Solid phase extraction and trace monitoring of cadmium ions in environmental water and food samples based on modified magnetic nanoporous silica

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A R T I C L E   I N F O
Article history:
Received 18 June 2015
Received in revised form 14 July 2015
Accepted 25 July 2015
Available online 29 July 2015
Keywords:
Pyridine-functionalized magnetic mesoporous silica
Solid phase extraction
Cadmium ions
Environmental samples

A B S T R A C T
A new method has been developed for trace separation/preconcentration of cadmium ions using pyridine-functionalized magnetic nanoporous silica material (called Py-Fe3O4@MCM-41) as a new magnetic sorbent and their determination by flame atomic absorption spectrometry (FAAS). The Py-Fe3O4@MCM-41 sorbent was characterized by thermogravimetric analysis, differential thermal analysis, transmission electron microscopy, Fourier transform infrared spectrometry and X-ray diffraction. The modified Fe3O4@MCM-41 can be easily separated from an aqueous solution by applying an external magnetic field. Effects of pH, amount of functionalized Fe3O4@MCM-41, extraction time, type and quantity of eluent, desorption time, and interfering ions on the extraction efficiency were evaluated and optimized. Under the optimized conditions, the detection limit and relative standard deviation was 0.04 μg L−1 and 2.9%, respectively and the maximum adsorption capacity of the synthesized sorbent for cadmium ions was 154 mg g−1. The proposed method has been applied to the determination of Cd ions at trace levels in real samples such as, rice, onion, carrot, lettuce, parsley, basil, tap water, river water and seawater with satisfactory results.

1. Introduction
Cadmium is among thirteen toxic metal species on the priority pollutant list of the Environmental Protection Agency (EPA) [1,2]. Cadmium presence in biosphere is related to both natural (mainly volcanic activity and rock weathering) and anthropogenic emission sources. Elevated cadmium concentration in waters, soil and as a consequence in food is caused by its various applications in many branches of industry. The metal is used in electroplating, in nickel–cadmium batteries, alloys and as a coating for other metals. Cadmium compounds have been mainly applied as pigments, they are also used as semiconductors [3]. Exposure to cadmium has been proved to have adverse effect on heart, lungs, bones and especially kidneys. Having been accumulated in liver and kidneys it is excreted very slowly and the process may last even for 20–30 years [4,5]. Moreover, cadmium has been classified as a carcinogen (Group IA) by International Agency for Research on Cancer [6]. Due to its toxicity both to humans and animals cadmium concentration in the environment should be monitored, hence appropriate guideline values for cadmium content have been introduced; for drinking water they are as follow:

WHO 3 μg L−1 [7], EU 5 μg L−1 [8], US EPA 5 μg L−1 [9]. For many years flame atomic absorption spectrometry (FAAS) has been a standard analytical tool for determination of metals in various matrices owing to its wide application range, simplicity in operation and low cost of analysis [10]. However, cadmium content in many natural water samples is frequently below the quantification limit achieved with this technique; therefore introducing a preconcentration step prior to FAAS determination is required.

Solid phase extraction (SPE) is an efficient separation-preconcentration technique for heavy metals since it has many important advantages including simplicity, flexibility, economic, rapid, and higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, and more importantly it is environment friendly. Various SPE materials have been

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successfully used for preconcentration and separation of heavy metal ions at trace levels [11–19].

Since the synthesis of M41S materials in 1992, mesoporous silica materials, due to their high surface areas, well-defined pore size, and tunable pore sizes, have been widely utilized in the field of adsorption of heavy metal ions [20–24]. Many efforts have been devoted to synthesis, characterization, and applications of mesoporous silica materials. However, mesoporous silica powders are difficult to be separated and recovered because of their small sizes, which hinder their utilization in liquid–solid processes. On the other hand, magnetic nanoparticles have been intensively investigated in recent years [25–28]. A novel material can be obtained by combining mesoporous silica materials with magnetic nanoparticles. Through a magnetic field, the magnetic mesoporous silica can be easily separated and recovered in liquid–solid processes.

