

# 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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(Received: 15 November 2014 and Accepted: 21 February 2016)

## Abstract

*A facile method for synthesis of amino functionalized silica coated Fe<sub>3</sub>O<sub>4</sub> 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 ( $\text{Fe}_3\text{O}_4$  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,  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  particles to form a core-shell  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  structure. Furthermore, silica shell prevents the aggregation of the  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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 ( $1000 \text{ mg L}^{-1}$ ), Cadmium standard solution ( $1000 \text{ mg L}^{-1}$ ), 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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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 N<sub>2</sub> 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 Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles**

Fe<sub>3</sub>O<sub>4</sub>@silica MNPs were prepared via the simple method. The Fe<sub>3</sub>O<sub>4</sub> 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, NH<sub>4</sub>OH (25% w/w, 8 mL), ddH<sub>2</sub>O (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 ddH<sub>2</sub>O (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 (Fe<sub>3</sub>O<sub>4</sub>@silica MNPs) was washed with ddH<sub>2</sub>O 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**

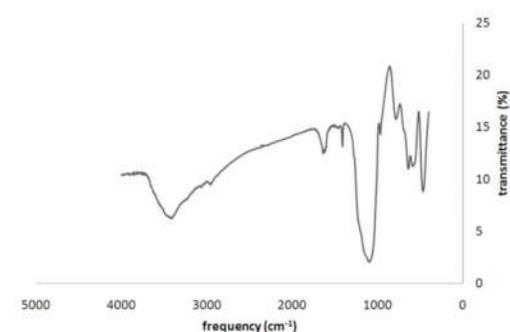
The adsorption of lead and cadmium ions by using amino-vinyl functionalized magnetic nanoparticles was investigated in aqueous solution at 25 °C. In general, the modified magnetic nanoparticles (15.0 mg) were put into 50.0 mL of aqueous solution containing metal ions (5.0 mg L<sup>-1</sup>). The pH of 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<sup>-1</sup> HNO<sub>3</sub> 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 $\text{Fe}_3\text{O}_4$ Magnetic Nanoparticles

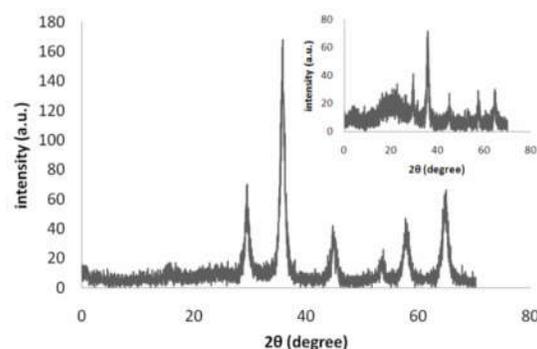
Fig. 1 shows the FT-IR spectra of the synthesized amino-vinyl functionalized  $\text{Fe}_3\text{O}_4$  MNPs. The peak at  $588\text{ cm}^{-1}$  is assigned to the stretching of Fe–O bond. The bands at  $960$  and  $1085\text{ cm}^{-1}$  were assigned to the vibration of the Si–O bonds which indicate the formation of silica shells on the surface of  $\text{Fe}_3\text{O}_4$ . The broad band at  $3400\text{ cm}^{-1}$ , can be assigned to the hydrogen-bonding silanol groups and adsorbed water and the band at  $2950\text{ cm}^{-1}$  is associated with the  $\text{CH}_2$  vibrations corresponding to the C–H stretching. The observed absorption peak at  $1602\text{ cm}^{-1}$  is related to the N–H bending vibration and those appeared at  $1410$  and  $1644\text{ cm}^{-1}$  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  $\text{Fe}_3\text{O}_4$ @silica MNPs.

