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The Use of Non-Modified Magnetic Nanoparticles for Fast and Efficient Separation and Preconcentration of Trace Amounts of Cadmium (II) Ions from Food and Water Samples

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ABSTRACT

A new method for the separation and preconcentration of trace amounts of cadmium in food and water samples by magnetic solid phase extraction (MSPE) with Fe_3O_4 magnetic nanoparticles (Fe_3O_4-MNPs) and its determination by flame atomic absorption spectrometry has been developed. For this purpose, Fe_3O_4-MNPs were synthesized via chemical precipitation method. The extraction of cadmium ions from the aqueous solution was performed with dithizone (DTZ) as the chelating agent. The various parameters affecting the extraction and preconcentration of cadmium were investigated and optimized. In this method, the analyte ions were quantitatively adsorbed on Fe_3O_4-MNPs and then, Fe_3O_4-MNPs were easily separated from the aqueous solution by applying an external magnetic field. After extraction and collection of Fe_3O_4-MNPs, the analyte ions were eluted using 1.0 mol L^{-1} HNO_3 in methanol. Under the optimal conditions, the calibration curve showed an excellent linearity in the concentration range of 0.3–24.0 µg L^{-1} and the limit of detection was 0.1 µg L^{-1} of cadmium. The developed method was successfully applied to the determination of cadmium in food and water samples. The results show that, magnetic nanoparticles can be used as a cheap and efficient adsorbent for the extraction and preconcentration of cadmium from real samples for Loratadine.

KEYWORDS: Magnetic Solid Phase Extraction; Fe_3O_4 Magnetic Nanoparticles; Cadmium; Food and Water Samples.

1. INTRODUCTION

Cadmium is a very toxic metal which naturally exists as a contaminant of zinc, copper and lead ores as well as phosphate rock. Cadmium is also a component of alloys, protective metal plating, dental materials, pigments and nickel–cadmium batteries. Cadmium is not regarded as essential to human life and is known to damage organs including the kidneys, liver and lungs [1]. According to World Health Organization (WHO) the upper permissible level of cadmium in drinking water is 3.0 µg L^{-1} [2]. Consequently, the determination of this element, at trace level, in food and water samples is of great interest from public health and environmental point of view.

In spite of the increase in sophisticated analytical instrumentation aiming to improve the detection limits, many methods for metal determination at µg L^{-1} levels are still commonly performed using preconcentration procedures associated with techniques with moderate detectability such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) [3]. Among peconcentration methods, adsorption has increasingly received more attention in recent years because it is simple, relatively low-cost, and effective in removing heavy metal ions from wastewaters [4]. Several adsorbent materials, such as activated carbon [5], zeolites [6], functionalized polymers [7] and those based on Amberlite immobilized with chelating agents [8], as well as ionexchange resins [9] have been used for preconcentration purposes. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of enough active surface sites) or have shown problems like high cost, difficulties of separation from wastewater or generation of secondary wastes.

Recently, adsorption using magnetic nano-sized adsorbents has attracted significant attention due to its specific characteristics [10-12]. It adopts magnetic particles as sorbents, which endow some unique features in extraction. For instance, after extraction, the magnetic particles can be readily isolated from sample matrix with a magnet. Compared with isolation of conventional sorbents by filtration or centrifugation, magnetic isolation is obviously much more convenient, economic and efficient. In addition, in MSPE, the sorbents are universally dispersed into sample solution to achieve extraction. In such a dispersive mode, the contact area between the sorbents and the analytes is large enough to ensure a fast mass transfer, which is beneficial to guarantee high extraction efficiency of this method. Moreover, MSPE is suitable for direct analysis of samples containing particles or microorganisms, which widely exist in environmental or biological matrices and may arouse blockage and lead to extraction failure on conventional SPE cartridges. Magnetic nano-adsorbents have the advantages of both magnetic separation techniques and nano-sized materials, which can be easily recovered or manipulated with an external magnetic field. Moreover, the incorporation of magnetic particles with other functionalized materials such as multi-walled carbon nanotubes (MWCNT) [13], zeolites [14], activated carbon [15] etc., which are effective for the removal of both organic and inorganic pollutants is potentially a promising method to facilitate the separation and recovery of the adsorbents. All of these merits render MSPE a promising technique for sample preparation.