In the present study, the synthesized modified magnetic nanoporous silica (Py-Fe3O4@MCM-41) was used for selective solid phase extraction and ultra-trace determination of cadmium ions in environmental water and food samples. The mentioned sorbent was characterized using transmission electron microscopy (TEM), thermal analysis (TGA/DTA), Fourier transform infrared spectrometry (FT-IR), and X-ray diffraction (XRD).

2. Experimental

2.1. Reagents and materials

All analytical grade reagents were purchased from Merck (Darmstadt, Germany, www.merck.de) or from Fluka (Buchs SG, Switzerland, www.sigmaaldrich.com) and used without further purification. 3-aminopropytriethoxysilane, oxalyl chloride and 4-pyridine carboxylic acid were purchased from Merck. Double-distilled water from a Millipore-Q purification system (Millipore, Bedford, MA, USA) was used for the preparation of solutions. A stock solution (100.0 mg L−1) of cadmium ions was prepared by dissolving an appropriate amount of corresponding nitrate salts in double-distilled water. Working standard solutions were prepared daily through serial dilutions of the stock solution with deionized water prior to analysis. Soil (NCS DC 73323) from Bulgaria was used as the reference material for validation of the proposed technique.

2.2. Apparatus

Cadmium concentration was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air–acetylene flame, according to the user’s manual, provided by the manufacturer. Cadmium hollow cathode lamps (HCL) was used as the radiation source with wavelengths of 283.3 nm. The pH was measured at 25 ± 1 °C with a digital WTW Metrohm 827 ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. IR spectra were recorded on a Bruker IFS-66FT-IR Spectrophotometer. Transmission electron microscopy (TEM) analysis was performed on a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a STOE diffractometer with Cu Kα radiation (λ=1.5418 Å). Thermal analysis (TGA-DTA) was carried out on a Bahr STA-503 instrument in air at a heating rate of 10 °C/min. 1H spectrum was recorded on a Bruker AVANCE 300-MHz instrument using TMS as internal reference. Data for 1H NMR are reported as follows: multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet).

2.3. Synthesis of MCM-41

MCM-41 mesoporous silica was prepared by sol–gel method according to previous report [29] and its formation was confirmed by low angle X-ray powder diffraction.

2.4. Synthesis of Fe3O4@MCM-41

For synthesis of Fe3O4@MCM-41, the prepared mesoporous material was added while preparing Fe3O4. In a typical procedure, 0.07 g of FeCl3 and 0.043 g of FeCl2.4H2O were dissolved in 30 mL of deionized water, degassed with nitrogen gas for 15 min and heated to 80 °C. Then, 0.13 mL of NH4OH (25% solution) was added drop-wise to the solution until the brown color solution turned to black. After that 0.5 g MCM-41 was added to the black solution and the reaction mixture was stirred at room temperature for 20 h. Then the solid phase was filtered and washed by deionized water, and the resulting black powder dried under room temperature. The synthesis of Fe3O4@MCM-41 was confirmed by FT-IR and low and high angle X-ray powder diffraction.

2.5. Synthesis of pyridine functionalizing agent

N-(3-(triethoxysilyl)propyl)isonicotinamide (TPI) was synthesized according to the previously reported procedure [30] and characterized by 1H NMR. Briefly, in a 250 mL round-bottomed two-necked flask equipped with a magnetic stirrer and a condenser, 5 g (40.5 mmol) of pyridinoic acid were suspended in 150 mL of dry CH2Cl2 at 0 °C under N2 atmosphere. A total of 10 mL of oxalyl chloride was slowly added from a dropping funnel. After 1 hour the reaction mixture was left to room temperature and held at the same temperature overnight. Then, the solvent was removed under reduced pressure, and the residue was suspended again in 150 mL of dry CH2Cl2. After the addition of 17 mL triethylamine to the suspended reaction system, 9 g 3-aminopropyltriethoxysilane was slowly added. The reaction mixture was stirred at room temperature for a further 4 h. The mixture was suspended in water to remove impurities. The organic phase separated and the solvent was removed under reduced pressure to obtain brownish viscous oil. The synthesis of TPI was confirmed by 1H NMR (CDCl3): 0.61 ppm (t, 2H), 0.61 ppm (t, 2H), 1.65 ppm (m, 2H), 3.36 ppm (m, 2H), 3.72 ppm (q, 6H), 7.24 ppm (s, 1H), 7.57 ppm (d, 2H), 8.60 ppm (d, 2H).