Fig. 2 shows a typical XRD pattern of modified  $\text{Fe}_3\text{O}_4$  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

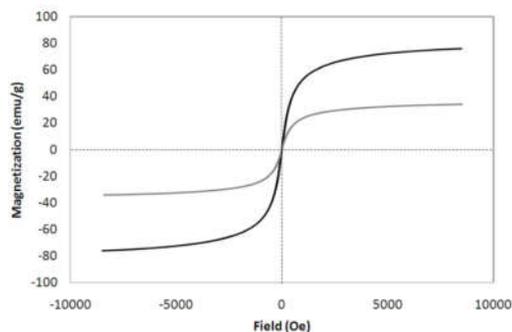
observed in the case of  $\text{Fe}_3\text{O}_4$  nanoparticles, respectively. Deduced from Debye–Scherrer’s formula, the average size of the  $\text{Fe}_3\text{O}_4$  MNPs is about  $12.6\text{ nm}$ . Fig. 2, inset displays the XRD pattern of the  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  MNPs, which shows almost the same feature of unmodified  $\text{Fe}_3\text{O}_4$  MNPs. However, the broad peak at  $2\theta$  of  $18$ – $26$  corresponds to the amorphous structure of silica shell [48].



**Figure 2.** XRD pattern of  $\text{Fe}_3\text{O}_4$  MNPs.

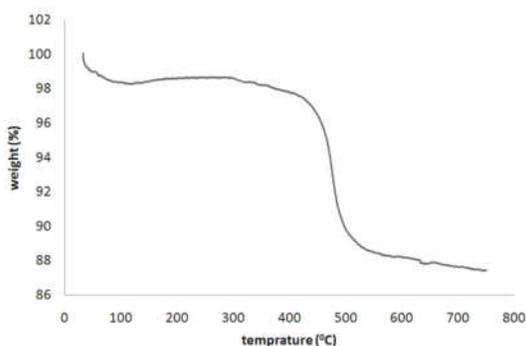
The inset: XRD pattern of  $\text{Fe}_3\text{O}_4$ @silica MNPs.

The magnetic properties of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  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  $34.6\text{ emu g}^{-1}$ , for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  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  $\text{Fe}_3\text{O}_4$  MNPs, still show the strong magnetization, which suggests their suitability for magnetic separation and targeting.



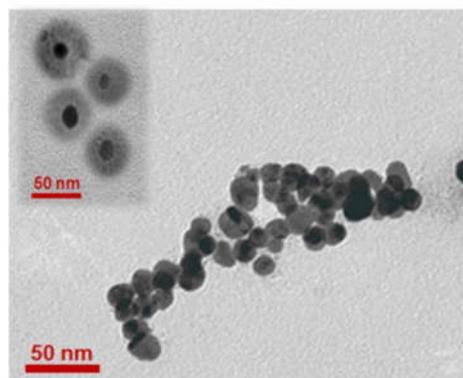
**Figure 3.** Magnetization curves of  $Fe_3O_4$  MNPs (black line) and  $Fe_3O_4@silica$  MNPs (gray line).

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.

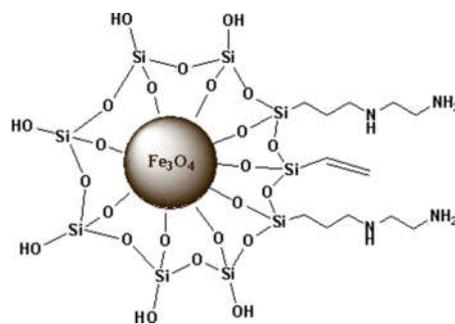
Transmission electron microscopy image (Fig. 5) of  $Fe_3O_4$  MNPs indicates the formation of spherical particles with average particle size of 15 nm. As seen in Fig. 5 inset, the silica coated magnetic nanoparticles exhibit perfectly spherical with smooth surface and represent clear core-shell structure. 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.

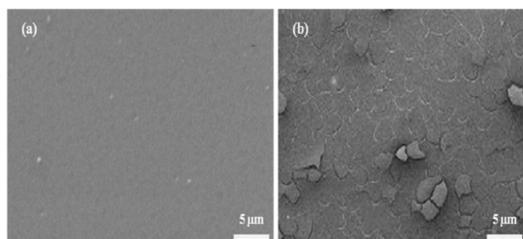
These results indicate the formation of silica shell containing amine and vinyl functional groups on the surface of the  $Fe_3O_4$  MNPs (Fig.6). According to our previous report [45], in the presence of vinyl precursor in the silica matrix, the stability of silica shell clearly improved.



**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<sub>3</sub>O<sub>4</sub> 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<sub>2</sub> groups were protonated and the numbers of free NH<sub>2</sub> groups on the outer surface of the adsorbent decreased, consequently their adsorption capacity towards the metal ions decreased [38].

