

Determination of Lead and Cadmium in Various Food Samples by Solid Phase Extraction Using a Novel Amino-Vinyl Functionalized Iron Oxide Magnetic Nanoparticles

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Abstract

A facile method for synthesis of amino functionalized silica coated Fe₃O₄ magnetic nanoparticles is introduced. For this purpose, the surface of magnetic nanoparticles (MNPs) was modified with two precursors of silica which produced amine and vinyl functional groups on the surface of magnetic nanoparticles. The modified magnetic nanoparticles were characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), vibrating sample magnetometry (VSM) and thermogravimetric analysis (TGA). Results showed that, in the presence of vinyl precursor, the stability of silica matrix clearly improved. Moreover, the amino functionalized magnetic nanoparticles were used as a sorbent for solid-phase extraction of trace lead and cadmium in different food samples such as rice, wheat, milk and shrimp. The effects of various parameters such as pH, extraction time and adsorbent content were investigated in order to establish the optimum conditions for the extraction and determination of lead and cadmium. The regeneration studies also showed that modified magnetic nanoparticles can be used several times for the adsorption of lead and cadmium without loss of their magnetization properties.

Keywords: Solid phase extraction, Lead, Cadmium, Amino-vinyl functionalized magnetic nanoparticles.

1. INTRODUCTION

Heavy metals contamination is known to be a significant problem, which threatens the environment and human life. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic [1-3]. Lead poisoning (also known as plumbism) is a medical condition in humans and other vertebrates caused by increasing the level of lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, reproductive and nervous systems. It interferes with the development of the

nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders [4, 5]. Cadmium and its compounds are highly toxic and exposure to this metal is known to cause cancer and targets the body's cardiovascular, renal, gastrointestinal, neurological, reproductive and respiratory systems [6, 7]. Therefore, the effective removal of lead and cadmium ions from the environmental, food and biological samples has been a crucial issue related to the quality of human life.

Several analytical methods including inductively coupled plasma optical

emission spectrometry [8,9], inductively coupled plasma-mass spectrometry [10-12], flame atomic absorption spectrometry [13-14], electrothermal atomic absorption spectrometry [15-16] and graphite furnace atomic absorption spectrometry [17-18], have been proposed for the determination of lead and cadmium in various matrices. However, the direct determination of these metal ions in real samples with above techniques in most cases was very difficult because of matrix effect and low existing level. Under these circumstances, in order to determine trace levels of lead and cadmium a separation and enrichment step prior to the determinations may be beneficial. For this purpose, several methods have been applied, including, liquid-liquid extraction [19-20], cloud point extraction [21, 22], liquid-phase microextraction [23,24] and solid-phase extraction [25-29]. Among these techniques, solid-phase extraction (SPE) as a popular technique for achieving separation and preconcentration of metal ions in environmental samples has been developed and widely used because of its high enrichment factor, simple operation, minimal cost, reusability of the adsorbent and the ability to combine with different detection techniques whether in on-line or off-line mode. In this sense, functionalized iron oxide magnetic nanoparticles (Fe_3O_4 MNPs) with chelating species such as thiol [30], imidazole [31], amine [32-38] and carboxylic [39] have attracted more attentions as they can be easily recovered from the reaction mixture by using an external magnet. However, Fe_3O_4 MNPs are not highly stable and they may lose their magnetic properties, especially in acidic environments. In order to overcome this problem, silica as a protecting shell is usually utilized to coat the Fe_3O_4 particles to form a core-shell $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ structure. Furthermore, silica shell prevents the aggregation of the Fe_3O_4 particles and provides numerous surface Si-OH groups for further modification [40-44].