2.6. Synthesis of pyridine-functionalized Fe3O4@MCM-41 (Fe3O4@MCM-TPI)

0.1 g as-prepared Fe3O4@MCM-41 particles were first evenly dispersed in 50 mL toluene, and then added 1.0 g TPI and the mixture was refluxed for 24 h. The solid phase was filtered and washed 3-times with acetone (20 mL each) to remove impurities and dried at room temperature. The products obtained are referred to as Fe3O4@MCM_TPI sample. Fig. 1 provides a scheme for synthesis of the sorbent.

2.7. Extraction procedure

A portion of sample solution containing the studied ions was transferred to a 100 mL beaker, the pH values was adjusted to desired value by adding HCl or NaOH solution. Then, 10 mg of adsorbent was added, and the solution was shaken for 5 min to facilitate adsorption of the cadmium ions onto the modified Fe3O4@MCM-41. Then the magnetic adsorbent was separated easily and fast by using a strong flat permanent magnet and the supernatants were decanted directly. 5 mL deionized water was added for washing and then decanted directly. 1.0 mL of 1.0 mol L−1 HCl was
added as eluent and shaken for 5 min. Finally, the eluted ions were detected by FAAS. Fig. 2 provides a scheme to illustrate the extraction procedure for selective preconcentration of cadmium ions by proposed solid phase extraction method.

2.8. Sample pre-treatment for cadmium analysis

2.8.1. Rice, onion, carrot, lettuce, parsley and basil

Food products, including green tea, rice, tobacco, carrot, lettuce,
ginseng and spice were collected from an agricultural land in south of Tehran, Iran. All of the samples were stored in plastic bags and brought to the laboratory for preparation and treatment. After washing the samples with distilled water, 5.0 g of each sample was grounded, homogenized and dried at 80 °C and triturated in porcelain mortar. After fractionation of samples by sieving, sizes less than 20 μm were dissolved in 10 mL of 3 mol L\(^{-1}\) HNO\(_3\) solution and diluted with distilled water to a final volume of 100 mL, then the pH was adjusted to 7.0 for further experiments.

2.8.2. Tap, river and sea water
The sorbent was successfully used for determination of cadmium in tap, river (from Siahrood river) and sea water (Caspian sea water) samples. The polyethylene bottles filled with the samples were cleaned with detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm), and were acidified to pH of 2.0 for storage. Before analysis, the water samples (100 mL) were adjusted to pH of 7.0 according to optimized experimental conditions.

3. Results and discussion

3.1. Characterization of the multifunctional magnetic mesoporous composite

3.1.1. Morphology analysis
The synthetic strategy to prepare Fe\(_3\)O\(_4\)@MCM-41 with 10 wt% of loaded iron oxide nanoparticles is designed and presented in Fig. 1. This figure has three parts containing the synthesis of N-(3-(triethoxysilyl)propyl)isonicotinamide (TPI), the one of Fe\(_3\)O\(_4\)@MCM-41 and the reaction between them to prepare the perspective composite. Fig. 3 shows TEM images of the pyridine-functionalized Fe\(_3\)O\(_4\)@MCM-41. As seen in this figure, Fe\(_3\)O\(_4\) nanoparticles are placed on the surface of the MCM-41 support. Since the average size of magnetic nanoparticles (about 55 nm) are bigger than the pore size of MCM-41 (about 2–3 nm), so nanoparticles could not go into the pores [29,31]. Fig. 3 clearly exhibits that the mesoporous structure is maintained after condensation between OH groups on both MCM-41 and Fe\(_3\)O\(_4\) nanoparticles and modifying Fe\(_3\)O\(_4\)@MCM-41 with TPI. Although some OH groups on MCM-41 are utilized for condensation with OH groups on the surface of magnetic nanoparticles, there is still OH ones which are access for functionalizing by condensation between ethoxy of TPI and OH groups on MCM-41. As seen in scheme, pyridine agents could be placed on both Fe\(_3\)O\(_4\) nanoparticles and MCM-41 surface which cause the high loading on Fe\(_3\)O\(_4\)@MCM-41. In addition, the presence of Fe\(_3\)O\(_4\) in the resulting compound creates magnetic property which can be removed from the reaction system by an external magnetic field and the pyridine agents on it provide the opportunity to adsorb heavy metal ions.

