Solid phase extraction of trace amounts of cadmium(II) ions in water and food samples using iron magnetite nanoparticles modified by sodium dodecyl sulfate and 2-mercaptobenzothiazole

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ABSTRACT

A new, simple and rapid method for solid phase extraction and preconcentration of trace amounts of cadmium ions using 2-mercaptobenzothiazole/sodium dodecyl sulfate immobilized on magnetite nanoparticles (MBT-SDS-MNPs) was proposed. The method is based on the extraction of cadmium ions via complexation with MBT immobilized on SDS-coated MNPs and their determination by flame atomic absorption spectrometry. The effects of different parameters – pH; eluent type, concentration and volume; amounts of salt and adsorbent; contact time and interfering ions – on the adsorption of cadmium ions were studied. Under optimized conditions, the calibration curve was linear in the range of 10–5,000 μgL⁻¹. Detection limit and relative standard deviation of the proposed method were 0.009 μgL⁻¹ and 2.2%, respectively. The adsorption data were analyzed by Langmuir and Freundlich isotherm models and a maximum adsorption amount of 24.80 mg g⁻¹, a Langmuir adsorption equilibrium constant (b) of 4.62 and Freundlich constants Kf and n of 6.075 mg¹⁻¹L¹/n g⁻¹ and 2.391, respectively, were obtained. Finally, this adsorbent was successfully used for extraction of cadmium from water and food samples.

Key words | cadmium, flame atomic absorption spectrometry (FAAS), magnetite nanoparticles (MNPs), 2-mercaptobenzothiazole (MBT), sodium dodecyl sulfate (SDS)

INTRODUCTION

Important roles of trace heavy metal ions in human life are known. Heavy metals are harmful to human health and the environment, even at low concentrations (Mashhadizadeh & Karami 2011; Bagheri et al. 2012). Cadmium as a heavy metal is highly toxic and can cause a serious threat to living organisms. The major sources of cadmium are corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries, mining, smelting and refining of non-ferrous metals. Therefore, an efficient and economic process for determination of cadmium from water and food samples is a pressing need (Purkayastha et al. 2014).

Several methods have been developed for the determination of metal ions. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions. However, direct determination of metal ions at trace amounts by FAAS is limited due to their low concentrations and matrix interferences. Therefore, a preconcentration/separation step is required (Duran et al. 2007). A number of separation/preconcentration procedures have been used for trace metal determinations; these include co-precipitation (Soylak et al. 2005; Soylak & Erdogan 2006), liquid-liquid extraction (Mirzaei et al. 2014), flotation (Mizuike et al. 1984; Nović & Gućek 2000), electrochemical deposition (Matusiewicz & Lesiński 2002; Mashkouri Najafi et al. 2009, 2010), cloud point extraction (Liang & Sang 2008) and solid phase extraction (SPE) (Khazaei et al. 2013; Sun et al. 2015). SPE has several important advantages over other methods: simplicity, flexibility, high preconcentration factor, consumption of small volumes of organic solvent, low cost, and short extraction time for sample preparation (Yang et al. 2009; Mashhadizadeh & Karami 2011).

Recently, use of nanoparticles (NPs) for sample extraction in SPE is gaining research interest (Faraji et al. 2010;...
Nanomaterials can offer several advantages over traditional SPE sorbents, such as having very high surface areas and a short diffusion route, which results in high extraction capacity and efficiency (Kalfa et al. 2009). Also, NPs’ surface functionality can be easily modified to achieve the selective sample extraction. Moreover, using superparamagnetic NPs such as Fe$_3$O$_4$ can achieve a shorter analysis time, due to the magnetically assisted separation of these particles from the sample solution. The NPs are attracted to a magnetic field but retain no magnetic charge after the field is removed. This property makes them particularly suitable for sample preparation because no centrifugation or filtration of the sample is needed after extraction in comparison with non-magnetic adsorbents (Faraji et al. 2010a).

In this research, magnetite nanoparticles (MNPs) modified by sodium dodecyl sulfate (SDS) and 2-mercapto-benzothiazole (MBT), as the adsorbent for the separation and preconcentration of cadmium ions from water and food samples, and later determination by FAAS, have been presented.

**EXPERIMENTAL**

**Chemicals and reagents**

All chemicals were of analytical reagent grade, and all solutions were prepared with deionized water. Stock solutions of cadmium (1,000 mg L$^{-1}$) were prepared by dissolving appropriate amount of cadmium nitrate salts in water and diluting to 100.0 mL in a volumetric flask (to prevent the hydrolysis of lead and cadmium nitrate salts, two drops of nitric acid 0.02% were added). Other reagents used were sodium dodecyl sulfate (SDS), 2-mercaptop-benzothiazole (MBT), ferrous chloride (FeCl$_2$·4H$_2$O), ferric chloride (FeCl$_3$·6H$_2$O), cadmium nitrate (Cd(NO$_3$)$_2$·4H$_2$O), ethanol, ammonia, hydrochloric acid, nitric acid and sodium hydroxide. All chemicals were obtained from Merck and Fluka.