(Fe_3O_4-MNPs) are magnetic iron oxides that have a super paramagnetic behavior under certain particle sizes, which can be easily magnetized with an external magnetic field and redispersed immediately, once the magnetic field is removed [16]. Fe_3O_4-MNPs have been widely used in various industrial products, such as pigments, recording materials, printing and electro photography, copying toner and carrier powders, etc. [17], due to their excellent physicochemical properties. In recent years, Fe_3O_4-MNPs have been used in the separation of trace organic compounds and metal ions in various samples [18-19].

In this study, Fe_3O_4-MNPs were synthesized and were employed as an SPE adsorbent for separating and concentrating trace amounts of cadmium from food and water samples. Cadmium was then determined by flame atomic absorption spectrometry (FAAS). FAAS is used for determination because of its fast analysis time, relative simplicity and lower cost. In the current study, the effect of different experimental conditions on the preconcentration and separation of cadmium was investigated. Under the optimum conditions, the developed method was used for the preconcentration, separation and determination of cadmium from food and water samples with satisfactory results.

2. EXPERIMENTAL

2.1. Chemicals and Materials

All chemicals were of analytical reagent grade. Stock standard solution (1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3) of cadmium was prepared using $Cd(NO_3)_2$, $4H_2O$ that was obtained from Merck (Darmstadt, Germany). The working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution with deionized water. Other reagents used namely ferric chloride ($FeCl_3$, $6H_2O$), ferrous chloride ($FeCl_2$, $4H_2O$), dithizone (DTZ), sodium hydroxide, hydrochloric acid, nitric acid, ethanol, methanol, acetone and sodium nitrate were obtained from Merck (Darmstadt, Germany). A solution of 1×10^{-2} mol L^{-1} DTZ was prepared by dissolving an appropriate amount of DTZ in methanol. All glassware was rinsed with deionized water, decontaminated for at least 24 h in 10 % (v/v) nitric acid solution and rinsed again five times with deionized water.

2.2. Instruments

A SensAA (GBC, Australia) atomic absorption spectrometer equipped with deuterium background correction and cadmium hollow cathode lamp was used for the determination of cadmium at a wavelength of 228.8 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. The pH-meter model 827 from Metrohm (Herisau, Switzerland) with combined glass electrode was used for pH measurements. A stirrer model 1203 from Jenway (Leeds, UK) was applied to stir solutions in the preparation of Fe_3O_4-MNPs step with a magnet. Magnetic separation was carried out with a strong super magnet with a 1.4 T magnetic field (5×5×4 cm). A shaker (Jal Tajhiz model JTSL20, Iran) was applied for shaking the solutions. X-ray powder diffraction (XRD) measurements were performed using a Bruker diffractometer model D8 Advance (Germany) with mono chromatized Cu kα radiation. The morphology of synthesized samples was characterized with Tescan scanning electron microscope (SEM) model Vega II (Brno, Czech) .

2.3. Synthesis of Fe_3O_4-MNPs nanoparticles

Fe_3O_4-MNPs were prepared by chemical coprecipitation method [19]. During the whole process, the solution temperature was maintained at 80°C and nitrogen gas was used to prevent the intrusion of oxygen. The bubbling of nitrogen gas through the solution protects Fe_3O_4-MNPs against critical oxidation and reduces the particle size when compared to synthesis methods without oxygen removal [20]. the obtained Fe_3O_4-MNPs were separated from the reaction medium by a magnetic field (with 1.4 T magnetic strength) and then were washed with 500 mL deionized water two times. Finally, the obtained Fe_3O_4-MNPs were resuspended in 500 mL of degassed deionized water. The pH of suspension after the washings was 11.0 and concentration of the generated Fe_3O_4-MNPs in suspension was estimated to be about 10 g L^{-1}. The obtained Fe_3O_4-MNPs were stable in this condition up to one month.