In the present work, the solid phase extraction by using amino-vinyl functionalized Fe_3O_4 MNPs as a sorbent was investigated for extraction, preconcentration and determination of trace amounts of lead and cadmium in food samples. For this purpose, two different precursors of silica, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) and Triethoxyvinylsilane (VTEOS) were used to form silica shell on the surface of Fe_3O_4 MNPs. As reported in our previous work, in the presence of vinyl precursor, the stability of silica shell improved clearly due to the hydrophobicity of VTEOS [45]. The amino functionalized magnetic nanoparticles were successfully applied for extraction and determination of lead and cadmium in rice, wheat, milk and shrimp samples.

2. EXPERIMENTAL

2.1. Apparatus and Reagents

Iron(II) chloride tetrahydrate, Iron(III) chloride hexahydrate, Lead standard solution (1000 mg L^{-1}), Cadmium standard solution (1000 mg L^{-1}), Triethoxyvinylsilane (VTEOS), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS), Tetraethyl orthosilicate (TEOS) and all of the chemical reagents were purchased from Sigma-Aldrich and Merck and were used without further treatment. Ultrapure water (Millipore) was used throughout the whole experiment.

The structure and morphology of Fe_3O_4 and $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ MNPs were characterized by X-ray diffraction (XRD-D8, BRUKER) and transmission electron microscopy (TEM-CM10, Philips). Magnetic properties of Fe_3O_4 and $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ MNPs were investigated using a vibrating sample magnetometer (VSM) with an applied field between 10000 and 10000 Oe at room temperature (MDKF, Iran). Thermal stability of functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ MNPs was investigated by thermo-gravimetric analysis (STA 503, Bahr, Germany) at a

heating rate of 10 °C/min under N₂ flow (10 ml/min). The concentrations of lead and cadmium were analyzed via an ICP–AES spectrophotometer (Thermo Scientific, IRIS Intrepid II, USA). An Ethos Plus microwave digester (Preekem, Exel, China) equipped with a carousel provided with ten 100-mL high pressure Teflon vessels with cover, HTC adapter plate and HTC safety springs was used. The acid microwave digestion performed at a maximum power of 1000 W.

2.2. Preparation of Amino-Vinyl Functionalized Fe₃O₄ Magnetic Nanoparticles

Fe₃O₄@silica MNPs were prepared via the simple method. The Fe₃O₄ MNPs (600 mg) prepared according to the previous report [46], were suspended in 1-propanol (60 mL) by sonication for 30 min at room temperature. Then, NH₄OH (25% w/w, 8 mL), ddH₂O (6 mL), and TEOS (1 mL) were added to the above solution and the mixture was stirred at 50 °C for 1 h. The black precipitate was washed three times with 1-propanol and then added to a mixture of AEAPS (0.5 ml) and VTEOS (0.5 ml) in ddH₂O (60 mL) followed by the addition of 0.01M HCl (30 mL). The mixture was shaken at room temperature for 24 h. The resulted dark brown precipitate (Fe₃O₄@silica MNPs) was washed with ddH₂O and kept in an oven at 80 °C for 48 h until complete drying.

Also, to elucidate the role of VTEOS in the stability of silica shell, two glass slides were coated with thin layer of silica, with and without vinyl precursor in silica matrix. For this purpose, the surface of the glass slides was coated according to our previous report, with the slight modification [47]. The sol solution was prepared by mixing of VTEOS (0.5 mL), AEAPS (0.5mL), HCl (0.5 mL of 1mM) and 1.5 ml of ethanol. The mixture was then stirred for 30 min and allowed to gelate at room temperature for 24 h. The formed sol solution was coated on a glass slide by immersion of the glass into the sol

solution for 15s and drying at room temperature under an ambient atmosphere for 3 days. Finally it was kept in an oven at 100 °C for 48 h for complete drying. Also, a coated glass slide with no vinyl precursor in the silica matrix was prepared via the same method.