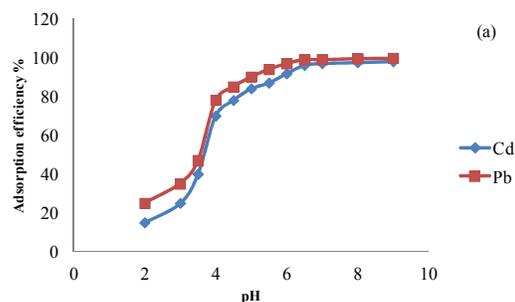
#### 3.2.2. Effect of Ultrasonic Time and Sample Volume

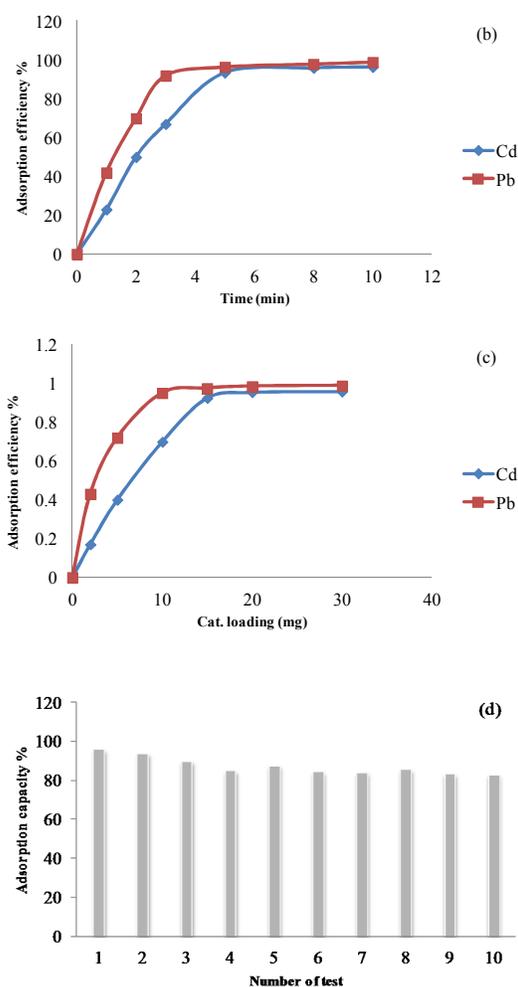
In order to obtain an appropriate experimental time, the effects of ultrasonic time on the adsorption and desorption of lead and cadmium were examined, respectively. For this purpose, the ultrasonic time varied in the range of 1–10 min for both adsorption and desorption experiments. Satisfactory results 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 mol L<sup>-1</sup> HNO<sub>3</sub> 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<sub>3</sub>O<sub>4</sub> 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<sup>-1</sup>), 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:  $[Pb^{2+}]$ :  $5 \text{ mg L}^{-1}$ ,  $[Cd^{2+}]$ :  $5 \text{ mg L}^{-1}$ , solution volume:  $50 \text{ mL}$ .

### 3.2.4. Regeneration Study

In order to evaluate the possibility of regeneration and reusability of modified  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ; 1000 for  $\text{Mg}^{2+}$ , 500 for  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ; 100 for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ . 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 $\text{ml}^{-1}$ )	Found (ng $\text{ml}^{-1}$ )	Recovery (%)
Rice	0	B.D.L.*	-
	5	$4.90 \pm 0.12$	98.0
	10	$9.62 \pm 0.31$	96.2
Wheat	0	B.D.L.	-
	5	$4.88 \pm 0.23$	97.7
	10	$9.64 \pm 0.27$	96.4
Milk	0	B.D.L.	-
	5	$4.91 \pm 0.17$	98.3
	10	$9.67 \pm 0.43$	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 <sup>-1</sup> )	Found (ng ml <sup>-1</sup> )	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 Fe<sub>3</sub>O<sub>4</sub> 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.

#### ACKNOWLEDGEMENT

The authors wish to express their gratitude to the Research Council of Standard Research Institute for the support of this work.