2.4. Sample preparation

Spinach, lettuce and radish samples were purchased from the local supermarket at Sari in Iran. First, spinach sample was cleaned with tap water and deionized water. Then, this sample was dried at 110°C. The dried sample was ground to reduce particle size and then thoroughly mixed to ensure the homogeneity of the sample. A mass of 500 mg of spinach was transferred into a 250 mL beaker and 5 mL of 0.5 mol L^{-1} nitric acid was added to moisten the sample thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate

(130°C) for 3 h. After cooling to room temperature, 5 mL of concentrated perchloric acid was added drop wise. The beaker was heated gently until the completion of sample decomposition resulting in a clear solution. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 mol L^{-1} nitric acid and the solution was filled to the mark with the same acid [21]. The same method was done for the preparation of lettuce and radish samples.

2.5. Extraction procedure

The extraction procedure was carried out in a batch process. All standards and samples were prepared for analysis according to the following procedure. 200 mL of sample containing analyte, 2.0×10^{-2} mol L^{-1} acetate buffer (pH=5), 8.0×10^{-5} mol L^{-1} DTZ and 50 mg Fe_3O_4-MNPs were placed in a beaker and shook for 5 min. Then, the beakers were placed on the magnet and the nanoparticles were collected. After decanting the supernatant solution, the collected Fe_3O_4-MNPs were washed with 3.0 mL of 1.0 mol L^{-1} HNO_3 in methanol solution in order to elute the adsorbed analyte. Then, cadmium in the eluent was determined by FAAS. The percent extraction (E (%)) of cadmium was calculated from the following equation:

$$E(\%) = 100 \times (Co.Vo) / (Caq.Vaq) \qquad \text{(Eq. 1)}$$

where Caq and Co are the concentrations of cadmium ions before and after the extraction in the solution and Vaq and Vo are the volume of aqueous solution and organic solution.

3. RESULTS AND DISSCUTIONS

The extraction efficiency depends on some important experimental parameters. In order to obtain the maximal extraction efficiency, various parameters such as sample pH, DTZ concentration, amounts of adsorbent, type and concentration of eluent, extraction time and ionic strength were investigated in detail. Triplicate extractions were performed for all experiments and the average of these results was reported in figures or tables. Finally, these optimal conditions were applied to extract and detect cadmium in food and various water samples.

3.1. Characterization of the Fe_3O_4-MNPs

Characterization of Fe_3O_4-MNPs was studied using XRD and SEM. Fig. 1 shows the XRD pattern of the synthesized Fe_3O_4-MNPs, which was quite identical to pure Fe_3O_4-MNPs and matched well with its (JCPDS No. 19-629) XRD pattern, Indicating that the sample has a cubic crystal system. Also, we can see that no characteristic peaks of impurities were observed.

SEM image of the prepared Fe_3O_4-MNPs was obtained as shown in Fig. 2. Fe_3O_4 surface morphology analysis demonstrated the agglomeration of many ultrafine particles with a diameter of about 40 nm.

The FT-IR spectra of Fe_3O_4-MNPs before and after adsorption of Cd-DTZ complex are shown in Fig. 3. As could be seen, S–H bond stretching vibration around 1998.12 cm^{-1} and S–C=N bond stretching vibration around 1380.94 cm^{-1} was obviously observed in the FT-IR spectra of Cd-DTZ adsorbed on Fe_3O_4-MNPs, indicating that Cd-DTZ has been successfully adsorbed on surface of the Fe_3O_4 magnetic nanoparticles.

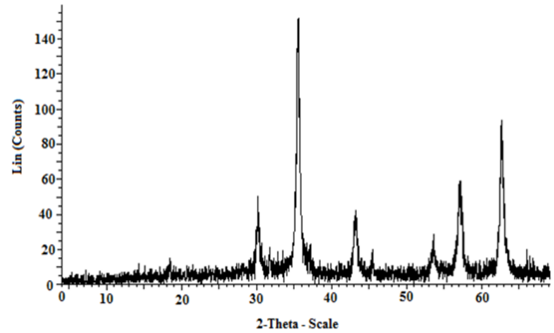

Fig. 1. XRD pattern of synthesized Fe_3O_4-MNPs.

