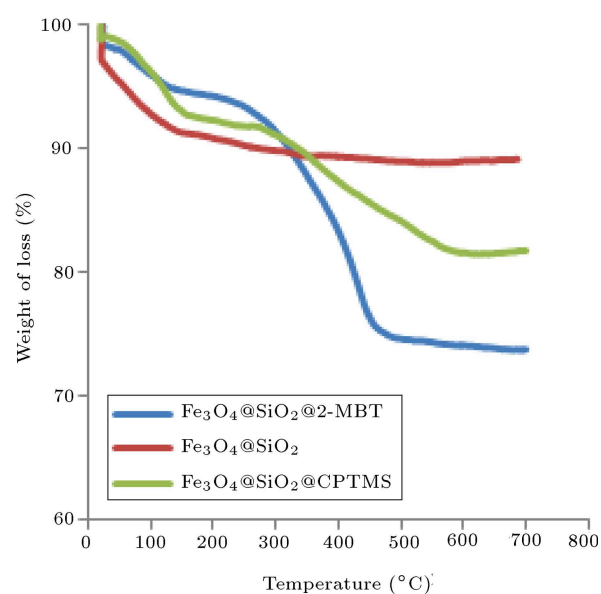


Figure 6. The TGA plots of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CPTMS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanocomposites.

Table 1. Experimental variables and levels of the Box-Behnken Design (BBD).

	Variable	Level		
		Lower	Central	Upper
Sorption step	A: pH	3.0	6.5	10.0
	B: Sorption time (min)	2.0	6.0	10.0
	C: Magnetic nanosorbent amount (mg)	2.0	6.0	10.0
Elution step	A: Eluent concentration (mol L ⁻¹)	0.2	0.6	1.0
	B: Eluent volume (mL)	2.0	4.0	6.0
	C: Elution time (min)	1.0	5.5	10.0

Table 2. BBD and results for the study of three experimental variables in the sorption step.

Runs	pH	Sorption time (min)	Magnetic nanosorbent amount (mg)	Recovery (%)
1	6.5	2	10	95.8
2	6.5	6	6	96.5
3	3	6	2	65.5
4	3	2	6	68.9
5	10	10	6	76.1
6	10	6	10	77.3
7	10	6	2	79.2
8	6.5	6	6	97.5
9	3	10	6	67.4
10	6.5	6	6	98.7
11	3	6	10	70.2
12	6.5	2	2	87.6
13	6.5	10	10	94.4
14	10	2	6	67.2
15	6.5	10	2	86.3

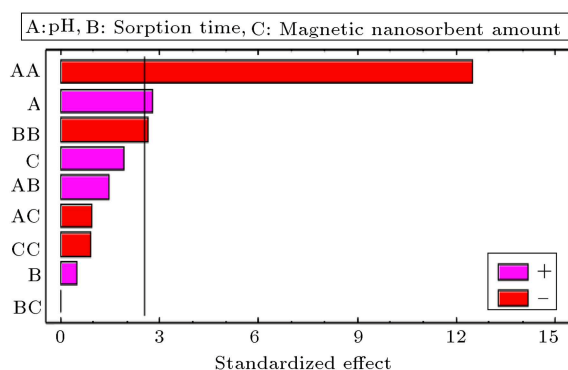
**Figure 7.** The standardized Pareto chart of the main effects in the BBD (sorption step). AA, BB, and CC are the quadratic effects of pH, sorption time, and amount of magnetic nanosorbent, respectively. AB, AC, and BC are the interaction effects between pH and sorption time, pH and amount of magnetic nanosorbent, and sorption time and amount of magnetic nanosorbent, respectively.

Figure 8(a) shows the response surface obtained by plotting the pH of sample and amount of magnetic nanosorbent with a fixed sorption time (6 min). Figure 8(b) shows the response surface plot of the solution pH and sorption time, with the amount of magnetic nanosorbent fixed at 6.0 mg. Figure 8(c) shows the response surface developed for the amount of magnetic nanosorbent and sorption time for pH = 6.7. Based on maxims, the equations' optimum condition is when pH = 6.7, extraction time is 6 min, and the amount of magnetic nanosorbent is 8.7 mg.