2.3. Sample preparation

Rice, wheat, milk and shrimp samples were purchased from local markets in Tehran (Iran). Where possible, each product was chosen from a different manufacturer. The procedure used for preparing samples for determination of metal ions was as follows: 0.4 g of each sample was weighed accurately and transferred into a Teflon vessel and 5 mL of concentrated nitric acid was then added. The vessels were sealed and placed into the microwave oven. Acid digestion was performed with the heating programme, which consists of three successive steps at maximum power. First, the temperature was increased to 120 °C and kept for 5 min. Next, the temperature was increased to 180 °C and kept for 10 min for complete digestion. Finally the digests were cooled to reach room temperature, transferred to a 50 mL volumetric flask and the volume was completed to the mark with phosphate buffer solution (pH 6.5).

2.4. Procedure of Magnetic Solid Phase Extraction

The adsorption of lead and cadmium ions by using amino-vinyl functionalized magnetic nanoparticles was investigated in aqueous solution at 25 °C. In general, the modified magnetic nanoparticles (15.0 mg) were put into 50.0 mL of aqueous solution containing metal ions (5.0 mg L⁻¹). The pH of the solution was adjusted to the certain value with phosphate buffer solution and mixed by ultrasonication for several minutes until the equilibrium was established and then magnetically separated via an external magnetic field. Next, 5 mL of 1 mol L⁻¹ HNO₃ was added as eluent and the mixture was

ultrasonicated again for 5 min. Finally, the adsorbent was removed via an external magnetic field and the supernatant was collected for the determination of lead and cadmium by ICP-AES.

3. RESULTS AND DISCUSSION

3.1. Characterization of Amino-Vinyl Functionalized Fe_3O_4 Magnetic Nanoparticles

Fig. 1 shows the FT-IR spectra of the synthesized amino-vinyl functionalized Fe_3O_4 MNPs. The peak at 588 cm^{-1} is assigned to the stretching of Fe–O bond. The bands at 960 and 1085 cm^{-1} were assigned to the vibration of the Si–O bonds which indicate the formation of silica shells on the surface of Fe_3O_4 . The broad band at 3400 cm^{-1} , can be assigned to the hydrogen-bonding silanol groups and adsorbed water and the band at 2950 cm^{-1} is associated with the CH_2 vibrations corresponding to the C–H stretching. The observed absorption peak at 1602 cm^{-1} is related to the N–H bending vibration and those appeared at 1410 and 1644 cm^{-1} are attributed to the =C–H bending and C=C stretching, respectively. These results indicate that the amine and vinyl functional groups are present on the surface of the modified MNPs.

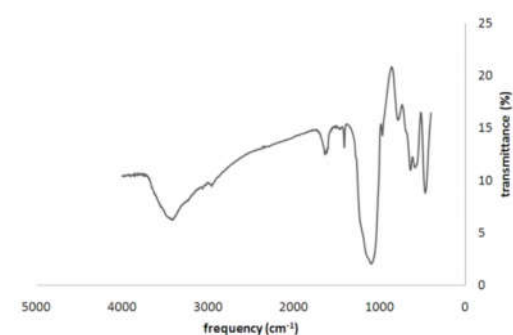


Figure 1. FT-IR spectrum of Fe_3O_4 @silica MNPs.

Fig. 2 shows a typical XRD pattern of modified Fe_3O_4 MNPs. Six characteristic peaks ($2\theta = 30.1$, 35.8 , 43.3 , 53.7 , 57.7 , and 63.1), related to their corresponding indices (($2\ 2\ 0$), ($3\ 1\ 1$), ($4\ 0\ 0$), ($4\ 2\ 2$), ($5\ 1\ 1$) and ($4\ 4\ 0$)) were

observed in the case of Fe_3O_4 nanoparticles, respectively. Deduced from Debye–Scherrer’s formula, the average size of the Fe_3O_4 MNPs is about 12.6 nm . Fig. 2, inset displays the XRD pattern of the Fe_3O_4 @ SiO_2 MNPs, which shows almost the same feature of unmodified Fe_3O_4 MNPs. However, the broad peak at 2θ of 18 – 26 corresponds to the amorphous structure of silica shell [48].