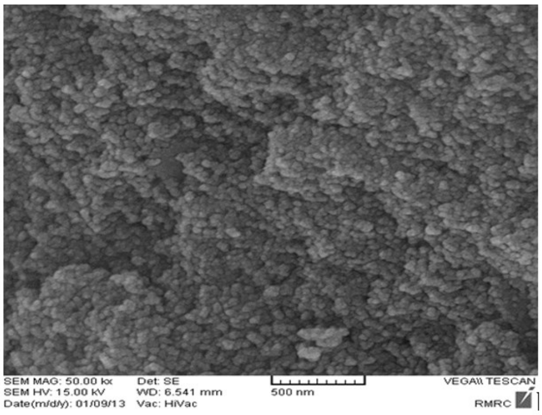

Fig. 2. SEM image of synthesized Fe_3O_4-MNPs.

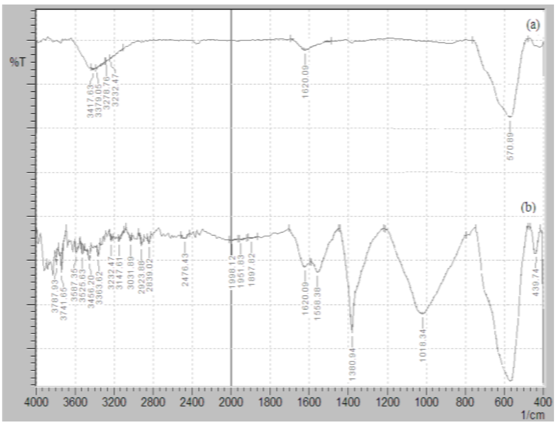

Fig. 3. The FT-IR spectra of Fe_3O_4-MNPs (a) before and (b) after adsorption of Cd-DTZ complex.

3.2. The Effect of pH

Since the pH of the aqueous sample solutions plays a unique role in metal chelate formation and is an important analytical factor in SPE, the adsorption of cadmium by Fe_3O_4-MNPs was investigated at pH range of 1-11. The pH of sample solutions was adjusted by NaOH and HNO_3. The results illustrated in Fig. 4 reveal that the recovery is nearly constant in the pH range of 3-6. At the pH values below 3, however, the percent recovery decreased, most probably due to the competition of H^+ with Cd^{2+} for DTZ and the formation of acidic form of DTZ that prevents Cd^{2+} from extraction. This phenomenon has been used for back extraction of cadmium ions. Accordingly, further studies were done at pH 5 using a 1.0 mol L^{-1} acetate buffer solution. Additional experiments on the volume of buffer showed that 4 mL of buffer solution give the best results. Therefore, 4 mL of 1.0 mol L^{-1} acetate buffer solution were used in all subsequent experiments.

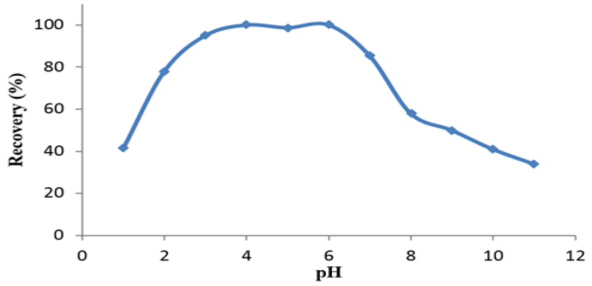

Fig. 4. The effect of pH on recovery of cadmium. (Sample volume: 200 mL; DTZ: 8.0×10^{-5} mol L^{-1}; Fe_3O_4-MNPs: 50 mg; Cd: 10 μg L^{-1}).

3.3. The Effect of DTZ concentration

The influence of the amount of DTZ was also evaluated in the range of 0.0 – 1.0×10^{-4} mol L^{-1}. The results are shown in Fig. 5. It was observed that cadmium extraction improved, by increasing the DTZ concentration, up to 5.0×10^{-5} mol L^{-1} and remained constant. Lower extraction recovery at a concentration below 5.0×10^{-5} mol L^{-1} is due to insufficient DTZ concentration and incomplete formation of the complex. No significant changes were observed when higher concentrations of DTZ were employed. Thus, 8.0×10^{-5} mol L^{-1} DTZ was chosen as the optimum to account for other extractable species.