3.2.2. Selection of eluent

In this work, the effect of elution solvent for elution of target ions from Fe₃O₄@SiO₂@MBT nanosorbent was investigated; in addition, four types of eluents, such as HNO₃, HCl, NaOH, and H₂SO₄ solutions, were selected. The results showed that the best eluent for simultaneous quantitative recovery of cadmium and copper ions from the magnetic nanosorbent was HCl.

3.2.3. Elution step

In the elution step, different parameters (eluent concentration, eluent volume, and elution time) that significantly affect this method were optimized by BBD. Other parameters involved in this step were kept constant. The number of experiments (15 runs) is then defined as the sorption step (Table 3).

According to Pareto chart in Figure 9, elution time is the main factor in the extraction efficiency of target ions. The 3D response surfaces representing the simultaneous influence of independent variables studied in the elution step are shown in Figure 10.

According to the analysis of variance (ANOVA) method, the lack of fit 0.10 (more than 0.05) implied that the quadratic model was valid for this work. The conditions of a maximum integrated absorbance value include concentration of eluent, 0.62 mol L⁻¹ HCl, eluent volume of 4.3 mL, and elution time of 7 min.

3.3. Effect of breakthrough volume

In a condition where all solutions are adjusted according to the optimum condition obtained for this

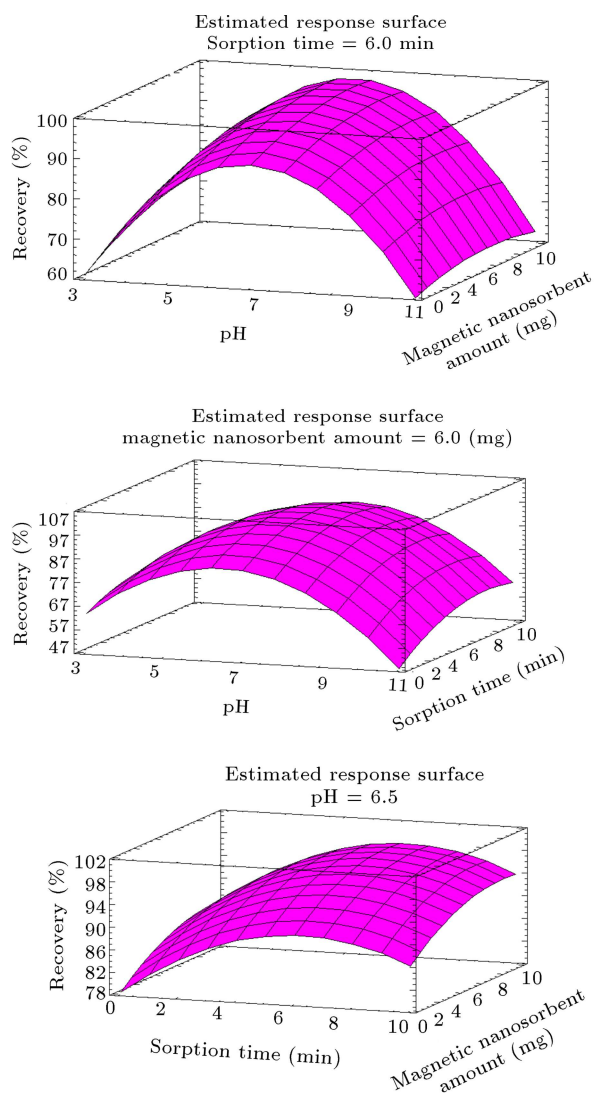


Figure 8. The estimated response surfaces methodology using the BBD for sorption step: (a) Response surface plot of solution pH and amount of magnetic nanosorbent vs. extraction recovery, (b) response surface plot of solution pH and sorption time vs. extraction recovery, and (c) response surface plot of sorption time and amount of magnetic nanosorbent vs. extraction recovery.