#### REFERENCES

- Jang, D. H., Hoffman, R. S. (2011). "Heavy Metal Chelation in Neurotoxic Exposures", *Neurologic Clinics*, 29: 607-622.
- Demirbas, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review", *Journal of Hazardous Materials*, 157: 220-229.
- Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G., Gardea-Torresdey, J. (2009). "The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain", *The International Journal of Biochemistry & Cell Biology*, 41: 1665.
- Liu, J., Hao, H., Zeng, Y., Dai, F. C., Gu, P. Q. (2013). "Neurotoxicity and Biomarkers of Lead Exposure: a Review", *Chinese Medical Sciences Journal*, 28: 178-188.
- Riva, M. A., Lafranconi, A., Dorso, M. I., Cesana, G. (2012), "Lead Poisoning: Historical Aspects of a Paradigmatic "Occupational and Environmental Disease"", *Safety and Health at Work*, 3: 11.
- Rodríguez-Barranco, M., Lacasaña, M., Aguilar-Garduño, C., Alguacil, J., Gil, F., González-Alzaga, B., Rojas-García, A. (2013), "Association of arsenic, cadmium and manganese exposure with

- neurodevelopment and behavioural disorders in children: A systematic review and meta-analysis”, *Science of the Total Environment*, 454: 562-577.
7. Templeton, D. M., Liu, D. M. (2010), “Multiple roles of cadmium in cell death and survival”, *Chemico-Biological Interactions*, 188: 267-275.
  8. Zhao, L., Zhong, S., Fang, K., Qian, Z., Chen, J. (2012). “Determination of cadmium (II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry”, *Journal of Hazardous Materials.*, 239: 206-212.
  9. Yilmaz, V., Arslan, Z., Rose, L. (2013). “Determination of lead by hydride generation inductively coupled plasma mass spectrometry (HG-ICP-MS): On-line generation of plumbane using potassium hexacyanomanganate(III)” *Analytica Chimica Acta.* 761: 18-26.
  10. Resano, M., Marzo, M. P., Alloza, R., Saénz, C., Vanhaecke, F., Yang, L., Willie, S., Sturgeon, R. E. (2010). “Laser ablation single-collector inductively coupled plasma mass spectrometry for lead isotopic analysis to investigate evolution of the Bilbilis mint” *Analytica Chimica Acta*, 677: 55-63.
  11. Vassileva, E., Hoenig, M. (2011). “Determination of the total and extractable mass fractions of cadmium and lead in mineral feed by using isotope dilution inductively coupled plasma mass spectrometry”. *Analytica Chimica Acta*, 701: 37-44.
  12. Djedjibegovic, J., Larssen, T., Skrbo, A., Marjanović, A., Sober, M. (2012). “Contents of cadmium, copper, mercury and lead in fish from the Neretva river (Bosnia and Herzegovina) determined by inductively coupled plasma mass spectrometry (ICP-MS)” *Food Chemistry*, 131: 469-476.
  13. Wang, Y., Gao, S., Zang, X., Li, J., Ma, J. (2012). “Graphene-based solid-phase extraction combined with flame atomic absorption spectrometry for a sensitive determination of trace amounts of lead in environmental water and vegetable samples” *Analytica Chimica Acta.*, 716: 112-118.
  14. Mirzajani, R., Pourreza, N., Kiasat, A. R., Najjar, S. S. (2013), “Application of  $\beta$ -cyclodextrin in polymeric solid phase for separation and determination of lead in different environmental matrices” *International Journal of Environmental Analytical Chemistry*, 93: 800-810.
  15. Hagarová, I., Bujdoš, M., Matúš, P., Kubová, J. (2013). “Coacervative extraction of trace lead from natural waters prior to its determination by electrothermal atomic absorption spectrometry” *Spectrochimica Acta Part B: Atomic Spectroscopy*, 88: 75-79.
  16. López-García, I., Vicente-Martínez, Y., Hernández-Córdoba, M. (2013). “Determination of lead and cadmium using an ionic liquid and dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry” *Talanta.* 110: 46-52.
  17. Dessuy, M. B., Vale, M. G. R., Welz, B., Borges, A. R., Silva, M. M., Martelli, P. B. (2011) “Determination of cadmium and lead in beverages after leaching from pewter cups using graphite furnace atomic absorption spectrometry” *Talanta.* 85: 681-686.
  18. Duarte, A. T., Dessuy, M. B., Silva, M. M., Vale, M. G. R., Welz, B. (2010).”Determination of cadmium and lead in plastic material from waste electronic equipment using solid sampling graphite furnace atomic absorption spectrometry” *Microchemical Journal*, 96: 102-107.
  19. Carletto, J. S., Carasek, E., Welz, B. (2011).” Hollow-fiber liquid-liquid-solid micro-extraction of lead in soft drinks and determination by graphite furnace atomic absorption spectrometry” *Talanta.* 84: 989-994.
  20. Boulkroune, N., Meniai, A. H. (2012).”Modeling Purification of Phosphoric Acid Contaminated with Cadmium by Liquid-liquid Extraction” *Energy Procedia.* 18: 1189-1198.
  21. X. Wen, Q. Deng, S. Ji, S. Yang, L. Peng, (2012). “Design of rapidly synergistic cloud point extraction of ultra-trace lead combined with flame atomic absorption spectrometry determination” *Microchemical Journal*, 100: 31-35.
  22. Citak, D., Tuzen, M. (2010),”A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry” *Food and Chemical Toxicology*, 48; 1399-1404.
  23. Bai, H., Zhou, Q., Xie, G., Xiao, J. (2010), “Temperature-controlled ionic liquid-liquid-phase microextraction for the pre-concentration of lead from environmental samples prior to flame atomic absorption spectrometry” *Talanta*, 80: 1638-1642.
  24. Abulhassani, J., Manzoori, J. L., Amjadi, M. (2010). “Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry” *Journal of Hazardous Materials*, 176: 481-486.
  25. Barciela-Alonso, M. C., Plata-García, V., Rouco-López, A., Moreda-Piñeiro, A., Bermejo-Barrera, P. (2014). “Ionic imprinted polymer based solid phase extraction for cadmium and lead pre-concentration/determination in seafood” *Microchemical Journal*, 114: 106-110.