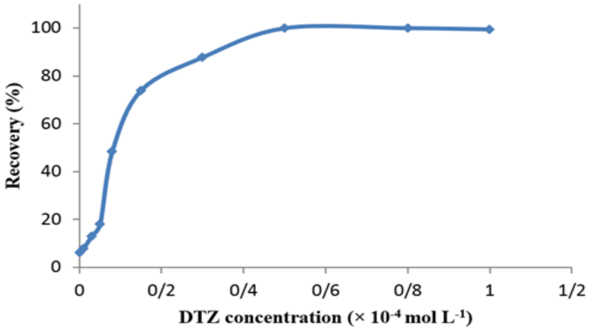

Fig. 5. The effect of DTZ concentration on recovery of cadmium. (Sample volume: 200 mL; pH: 5; Fe_3O_4-MNPs: 50 mg; Cd: 10 μg L^{-1}).

3.4. The Effect of adsorbent amounts

To choose the optimum amount of the adsorbent, the amount of the Fe_3O_4-MNPs required for the quantitative extraction of cadmium was investigated with the extraction time of 5 min. According to the results shown in Fig. 6, among the amounts investigated, i.e., 1, 5, 10, 20, 30, 40, 50, 60, 80 and 100 mg, the maximum extraction efficiency was obtained in the range of 30-50 mg of Fe_3O_4-MNPs. When the amount of the adsorbents was above 50 mg, the extraction recovery decrease probably because of difficulty in desorption of cadmium from Fe_3O_4-MNPs. Therefore, 50 mg Fe_3O_4-MNPs was selected as optimum. The results proved that the adsorbent has a high adsorption capacity and good extraction efficiency can be achieved by using only a small amount of the sorbent.

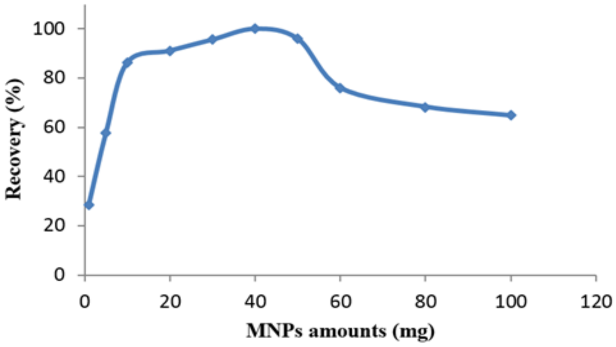

Fig. 6. The effect of MNPs amounts on recovery of cadmium. (Sample volume: 200 mL; pH: 5; DTZ: 8.0×10^{-5} mol L^{-1}; Cd: 10 μg L^{-1}).

3.5. The effect of type, concentration and volume of eluent

Since high extraction efficiency was achieved by the current method, an efficient back extraction stage for the stripping of cadmium from MNPs is required [30]. Several stripping solutions including 0.1 and 1.0 mol L^{1} HNO_3; 0.1 and 1.0 mol L^{-1} HNO_3 in ethanol and 0.1 and 1.0 mol L^{-1} HNO_3 in methanol were examined (Fig. 7). However, in this study, the 1.0 mol L^{-1} HNO_3 in methanol was the best eluent.

In a complementary experiment, the effect of volume of 1.0 mol L^{-1} HNO_3 in methanol in the quantitative stripping of cadmium from the MNPs was investigated. The stripping was conducted using 1.0, 2.0, 3.0, 4.0 and 5.0 mL portions of 1.0 mol L^{-1} HNO_3 in methanol. A 3.0 mL solution of 1.0 mol L^{-1} HNO_3 in methanol was sufficient for the full stripping of the cadmium.