procedure, 8.7 mg of the synthetic magnetic nanocomposite was tested with the aqueous solution of target metal ions with 0.01 mg of target ions in the volume range of 50–1000 ml. The obtained results of the analysis show that, up to 800 ml, extraction efficiency is relatively constant. At higher volumes, extraction efficiency decreases. Therefore, in our procedure, 800 ml is considered as the breakthrough volume. In fact, the breakthrough volume is the maximum volume of solution that can be used with the recovery percentage more than 95%. In our procedure, the pre-concentration factor calculated as the ratio of the highest sample volume (800 ml) to the eluent volume (4.3 mL) is 186.

Table 3. BBD and results for the study of three experimental variables in the elution step.

Runs	Eluent concentration (mol/L)	Eluent volume (mL)	Eluent time (min)	Recovery (%)
1	0.6	4.0	5.5	96.6
2	0.6	4.0	5.5	98.4
3	1.0	6.0	5.5	65.8
4	1.0	4.0	1.0	60.4
5	0.2	4.0	1.0	56.2
6	1.0	4.0	10.0	68.4
7	0.6	2.0	10.0	87.5
8	0.6	2.0	1.0	70.6
9	0.6	6.0	1.0	77.9
10	0.2	2.0	5.5	53.2
11	0.6	6.0	10.0	92.5
12	1.0	2.0	5.5	58.7
13	0.2	6.0	5.5	58.9
14	0.6	4.0	5.5	95.9
15	0.2	4.0	10.0	60.8

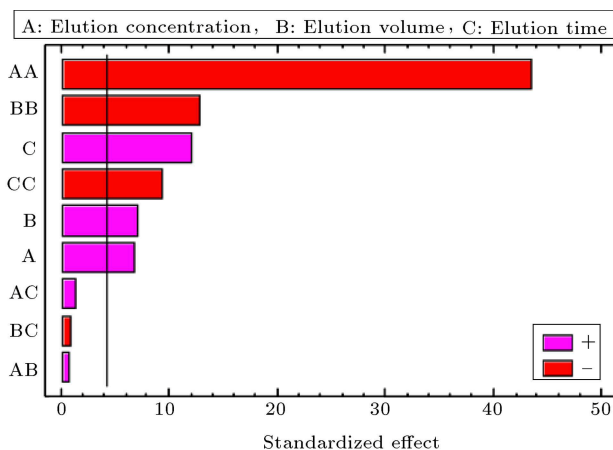


Figure 9. The standardized Pareto chart of the main effects in the BBD (elution step). AA, BB, and CC are the quadratic effects of eluent concentration, and eluent volume, elution time, respectively. AB, AC, and BC are the interaction effects between eluent concentration and eluent volume, eluent concentration and elution time, eluent volume and elution time, respectively.

3.4. Effect of potential interfering ions

Well-known problems in the FAAS determination of metals in natural samples are matrix effects [25–29]. To study this effect, some foreign salts with different concentrations were added to 100 mL of a solution containing 1 mg L⁻¹ of target ions. The ion that changes the sorption and elution of desired metal ions more than 5% is known as the interfering ion (Table 4). Results show the high selectivity of magnetic nanocomposite toward target ions.

Table 4. Influence of interfering ions.