26. Wadhwa, S. K., Tuzen, M., Kazi, T. G., Soylak, M., Hazer, B. (2014). "Polyhydroxybutyrate-b-polyethyleneglycol block copolymer for the solid phase extraction of lead and copper in water, baby foods, tea and coffee samples" *Food Chemistry*, 152: 75-80.
27. Sahmetlioglu, E., Yilmaz, E., Aktas, E., Soylak, M. (2014). "Polypyrrole/multi-walled carbon nanotube composite for the solid phase extraction of lead (II) in water samples" *Talanta*. 119: 447-451.
28. Nabid, M. R., Sedghi, R., Bagheri, A., Behbahani, M., Taghizadeh, M., Oskooie, H. A., Heravi, M. M. (2012). "Preparation and application of poly (2-amino thiophenol)/MWCNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction" *Journal of Hazardous Materials*, 203: 93-100.
29. Mashhadizadeh, M. H., Amoli-Diva, M., Shapouri, M. R., Afruzi, H. (2014). "Solid phase extraction of trace amounts of silver, cadmium, copper, mercury, and lead in various food samples based on ethylene glycol bis-mercaptoacetate modified 3-(trimethoxysilyl)-1-propanethiol coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles" *Food Chemistry*, 151: 300-305.
30. Hakami, T., Zhang, Y., Banks, C. J. (2012). "Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of Hg from water" *Water Research*, 46: 3913-3922.
31. Madrakian, T., Afkhami, A., Zolfigol, M. A., Ahmadi, M., Koukabi, N. (2012). "Application of Modified Silica Coated Magnetite Nanoparticles for Removal of Iodine from Water Samples" *Nano-Micro Letter* 4: 57-63.
32. Anbia, M., Lashgari, M. (2009). "Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media" *Chemical Engineering Journal*, 150: 555-560.
33. Wang, J., Zheng, S., Liu, J., Xu, Z. (2010). "Tannic acid adsorption on amino-functionalized magnetic mesoporous silica" *Chemical Engineering Journal* 165: 10-16.
34. Cestari, A. R., Vieira, E. F. S., Vieira, G. S., Costa, L. P., Tavares, A. M. G., Lohb, W., Airoidi, C. (2009). "The removal of reactive dyes from aqueous solutions using chemically modified mesoporous silica in the presence of anionic surfactant—The temperature dependence and a thermodynamic multivariate analysis" *Journal of Hazardous Materials*, 161: 307-316.
35. Wang, J., Zheng, C., Ding, S., Ma, H., Ji, Y. (2011). "Behaviors and mechanisms of tannic acid adsorption on an amino-functionalized magnetic nano-adsorbent" *Desalination*, 273: 285-291.
36. Tan, Y., Chen, M., Hao, Y. (2012). "High efficient removal of Pb (II) by amino-functionalized Fe<sub>3</sub>O<sub>4</sub> magnetic nano-particles" *Chemical Engineering Journal*, 191: 104-111.
37. Hao, Y. M., Chen, M., Hu, Z. B. (2010). "Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles" *Journal of Hazardous Materials*, 184: 392-399.
38. Wang, J., Zheng, S., Shao, Y., Liu, J., Xu, Z., Zhu, D. (2010). "Amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal" *Journal of Colloid and Interface Science*, 349: 293-299.