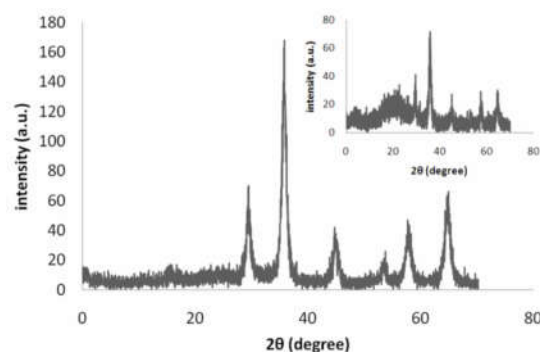


Figure 2. XRD pattern of Fe_3O_4 MNPs.

The inset: XRD pattern of Fe_3O_4 @silica MNPs.

The magnetic properties of Fe_3O_4 and Fe_3O_4 @ SiO_2 MNPs were characterized by using vibrating sample magnetometer (Fig.3). They exhibited superparamagnetic behavior and had little hysteresis, remanence and coercivity due to the fact that the particles are composed of ultra ne magnetic nanocrystals. The magnetic saturation (M_s) values are 76.3 and 34.6 emu g^{-1} , for Fe_3O_4 and Fe_3O_4 @ SiO_2 MNPs, respectively. As can be seen, in the presence of silica shell, the magnetic strength of the nano composite reduced [48]. It should be noted that the modified Fe_3O_4 MNPs, still show the strong magnetization, which suggests their suitability for magnetic separation and targeting.

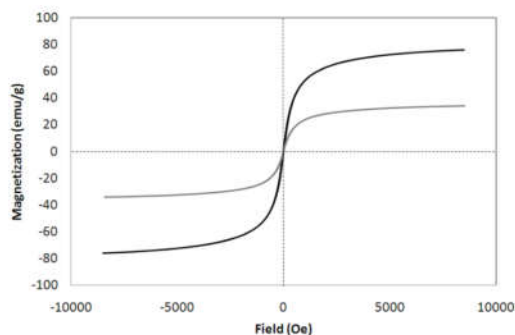


Figure 3. Magnetization curves of Fe_3O_4 MNPs (black line) and $Fe_3O_4@silica$ MNPs (gray line).

TGA was applied to assess the organic content over the surface of the synthesized magnetic nanocomposites. The TGA (Fig. 4) curve for the $Fe_3O_4@SiO_2$ MNPs presents the first weight loss below $120\text{ }^\circ\text{C}$ and this can be explained by the evaporation of the adsorbed solvent (water and ethanol) attached to the particle surfaces. After this slight weight loss, an unexpected weight gain is taken place within the temperature range from 120 to $200\text{ }^\circ\text{C}$. As reported by Caruntu et al. [49], this weight gain can be attributed to the oxidation of Fe_3O_4 to Fe_2O_3 . The approximately 9.5% weight loss from $390\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$ is presumably due to the decomposition of organic groups, while relatively slow weight loss at elevated temperatures can be related to the decomposition of silica shell.

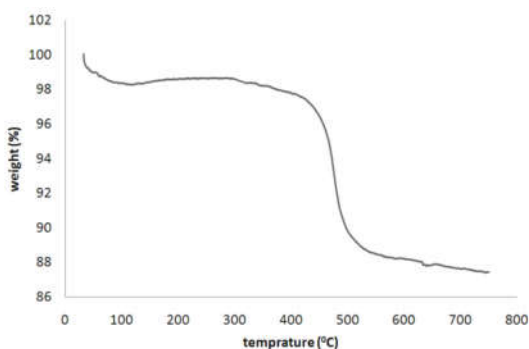


Figure 4. TGA curve of $Fe_3O_4@SiO_2$ MNPs.