Interfering ion	Tolerable concentration ratio X/Cd, Cu, Ni, Zn, Pb	$R^a \pm S^b$				
		Cadmium	Copper	Nickel	Zinc	Lead
K ⁺	10,000	89.0±1.5	98.0±2.0	98.0±2.2	95.0±1.8	97.0±1.2
Na ⁺	10,000	96.0±1.6	97.0±2.0	92.0±1.4	98.0±2.3	99.0±1.7
Al ³⁺	1,000	98.0±1.7	90.0±2.0	97.0±2.3	98.0±2.6	96.0±1.3
Co ²⁺	1,000	90.0±2.0	86.0±1.8	88.0±2.8	91.0±1.3	108.0±2.5
Cr ³⁺	1,000	91.0±1.7	98.0±1.6	97.0±1.5	97.0±2.4	96.0±1.3
Ag ⁺	1,000	96.0±2.1	97.0±1.7	98.0±1.8	95.0±2.5	97.0±1.5
Hg ²⁺	1,000	103.0±1.6	107.0±2.0	100.0±2.3	86.0±2.3	105.0±2.5
Mg ²⁺	1,000	97.0±2.3	95.0±1.8	98.0±1.5	98.0±1.6	97.0±1.8
Mn ²⁺	1,000	105.0±1.8	98.0±1.6	97.0±1.5	100.0±1.5	96.0±1.6
MnO ₄ ⁻	1,000	97.0±1.8	87.0±1.6	98.0±2.0	99.0 ±2.0	96.0±2.3
NO ₃ ⁻	1,000	95.0±2.0	90.0±1.8	87.0±1.8	98.0±1.8	91.0±1.6
CrO ₄ ²⁻	1,000	96.0±2.0	98.0±1.5	97.0±1.6	88.0±1.7	97.0±1.5
PO ₄ ³⁻	1,000	90.0±1.5	98.0±1.0	98.0±1.2	91.0±2.1	105.0±1.9

^a: Recovery; ^b: Standard deviation ($N = 3$).

3.5. Sorption capacity study

This parameter is calculated using the following equation:

$$Q = [(C_0 - C_A) \times V] / m,$$

where Q , C_0 , C_A , V , and m are the amount of metal ions sorbed onto the unit amount of the composites (mg g^{-1}), initial concentration (mg L^{-1}) of each ion, final concentrations (mg L^{-1}) of each ion, the volume of the aqueous phase (L), and the weight of the magnetic nanosorbent (g), respectively. To determine this parameter, the Batch MSPE procedure, 50.0 mg L^{-1} of target metal ions, was used. The obtained maximum sorption capacities of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanosorbent in optimum sorption conditions were obtained as 168, 138, 104, 120, and 220 mg g^{-1} for Cd(II), Cu(II), Ni(II), Zn(II), and Pb(II) ions, respectively.

3.6. Analytical performance

According to the mentioned method, linearity is within the range of 0.2-60 ng mL^{-1} for Cd(II), 0.2-70 ng mL^{-1} for Cu(II), 0.5-120 ng mL^{-1} for Ni(II), 0.3-100 ng mL^{-1} for Zn(II), and 1-200 ng mL^{-1} for Pb(II). LOD was computed based on $3S_b/m$ definition (where m represents the slope of the calibration curve after preconcentration, and S_b represents the standard deviation for 8 blank measurements); LODs were obtained as 0.14, 0.24, 0.30, 0.27, and 0.53 ng mL^{-1} for Cd(II), Cu(II), Ni(II), Zn(II), and Pb(II) ions, respectively. The precision of the method (RSD%) for a standard solution containing 25 ng mL^{-1} of target metal ions ($n = 5$) was found to be 3.2 for Cd(II), 3.7 for Cu(II), 3.5 for Ni(II), 3.9 for Zn(II), and 3.2 for Pb(II).

Table 5. Analytical characteristics of the proposed method for cadmium, copper, nickel, zinc, and lead.

Analyte	Detection limit (ng mL^{-1})	RSD (%)	R^2	Linear range (ng mL^{-1})
Cd(II)	0.14	3.2	0.9965	0.2-60
Cu(II)	0.24	3.7	0.9967	0.2-70
Ni(II)	0.3	3.5	0.9964	0.5-120
Zn(II)	0.27	3.9	0.9971	0.3-100
Pb(II)	0.53	3.2	0.9962	1-200

(Table 5). Moreover, under the chosen conditions, it was observed that $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-MBT}$ nanosorbent could be applied 5 times without considerable loss in their sorption capacity.