3.1.2. Porosity and pore size
Low-angle XRD patterns of Fe\(_3\)O\(_4\)@MCM-41 before and after pyridine-modified exhibit a single and strong diffraction peak between 2θ = 0.5° and 2θ as seen in Fig. 4, indicating the presence of mesoporous structure. Due to the grafting of pyridine groups, the diffraction peak of Fe\(_3\)O\(_4\)@MCM-TPI shifts to higher angle and becomes weaker compared with that of unmodified one. These results indicate that the mesoporous phase of the composites has been maintained, while the integrity of the mesopore structure was affected by the incorporation of TPI functionalizing agent. Fig. 4(c) shows the wide-angle XRD patterns of pyridine-functionalized Fe\(_3\)O\(_4\)@MCM-41 compound. The broad band centered at 2θ = 22° can be assigned to the characteristic reflection from amorphous SiO\(_2\) (JCPDS 29-0085). The wide-angle XRD patterns show (220), (311), (400), and (440) diffraction peaks, which are in accordance with that of magnetite (Fe\(_3\)O\(_4\)) (JCPDS 19-0629). The broad nature of the XRD patterns can be ascribed to the small size of Fe\(_3\)O\(_4\) [32].

3.1.3. TGA and DTA curves
The thermal stability of Fe\(_3\)O\(_4\)@MCM_TPI composite was studied by carrying out TGA-DTA analysis. A weight loss occurred between 200 °C and 600 °C which is accompanied with exothermic peaks at 400 °C and 500 °C in DTA curve, is corresponded to the oxidative decomposition of organic part of N-[3-(triethoxysilyl)propyl]isonicotinamide (TPI). Furthermore, according to thermal analysis, the prepared composite is stable up to 200 °C. According to the weight of loss in TGA curve, the amount of pyridine introduced into Fe\(_3\)O\(_4\)@MCM-41 is 1.6 m mol g\(^{-1}\).

3.1.4. IR spectra
FTIR measurements were performed for Fe\(_3\)O\(_4\)@MCM-41 and Fe\(_3\)O\(_4\)@MCM_TPI as shown in Fig. 1S (Electronic Supplementary Materials (ESM)). Both spectra present the typical Si–O–Si bands of the inorganic framework: symmetric vibration modes around 960 cm\(^{-1}\), asymmetric stretching vibration around 1080–1100 cm\(^{-1}\) [33]. The absorption peak of the Si–OH bands at 960 cm\(^{-1}\) in Fe\(_3\)O\(_4\)@MCM-41 turns into a shoulder upon functionalization, indicating that the TPI agents are substituting surface silanols. In Fig. 1S (ESM) (a), the bands at around 1700 and 3400 cm\(^{-1}\) can be assigned to the H–O–H stretching modes and bending vibration of the free or absorbed water, respectively.

Furthermore, Fe–O and FeO–H stretching vibration bands of
nanoparticles Fe₃O₄ were detected at 456, and > 3200 cm⁻¹, respectively and the band at 570 cm⁻¹ is an indication of the presence of Si–O–Fe [34]. The presence of organic groups is confirmed by C–H aromatic, C–H aliphatic, C=O and C=N around 3050, 2900, 1650 and 1500 cm⁻¹ region respectively, broad N–H stretching bands superimposed to those of water, in the 3000–3500 cm⁻¹ range [35]. All these results show that pyridine groups have been successfully grafted to the surface of Fe₃O₄@MCM-41.