Transmission electron microscopy image (Fig. 5) of Fe_3O_4 MNPs indicates the formation of spherical particles with average particle size of 15 nm. As seen in Fig. 5 inset, the silica coated magnetic nanoparticles exhibit perfectly spherical with smooth surface and represent clear core-shell structure. The core-shell $Fe_3O_4@SiO_2$ MNPs are uniform with a size of about 55 nm and the silica layer is about 20 nm in thickness.

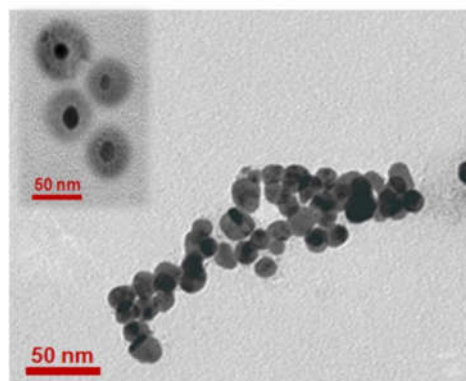


Figure 5. TEM image of Fe_3O_4 MNPs.

The inset: TEM.

These results indicate the formation of silica shell containing amine and vinyl functional groups on the surface of the Fe_3O_4 MNPs (Fig.6). According to our previous report [45], in the presence of vinyl precursor in the silica matrix, the stability of silica shell clearly improved.

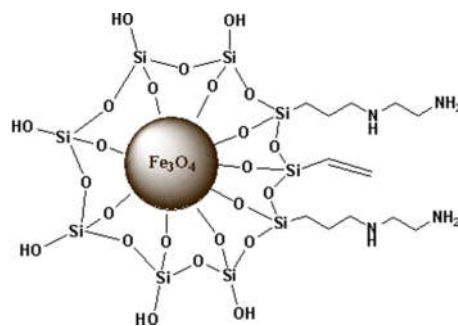


Figure 6. Structure of amino-vinyl functionalized Fe_3O_4 MNPs.

To elucidate this, two glass slides were coated with thin layer of silica, with and

without vinyl precursors in the silica matrix. Fig.7 shows the SEM images of two glass slides after immersion in aqueous solution for 1 h. As can be seen, no cracks were observed in the silica layer in presence of vinyl precursor. However, in the absence of vinyl precursor, some cracks were formed as a result of slight solubility of amine precursor.

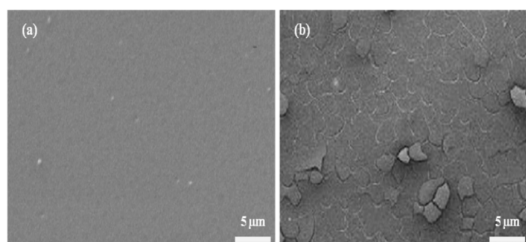


Figure 7. SEM images of silica coated glass slides (a) with and (b) without, vinyl precursor of silica.

3.2 Adsorption Studies

The amino-functionalized Fe_3O_4 MNPs was used as a sorbent for solid phase extraction of lead and cadmium in various food samples. For this purpose, the effect of different parameters such as pH, extraction time and adsorbent content were investigated in order to establish the optimum conditions for the extraction and determination of lead and cadmium.

3.2.1. Effect of pH

It is known that pH value has a critical role on solid phase extraction of metal ions. In order to determine the optimal pH, the effect of pH on adsorption of lead and cadmium were studied over the range of 2–9. As can be seen in Fig. 8a, the adsorption efficiency increased as the pH of the aqueous solution rise from 2 to 6.5 and the adsorption capacity of the adsorbent almost reaches a maximum. As reported previously, at lower pH values, more NH_2 groups were protonated and the numbers of free NH_2 groups on the outer surface of the adsorbent decreased, consequently their adsorption capacity towards the metal ions decreased [38].