3.7. Determining target ions in various real samples

The current method was applied to determine the level of target metal ions in different water and different food samples. Absorption data of solutions recovered from extraction were obtained by FAAS of each of ions in the real sample; the obtained results are shown in Table 6. As a result, the application of the synthetic nanocomposite is capable of very fast extraction of cadmium(II), copper(II), nickel(II), zinc(II), and lead(II) ions in different samples and has suitable efficiency.

3.8. Comparison of the method with other published methods

The comparison of the current method with other solid phases is summarized in Table 7. The current method suggests a good linear range, less RSD, acceptable

Table 6. Analysis of cadmium, copper, nickel, zinc, and lead ions in different food and agricultural products.

Sample	Analyte	Real sample (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Tap (laboratory water Semnan, Iran)	Cadmium	-	10.0	9.83	98.30
	Copper	9.3	10.0	18.11	88.1
	Nickel	-	10.0	9.92	99.20
	Zinc	-	10.0	9.81	98.10
	Lead	-	10.0	8.86	88.60
Distilled water	Cadmium	-	10.0	9.93	99.30
	Copper	-	10.0	9.71	97.10
	Nickel	-	10.0	10.9	100.90
	Zinc	-	10.0	9.8	98.00
	Lead	-	10.0	8.92	89.20
Solid sample	Analyte	Real sample (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Sugar	Cadmium	-	10.00	9.91	99.10
	Copper	3.40	10.00	13.12	97.20
	Nickel	-	10.00	10.95	109.50
	Zinc	5.30	10.00	15.25	99.50
	Lead	-	10.00	9.87	98.70
Edible Salts	Cadmium	6.70	10.00	15.56	88.6
	Copper	3.10	10.00	12.19	90.9
	Nickel	2.40	10.00	12.31	99.1
	Zinc	9.40	10.00	19.13	97.3
	Lead	2.00	10.00	11.12	91.2
Lettuce	Cadmium	3.4	10.00	14.28	108.8
	Copper	19.7	10.00	29.59	98.9
	Nickel	5.5	10.00	14.37	88.7
	Zinc	18.6	10.00	28.41	98.1
	Lead	6.4	10.00	16.10	97.0
Broccoli	Cadmium	2.20	10.00	12.91	107.1
	Copper	18.70	10.00	29.54	108.4
	Nickel	5.62	14.96	93.4	
	Zinc	17.89	10.00	27.51	96.2
	Lead	5.81	10.00	15.69	98.8
Tomato	Cadmium	-	10.00	9.82	98.20
	Copper	7.81	10.00	17.69	98.80
	Nickel	4.39	10.00	104.10	99.71
	Zinc	8.90	10.00	109.71	100.81
	Lead	6.57	10.00	15.40	88.30

Table 7. Analysis of cadmium, copper, nickel, zinc, and lead ions in different real samples.

Instrument		Analytical technique	Elements	LOD (ng mg ⁻¹)	PF ^a	MAC ^b (mg g ⁻¹)	Ref.
FAAS	XAD-2 functionalized with o-aminophenol		Cadmium	2.0	50	3.42	30
			Copper	4.0	50	3.37	
			Nickel	7.5	65	3.24	
			Zinc	-	-	-	
			Lead	25.0	40	3.32	
FAAS	4-(2-thiazolylazo)resorcinol-MWCNTs		Cadmium	2.8	-	3.9	31
			Copper	-	-	-	
			Nickel	-	-	-	
			Zinc	-	-	-	
			Lead	-	-	-	
FAAS	Functionalized amberlite XAD-16		Cadmium	1.19	100	4.436	32
			Copper	0.33	100	5.38	
			Nickel	-	-	-	
			Zinc	-	-	-	
			Lead	-	-	-	
FAAS	DHMP-activated carbon		Cadmium	-	-	-	33
			Copper	2.9	260	0.63	
			Nickel	3.5	260	0.54	
			Zinc	-	-	-	
			Lead	8.4	260	0.45	
FAAS	Fe ₃ O ₄ @IIP Cd ²⁺		Cadmium	0.6	-	-	34
			Copper	-	-	-	
			Nickel	-	-	-	
			Zinc	-	-	-	
			Lead	-	-	-	
FAAS	Fe ₃ O ₄ @SiO ₂ @2-mercaptobenzothiazole		Cadmium	0.14	186	168	This work
			Copper	0.24	186	138	
			Nickel	0.30	186	104	
			Zinc	0.27	186	120	
			Lead	0.53	186	220	