3.2. Optimization experiments

Extraction and preconcentration of cadmium ions on Py-Fe₃O₄@MCM-41 were highly dependent on the different parameters such as pH of the sample, extraction time, type, volume and concentration of eluent, desorption time, and concentration of potentially interfering ions. In this context, the procedure was optimized for the various analytical parameters.

3.2.1. Effect of pH

To study the effect of pH on the extraction, the pH of 25 mL of different sample solutions containing 1 mg L⁻¹ cadmium was adjusted in the range of 2–9. As shown in Fig. 5A, the adsorption of cadmium ions by the sorbent increased from pH 2.0 to 7.0 but decreased slightly from pH 7.0 to 9.0. By decreasing the pH value of the solution, the quantitative removal of the target ions was also decreased due to electrostatic repulsion of the protonated active sites on the sorbent with the positively charged cadmium species. Meanwhile, the observed decrease in retention percentage of cadmium ions on the sorbent at the pH values higher than 7.0, is most probably due to the precipitation of cadmium ions in the hydroxide form, which leads to decreasing the concentration of free cadmium ions in sample. Thus, the pH of 7.0 was chosen as the optimum pH for further experiments.

3.2.2. Effect of the adsorbent amounts

Compared to conventional sorbents (micron-sized adsorbents), magnetic mesoporous materials 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. Also, Py-Fe₃O₄@MCM-41 can be rapidly collected from sample solution by applying magnetically assisted separation, thus shorter extraction times can be achieved. Therefore, satisfactory results can be obtained with fewer amounts of these adsorbents. For the optimization of the amount of adsorbent, 5, 7, 10, 12 and 15 mg of the Py-Fe₃O₄@MCM-41 were tested. In the present work, by increasing amounts of the Py-Fe₃O₄@MCM-41 due to increase in the surface area and accessible sites to the adsorption of the analytes, the extraction efficiency increased. Quantitative extraction of cadmium ions was achieved using only 10 mg of the Py-Fe₃O₄@MCM-41. At higher amounts of the adsorbent, the extraction efficiency was almost constant. Therefore, 10 mg of the sorbent was used in the subsequent study.

3.2.3. Equilibrium sorption time

In order to investigate the effect of shaking time on the extraction efficiency, extraction experiments were carried out at 2, 4, 5, 7 and 10 min time intervals. According to the results, an equilibrium time of about 5 min was required for quantitative extraction of the analytes from solution into the solid phase. Thus, the mixtures have been shaken for 5 min to reach equilibrium in the subsequent experiments (Fig. 5B).
2.2.4. Desorption condition

As the surface of Fe₃O₄ nano-particles coated with a silica layer, this composite is stable in high concentrations of acids without any leak of Fe³⁺ or Fe²⁺ in solution. So a series of selected eluent solutions, including HNO₃, HCl, and CH₃COOH were used for elution of cadmium ions from Py-Fe₃O₄@MCM-41. The results show that 1 mol L⁻¹ of HCl is a suitable and effective eluent to elute cadmium ions from Py-Fe₃O₄@MCM-41. The effect of eluent volume on the recovery of cadmium ions was also studied. Also the results show, quantitative recovery could be obtained with 1.0 mL of 1 mol L⁻¹ of HCl. Therefore, 1 mL volume of eluent for desorption of cadmium ions was used in the following experiments (Table 1).

Desorption times were evaluated in the range of 2–10 min. The results showed that the time of 5 min is sufficient for quantitative desorption of the cadmium ions by 1 mL of the 1 mol L⁻¹ of HCl.