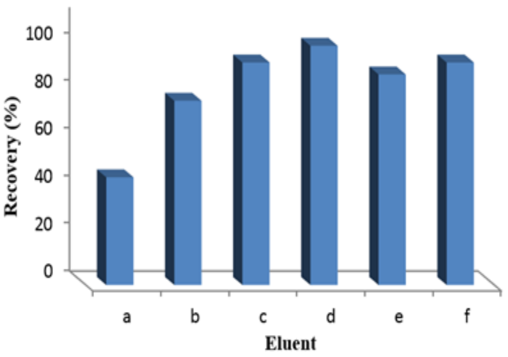

Fig. 7. The effect of eluent type and concentration on recovery of cadmium. ((a and b) HNO_3 0.1 and 1.0 mol L^{-1}; (c and d) HNO_3 in methanol 0.1 and 1.0 mol L^{-1}; (e and f) HNO_3 in ethanol 0.1 and 1.0 mol L^{-1}; Sample volume: 200 mL; pH: 5; DTZ: 8.0×10-5 mol L^{-1}; Fe_3O_4-MNPs: 50 mg; Cd: 10 μg L^{-1}).

3.6. The Effect of equilibrium time

Compared to ordinary sorbents (microsized adsorbents), NPs offer a significantly higher surface area-to-volume ratio and a short diffusion route, which results in high extraction capacity, rapid extraction dynamics and high extraction efficiencies. The effect of equilibrium time on the extraction of cadmium in the range of 2-15 min was studied. Results showed that 2 min provided quantitative extraction for cadmium. Therefore, to ensure complete extraction, 5 min was selected as the optimal equilibrium time.

3.7. The Effect of ionic strength

The influence of ionic strength (electrolyte concentration) on the extraction efficiency of cadmium ions was investigated in aqueous solutions containing various concentrations of sodium nitrate (0.0–25.0 %). Results showed that the quantitative extraction of cadmium was obtained in the 0.0–10.0 % $NaNO_3$ concentrations range. Lower extraction recovery at a concentration above 10% could be attributed to two reasons: Firstly, a decreasing electrolyte concentration favored the complexation tendency of cadmium ions with the functional groups of DTZ, which enhances the adsorption process. Secondly, an increasing ionic strength of solution influenced the activity coefficient of metal ions that may have limited their transfer to the adsorbent surfaces [22]. Thus, the strategy of no salt addition was selected for all experiments.

3.8. Breakthrough volume

The effect of sample volume on the adsorption of cadmium ions was studied in the range of 25-500 mL. In order to study the sample volume effect, 30 µL of 1.0 mgL^{-1} cadmium ions was diluted to 25, 50, 75, 100, 150, 200, 250, 350 and 500 mL with deionized water. Then adsorption and desorption processes were performed under the optimum conditions (pH 5, agitation time of 5 min) using 50 mg adsorbent. The results are shown in Fig. 8. It was observed that the cadmium ions present in various volumes of the solution in the range of 25-200 mL were completely and quantitatively adsorbed (>96%) with Fe_3O_4-MNPs. The adsorption then decreased at higher volumes. Therefore, for the determination of trace quantities of cadmium in food and water samples, a sample volume of 200 mL was selected. With respect to eluent volume (3.0 mL), a 66.7 preconcentration factor (the ratio of the highest sample volume to the lowest eluent volume) for the analyte ions was obtained.

3.9. Matrix effects

In order to investigate the selectivity of the developed method for the determination of cadmium, the effect of coexisting ions on the recovery of cadmium complex was evaluated. For this purpose, 200 mL of sample solutions containing 10 µg L^{-1} of cadmium and different quantities of coexisting ions were treated in accordance with the recommended procedure. An ion was considered to be interfering when it caused a variation greater than ± 5 % in the absorption of the sample. The results (Table 1) indicate that cadmium recoveries are almost quantitative in the presence of interfering ions.

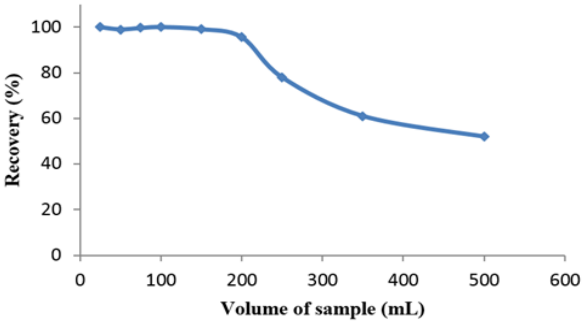

Fig. 8. The effect of volume of sample on recovery of cadmium. (pH: 5; DTZ: 8.0×10^{-5} mol L^{-1}; Fe_3O_4-MNPs: 50 mg; Cd: 10 µg L^{-1}).