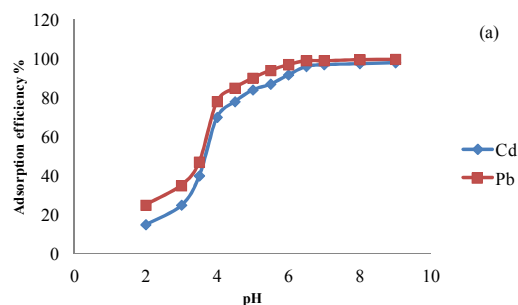
3.2.2. Effect of Ultrasonic Time and Sample Volume

In order to obtain an appropriate experimental time, the effects of ultrasonic time on the adsorption and desorption of lead and cadmium were examined, respectively. For this purpose, the ultrasonic time varied in the range of 1–10 min for both adsorption and desorption experiments. Satisfactory results for adsorption of lead and cadmium were obtained after 3 and 5 min, respectively (Fig. 8b). In addition, the results indicated that, the lead and cadmium ions could be desorbed completely by 5 min sonication in 5 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$ solution.

In order to determine the volume of the sample that can be used with acceptable recoveries, it was necessary to obtain the breakthrough volumes. The results showed that the recoveries are quantitative up to 500 mL sample volume. A preconcentration factor of 100 could be attained for quantitative recovery of metal ions when the sample volume was 500 mL.

3.2.3. Effect of Adsorbent Content

In order to investigate the optimum amount of adsorbent needed for the extraction of target analytes, the amount of modified Fe_3O_4 MNPs was varied from 1 to 30 mg. In general, increasing the amount of adsorbent would increase the number of available adsorption sites. Satisfactory recoveries were obtained by using 10 and 15 mg of sorbent for aqueous solution containing lead or cadmium (5 mg L^{-1}), respectively (Fig. 8c).



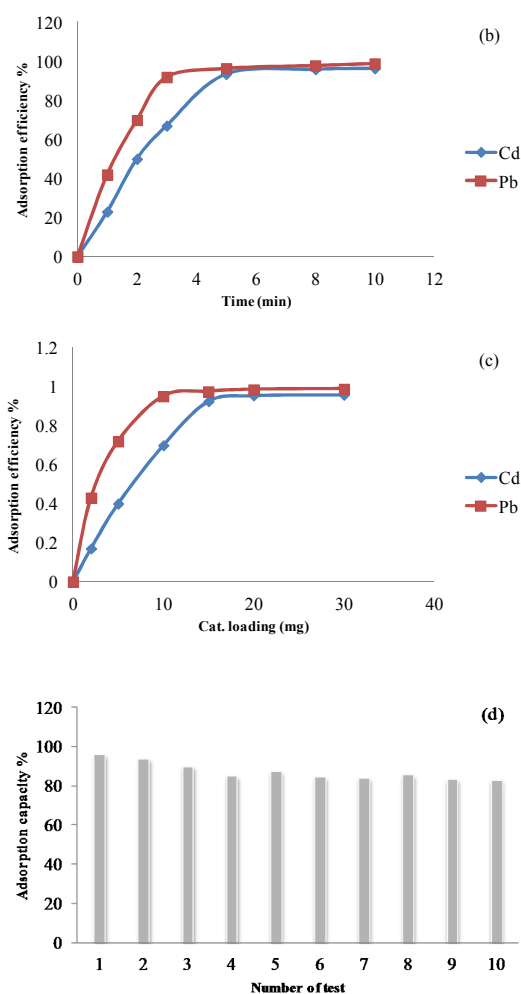


Figure 8. Effect of (a) pH (b) adsorption time (c) catalyst loading and (d) sorbent reusability, on lead and cadmium removal. Condition: $[Pb^{2+}]$: 5 mg L^{-1} , $[Cd^{2+}]$: 5 mg L^{-1} , solution volume: 50 mL .