3.3. Effect of potentially interfering ions

Because of the presence of other elements in real samples, selective preconcentration and determination of cadmium ion is difficult. So, the effects of common potentially interfering cations and anions on the adsorption of cadmium ions on the Py-Fe₃O₄@MCM-41 were investigated. Functionalized mesoporous silica by pyridine functional groups have been used for the selective sorption of cadmium ions (The selectivity of the sorbent was achieved by pyridine functional groups). In these experiments, 50 mL of solution containing 0.001 mg cadmium ions were added to interfering cations and anions and treated according to the recommended procedure. The results in Table 2 show that the vast majority of transition, alkaline, and earth alkaline metals do not interfere at environmentally relevant concentrations. This is due to the low capacity or rates of adsorption for interfering ions under optimum condition. Thus, these results confirm that the procedure using Py-Fe₃O₄@MCM-41 is independent of matrix interferences.

3.4. Maximum adsorption capacity

In order to determine how much sorbent was required to quantitatively remove a specific amount of a metal ion from the solution, the capacity of the sorbent was calculated. To evaluate this factor, 50 mL of a solution containing 2 mg cadmium ions underwent the extraction procedure (with 10 mg of the sorbent), and the maximum capacity was calculated. Maximum adsorption capacity for cadmium ions was 154 mg g⁻¹. In order to evaluate the maximum adsorption capacity, the difference between concentration of the solution before and the concentration of the solution after extraction by the sorbent was calculated.

![Figure 6](image-url)
3.6. Analytical performance

Volumes up to 400 mL for extraction of cadmium ions. The coefficient of determination ($r^2$) was 0.994. The limit of detection is defined as $C_{LOD} = 3Sb/m$, where Sb is the standard deviation of eight replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 100 mL, was found to be 0.04 $\mu$g L$^{-1}$ for cadmium ions. The relative standard deviations for eight separate extraction experiments for determination of 2.0 $\mu$g of cadmium ions in 100 mL of water was 2.9%.

3.7. Real samples analysis

Since environmental and food samples have complex matrices, non-specific background absorption was caused by interfering species of the sample matrix. To reduce this undesirable effect, Py-Fe$_3$O$_4$@MCM-41 was applied for selective extraction of cadmium ions in pH of 7.0. Table 3 shows the cadmium ions recoveries in food and environmental water samples.

3.8. Validation of the method

The concentration of cadmium ions obtained by Py-Fe$_3$O$_4$@MCM-41 was compared to the standard materials. For this reason, the concentration of the cadmium ions was determined at optimum conditions in standard reference material (Soil (NCS DC 73323)). As it can be seen in Table 1S (ESM), good correlation was achieved between estimated content by the present method and reference materials. Therefore, Py-Fe$_3$O$_4$@MCM-41 can be used as a reliable sample treatment technique for extraction and determination of cadmium ions in real samples.

4. Conclusion

In this work, for the first time, Fe$_3$O$_4$@MCM-41 was functionalized by pyridine and it was utilized as an adsorbent for the separation of ultra-trace amounts of cadmium ions. Such prepared adsorbent has not only the wormhole-like mesopore structure with large surface area and pore volume, but also the magnetic character. Through a magnetic field, the magnetic mesoporous silica can be easily separated and recovered in liquid–solid processes. This method is simple, rapid and reliable and found as a selective and sensitive method for the determination of trace levels of cadmium ions. The most important characteristic of the Py-Fe$_3$O$_4$@MCM-41 was shown excellent selectivity toward cadmium ions over other potentially interfering ions. The convenient data was found for detection limit and relative standard deviation in the determination of cadmium ions and confirmed that this method using modified Fe$_3$O$_4$@MCM-41 has high potential for extraction of metals. As a result, the LOD and maximum adsorption capacity of this method is comparable or better than some of the previously reported preconcentration methods. Table 4 provide a comparison between the proposed method and previous works for analysis of cadmium ions [23, 26, 36–39]. In conclusion, this pyridine functionalized magnetic mesoporous silica is a promising adsorbent for heavy metal detection in real samples.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jmmm.2015.07.093.

References


Table 4

A comparison between the proposed method and previous methods.

<table>
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<tr>
<th>Method</th>
<th>PF</th>
<th>LOD $^a$ (µg L$^{-1}$)</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>Refs.</th>
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$^a$ Limit of detection

$^b$ Preconcentration factor