^a: Preconcentration factor; ^b: Maximum adsorption capacity.

extraction recovery, and LOD. As observed, this magnetic nanocomposite sorbent in the current study is clearly different from other reports within the limit of detection [30-34].

4. Conclusions

In the present study, rapid and low-cost extraction of trace amounts of cadmium(II), copper(II), nickel(II), zinc(II), and lead(II) ions was described using the proposed magnetic nanosorbent. This magnetic nanosorbent is a confidential magnetic nanosorbent that ex-

hibits high sorption capacity and very low detection limits for the mentioned metal ions. Short separation process time (less than 13 min) and easy separation of magnetic nanosorbent without filtration are two advantages of this method. The Box-Behnken design was applied to optimize the extraction and elution steps. Finally, considering the obtained outcomes, effective and rapid extraction of trace quantities of the mentioned metal ions in various complex matrices (water samples, sugar and edible salts, and vegetable samples) was obtained, and the obtained results were good.

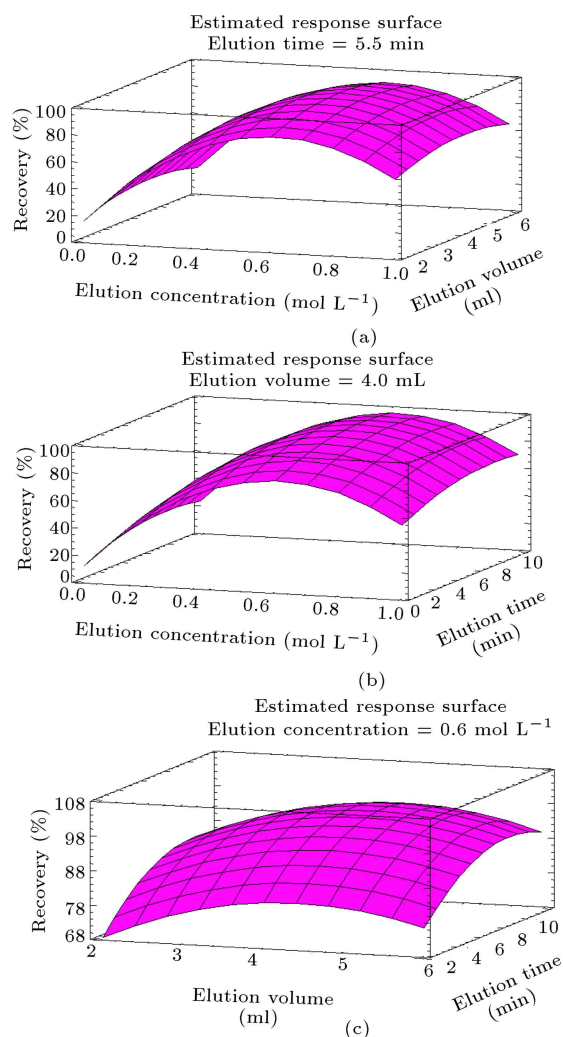


Figure 10. The estimated response surfaces methodology using the BBD for the elution step: (a) response surface of eluent volume and eluent concentration vs. extraction recovery, (b) Response surface plot of eluent concentration and elution time vs. extraction recovery, and (c) response surface plot of eluent volume and elution time vs. extraction recovery.

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