3.2.4. Regeneration Study

In order to evaluate the possibility of regeneration and reusability of modified Fe_3O_4 MNPs, repetitive adsorption-desorption cycles were performed. The results showed that, no significant difference in adsorption capacity was observed after 10 cycles and it remains almost constant (Fig.8d). The acceptable reusability and stability indicate that, the amino-vinyl functionalized Fe_3O_4 MNPs can be potential adsorbents in practical environmental remediation.

3.2.5. Effect of Co-Existing Ions

In order to study whether other ions could interfere during the extraction of the target analytes, the procedure was performed in presence of alkali, alkaline earth and heavy metals that often accompany analyte ions in real samples. A solution containing co-existing ions and $50 \mu\text{g L}^{-1}$ of each analytes was used. An ion was considered to interfere when its presence produce a variation of more than $\pm 5\%$ in the recovery of the analytes. The concentration ratio for each foreign ions was as follows: 10000 for Na^+ , K^+ , Ca^{2+} ; 1000 for Mg^{2+} , 500 for Ba^{2+} , Zn^{2+} ; 100 for Co^{2+} , Ni^{2+} , Al^{3+} , Cr^{3+} , Mn^{2+} , Fe^{3+} . The results obtained indicate that co-existing ions had no obvious influence on the recovery of the analytes and the method had good tolerance to matrix interference.

3.2.4. Applications to Real Samples

In order to investigate the accuracy and applicability of the optimized method in food samples, the concentration of lead and cadmium was determined in rice, wheat, milk and shrimp samples. The analytical results are shown in Tables 1 and 2. As can be seen, the recoveries for the target metal ions were in the range of 93.1–99.3%.

Table 1. Determination of cadmium in food samples (mean \pm S.D., $n = 3$)

Sample	Added (ng ml^{-1})	Found (ng ml^{-1})	Recovery (%)
Rice	0	B.D.L.*	-
	5	4.90 ± 0.12	98.0
	10	9.62 ± 0.31	96.2
Wheat	0	B.D.L.	-
	5	4.88 ± 0.23	97.7
	10	9.64 ± 0.27	96.4
Milk	0	B.D.L.	-
	5	4.91 ± 0.17	98.3
	10	9.67 ± 0.43	96.7

	20	19.02± 0.68	95.1
Shrimp	0	8.3± 0.48	-
	5	12.92± 0.53	97.2
	10	17.45± 0.57	95.4
	20	26.46± 0.84	93.5
*B.D.L.: Below Detection Limit			

Table 2. Determination of lead in food samples (mean ± S.D., n = 3)

Sample	Added (ng ml ⁻¹)	Found (ng ml ⁻¹)	Recovery (%)
Rice	0	12.30 ± 0.24	-
	5	17.07 ± 0.35	98.7
	10	21.72 ± 0.38	97.4
	20	31.04 ± 0.27	96.1
Wheat	0	6.40 ± 0.14	-
	5	11.32 ± 0.22	99.3
	10	16.08 ± 0.31	98.1
	20	25.55 ± 0.36	96.8
Milk	0	9.10± 0.46	-
	5	13.86± 0.43	98.3
	10	18.41± 0.53	96.4
	20	27.61± 0.58	94.9
Shrimp	0	14.80± 0.71	-
	5	19.36±	97.8

		0.84	
	10	23.51± 0.92	94.8
	20	32.39± 0.97	93.1

4. CONCLUSION

In this study, a novel amino-vinyl functionalized Fe₃O₄ magnetic nanoparticles with a core-shell structure were prepared for the effective removal of lead and cadmium from aqueous solutions. For this purpose, the surface of magnetic nanoparticles was modified with two precursors of silica which produced amine and vinyl functional groups on the surface of magnetic nanoparticles.

The results showed that, in the presence of vinyl precursor, the stability of silica matrix clearly improved. The modified magnetic nanoparticles were successfully applied for extraction and determination of lead and cadmium in rice, wheat, milk and shrimp samples. The regeneration studies also showed that modified magnetic nanoparticles can be used several times for the adsorption of lead and cadmium from aqueous solutions without loss of their magnetization properties.

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