Table 1. Effect of interfering ions on the extraction of cadmium

Interfering ions	Ion/Cd(II) ratio (w/w)	Recovery (%)
K^+, Na^+, Li^+ , Ca^{2+}, Ba^{2+}, Mg^{2+}, Br^-, F^-, I^-, Cl^-, NO_3^-	1000	99
PO_4^{3-}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}, CO_3^{2-}, As^{3+}, Cr (VI)	100	98
Fe^{3+}, Pb^{2+}, Ag^+	80	99
Fe^{2+}	50	100
Hg^{2+}	30	100
Cu^{2+}	10	98

3.10. Adsorption capacity

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ion from the solutions. The adsorption capacity was tested following the batch procedure. 50 mg of sorbent was equilibrated with 50 mL of solution containing 5 mg of cadmium, 8.0×10^{-5} mol L^{-1} DTZ and 2.0×10^{-2} mol L^{-1} acetate buffer, for 1 h. Then the mixture was filtered. 1.0 mL of the supernatant solution was diluted to 50.0 mL, then, the cadmium concentration was determined by FAAS. The capacity of the sorbent for cadmium was found to be 26.5 mg g^{-1}.

3.11. Figures of merit

The analytical performance of MSPE coupled with FAAS for the preconcentration and determination of cadmium was systematically investigated under optimized experimental conditions (Table 2). The results exhibited that there was an excellent linear correlation between the absorbance and the concentration of cadmium from 0.3 to 24.0 µg L^{-1} and a good correlation coefficient of 0.9988. The precision of this method was 2.6 % (RSD, n = 10) at the spiked concentration of 10 µgL^{-1}. The detection limit (calculated as the concentration corresponding to three times the standard deviation of 10 runs of the blank samples) of the proposed method was 0.1 µg L^{-1}. The preconcentration factor was 66.7 for 200 mL sample solution.

Table 2. Analytical characteristics of the method

Parameter	Analytical feature
Linear range, μg L^{-1}	0.3-24.0
Limit of detection, μg L^{-1} (n =10)	0.1
RSD [a] (%)	2.6
Preconcentration factor	66.7

[a] Cadmium concentration was 10 μg L^{-1} for which RSD was obtained

3.12. Comparison of the present method with other preconcentration methods

As shown in Table 3, in comparison with other reported methods, the proposed method has low LOD and a good preconcentration factor. The method developed in this work is proposed as a suitable alternative to more expensive instruments for cadmium determination at trace levels. This methodology is a reproducible, simple and low cost technique and does not require further instrumentation. These characteristics are of great interest for the routine laboratories in the trace analysis of metal ions.

3.13. Analysis of real samples

After the method was established, it was applied to determine cadmium concentration in food samples (spinach, lettuce and radish) as well as five kinds of water samples including tap, river, spring, mineral and sea water. All these samples were analyzed in triple replicates. The results are outlined in Table 4 and 5.

Before analysis, the collected water samples were filtered through a 0.45 µm Millipore membrane. The water samples were extracted using the proposed method and analyzed by FAAS. The results show that water samples were free of cadmium contamination. These samples were spiked with cadmium at different concentration levels to assess matrix effects. As can be seen from Table 4, the spiked recoveries were very good in the range of 93.0–102.7 %.