39. Fu, X., Chen, X., Wang, J., Liu, J. (2011). "Fabrication of carboxylic functionalized superparamagnetic mesoporous silica microspheres and their application for removal basic dye pollutants from water" *Microporous and Mesoporous Materials*, 139: 8-15.
40. Peng, X., Xu, F., Zhang, W., Wang, J., Zeng, C., Niu, M., Chmielewska, E. (2014). "Magnetic Fe<sub>3</sub>O<sub>4</sub> @ silica-xanthan gum composites for aqueous removal and recovery of Pb<sup>2+</sup>" *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 443: 27-36.
41. Mahmed, N., Heczko, O., Lancok, A., Hannula, S-P. (2014). "The magnetic and oxidation behavior of bare and silica-coated iron oxide nanoparticles synthesized by reverse co-precipitation of ferrous ion (Fe<sup>2+</sup>) in ambient atmosphere" *Journal of Magnetism and Magnetic Materials*, 353: 15-22.
42. Sun, N., Deng, C., Liu, Y., Zhao, X., Tang, Y., Liu, R., Xia, Q., Yan, W., Ge, G. (2014). "Optimization of influencing factors of nucleic acid adsorption onto silica-coated magnetic particles: Application to viral nucleic acid extraction from serum" *Journal of Chromatography A*, 1325: 31-39.
43. Yang, D., Wei, K., Liu, Q., Yang, Y., Guo, X., Rong, H., Cheng, M. L., Wang, G. (2013). "Folic acid-functionalized magnetic ZnFe<sub>2</sub>O<sub>4</sub> hollow microsphere core/mesoporous silica shell composite particles: Synthesis and application in drug release" *Materials Science and Engineering: C*, 33: 2879-2884.
44. Javidi, J., Esmaeilpour, M. (2013). "Synthesis of Fe<sub>3</sub>O<sub>4</sub>@silica/poly (N-isopropylacrylamide) as a novel thermo-responsive system for controlled release of H3PMo12O40 nano drug in AC magnetic field" *Colloids and Surfaces B: Biointerfaces*, 102: 265-272.
45. Safavi, A., Banazadeh, A., Sedaghati, F. (2013). "Synthesis of palladium nanoparticles on organically modified silica: Application to design of a solid-state electrochemiluminescence sensor for highly sensitive determination of imipramine" *Analytica Chimica Acta*, 796: 115-121.

46. Cheng, G., He, M., Peng, H., Hu, B. (2012). "Dithizone modified magnetic nanoparticles for fast and selective solid phase extraction of trace elements in environmental and biological samples prior to their determination by ICP-OES" *Talanta*, 88: 507-515.
47. Safavi, A., Maleki, N., Iranpoor, N., Firouzabadi, H., Banazadeh, A. R., Azadi, R., Sedaghati, F. (2008). "Highly efficient and stable palladium nanocatalysts supported on an ionic liquid-modified xerogel" *Chemical Communication*, 6155-6158.
48. Du, X., He, J., Zhu, J., Sun, L., An, S. (2012). "Ag-deposited silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles catalyzed reduction of p-nitrophenol" *Applied Surface Science*, 258: 2717-2723.
49. Caruntu, D., Caruntu, G., Chen, Y., Connor, C. J. O., Goloverda, G., Kolesnichenko, V. L. (2004). "Synthesis of Variable-Sized Nanocrystals of Fe<sub>3</sub>O<sub>4</sub> with High Surface Reactivity" *Chemistry of Material.*, 16: 5527-5534.