Table 3. Comparison of the presented method with other preconcentration methods for determination of cadmium

Method	LOD[a] (μg L^{-1})	R.S.D.[b] (%)	LDR[c]	PF[d]	Sample volume (mL)	Reference
On line-SPE-FAAS	0.11	4.1	1-50	38.4	-	23
On line-SPE-FAAS	0.25	2.2	1-30	50	10	24
SPE-ICP-OES	0.30	3.1	1-400	136[i]	47	25
SPE-FAAS	1.3	-	-	200	2000	26
SPE-FAAS	1.19	1.4	100-1500	100	500	27
SPE-FAAS	1.44	-	-	50	250	28
CPE[e]-ICP-OES	1.0	1.9	20-2000	9.36	15	29
CPE-FAAS	0.9	4	3-400	20	8	30
Coprecipitation-FAAS	0.27	7.2	20-2000	25	50	31
Coprecipitation-FAAS	0.34	10	-	50	100	32
Coprecipitation-FAAS	14.1	< 7	-	250	500	33
Coprecipitation-FAAS	2.0	-	-	100	200	34
SFOME[f]-FAAS	0.21	4.7	1-25	205[i]	100	35
UAEME[g]-ICP-OES	0.19	4.3	1-1000	17	-	36
MF[h]-FAAS	1.1	-	-	150	300	37
SPE-FAAS	0.1	2.6	0.3-24	66.7	200	This work

[a] Limit of detection, [b] Relative standard deviation, [c] Linear dynamic range, [d] Preconcentration factor, [e] Cloud point extraction, [f] Solidification of floating organic drop microextraction, [g] Ultrasound-assisted emulsification microextraction, [h] Membrane filtration, [i] Enhancement factor (the ratio of slopes of the preconcentration and direct calibration equations)

Table 4. Determination of Cadmium in water samples

Sample	Cadmium amount (μg L^{-1})		Recovery (%)
	Added	Found	
Tap water	0.0	n.d.[a]	–
(Drinking water system of Sari, Iran)	10.0	9.4 (2.5)[b]	94.0
	15.0	14.3 (2.5)	95.3
Spring water	0.0	n.d.	–
(Yakhkooh village spring, Savadkooh, Iran)	10.0	9.6 (2.6)	96.0
	15.0	14.6 (2.5)	97.3
Mineral water	0.0	n.d.	–
(Vata mineral water, Iran)	10.0	9.9 (2.7)	99.0
	15.0	14.7 (2.6)	98.0
River water	0.0	n.d.	–
(Siahrood river, Larim, Iran)	10.0	9.3 (3.1)	93.0
	15.0	14.2 (2.9)	94.7
Sea water	0.0	n.d.	–
(Caspian sea water, Noor, Iran)	10.0	10.1 (2.9)	101.0
	15.0	15.4 (3.0)	102.7

[a] Not detected, [b] RSD of three replicate experiments.

The results of the determination of cadmium in food samples are shown in Table 5. Relative recoveries of cadmium from food sample at spiking levels of 0.60 and 1.20 µg g^{-1} were between 93.3 and 99.2%. These results demonstrate that these water and food matrices, in our present context, had little effect on the proposed method.

Table 5. Determination of cadmium in food sample

Sample	cadmium amount (µg g^{-1})		Recovery
	Added	Found	(%)
Spinach	0.00	1.20	–
	0.60	1.79 (2.9)[a]	98.3
	1.20	2.39 (2.7)	99.2
Lettuce	0.00	1.80	–
	0.60	2.37 (3.0)	95.0
	1.20	2.96 (2.6)	96.7
Radish	0.00	0.24	–
	0.60	0.80 (2.7)	93.3
	1.20	1.37 (2.9)	94.2

[a] RSD of three replicate experiments

4. CONCLUSIONS

In the present work, the non-modified Fe_3O_4 NPs were successfully synthesized and used for the preconcentration and determination of cadmium ions in food and water samples by applying SPE method. Compared to traditional SPE methods with microsized sorbent materials, these types of SPE methods have advantages such as low time-consuming, higher surface areas of adsorbent and easy synthesizing of adsorbent. Due to very high surface areas, short diffusion route and magnetically-assisted separability of the Fe_3O_4 NPs, high adsorption capacities can obtain in a very short time. For cadmium ions, the detection limit obtained was 0.1 µg L^{-1}. The preconcentration factor of the proposed method was 66.7 and the RSD (C=10 µg L^{-1}, n=10) was 2.6 %. The results showed that our proposed SPE method can be used successfully for sensitive, simple and rapid extraction and determination of cadmium ions from food and water samples.

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