**Instruments**

A flame atomic absorption spectrometer (CTA 2000) equipped with a deuterium lamp background corrector, a cadmium hollow cathode lamp and an air-acetylene flame, was used for the determination of cadmium under the conditions suggested by the manufacturer. The wavelength, lamp current, slit width and acetylene flow rate were 228.8 nm, 4 mA, 0.3 nm and 2.2 L min$^{-1}$, respectively. The pHs of the solutions were measured with a pH/mV meter (Metrohm-827) which was supplied with a combined electrode. The surface morphology of the powders was observed by a scanning electron microscopy (SEM) (KYKY-EM3200). X-ray measurements were performed by using a Philips X-ray diffractometer. Other instruments used were an ultrasonic bath (S60H Elmasonic, Germany), a mechanical stirrer (Heidolph, RZR2020) and a magnet with strength of 1.4 tesla.

**PREPARATION OF ADSORBENT**

**Synthesis of MNPs**

As a first step, the Fe$_3$O$_4$ NPs were prepared by a chemical co-precipitation procedure (Xu et al. 2013). FeCl$_3$·6H$_2$O (8.5 g) and FeCl$_2$·4H$_2$O (3.0 g) were dissolved in 38 mL HCl (0.4 M) solution. Chemical precipitation was achieved under vigorous stirring for 30 min by adding 375 mL NH$_4$OH solution (0.7 M). During the whole process, the solution temperature was maintained at 80 °C and nitrogen gas was purged to remove the dissolved oxygen. After the reaction, the NPs were collected by a magnet and thoroughly washed with deionized water to remove excess amounts of ammonium hydroxide. Then, the NPs were dried in an oven for 5 h at 110 °C.

**Preparation of MBT-SDS-MNPs**

Firstly 10 mL of 3% (w/v) SDS solution and 10 mL of water containing 3 g of MNPs were placed in a beaker. The mixture was stirred at room temperature for 4 hours. Then, 50 mL of 0.4% (w/v) MBT solution was added to SDS-MNPs solution, and the mixture was stirred for 12 hours. Finally, after mixing, magnetite nano-adsorbents (MBT-SDS-MNPs) were separated from the solution using a magnet and then washed three times with deionized water and dried at room temperature.

**Extraction procedure**

Fifty millilitres of the sample solution containing 10 μg of cadmium ions was transferred into a beaker. One millilitre of 10% (w/v) NaCl, 5 mL of distilled water and 20 mg of sorbent were added to the solution. The pH of the solution was adjusted to 8.0 using 2 mL of 0.1 mol L$^{-1}$ phosphate buffer (pH = 8.0) and the mixtures were dispersed by
ultrasonication for 10 min at room temperature. Then, the beaker was placed on the magnet and the adsorbent containing adsorbed cadmium ions was collected. After decanting the supernatant solution, the magnet was removed, and a solution containing 1.0 mol L\(^{-1}\) (HNO\(_3\) in methanol) was added as eluent and ultrasonicated again for 5 min. Finally, the magnet was used to collect the adsorbent and then cadmium ions in the eluent were determined by FAAS.

Sample preparation

First, rice and macaroni samples were converted to a powder. One gram of powdered rice or macaroni was transferred to a beaker. In order to decompose the powdered samples, 10 mL of aqua regia was added to it and the mixture was heated almost to dryness. After this, 25 mL of deionized water was added to the beaker and the insoluble parts were filtered through a filter paper (blue band). The water samples were collected in cleaned polyethylene bottles. The only pretreatment was acidification to pH = 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls.

RESULTS AND DISCUSSION

Characteristics of modified magnetic nanoparticles

The adsorbent synthesized by the method given above was characterized by SEM and X-ray diffraction (XRD). Figure 1 displays the SEM image of MBT-SDS-MNPs, which shows the uniform size distribution of the NPs. Figure 2 shows the MBT-SDS-MNPs’ XRD pattern. The average crystallite size (D) was calculated to be 18.9 nm for MBT-SDS-MNPs using the Debye–Scherrer formula (\(D = K \lambda / (\beta \cos \theta)\)), where K is the Scherrer constant (K = 0.89), \(\lambda\) is the X-ray wavelength (\(\lambda = 1.5406\) Å), \(\beta\) is the full peak width at half maximum, and \(\theta\) is Bragg diffraction angle). From these results, it can be concluded that nanoscale material was obtained by the method described.

Effect of pH on the adsorption of cadmium

The pH of the sample solution plays an important role in the SPE procedure. An appropriate pH value can improve the adsorption efficiency, and also reduce interference from the matrix. The effect of pH on the extraction efficiency for cadmium was studied between the pH range of 4.0–11.0, adjusted by 0.1 mol L\(^{-1}\) NaOH or HCl, and the results are shown in Figure S1 (Supplementary Material (SM), available with the online version of this paper). It was found that the cadmium was maximally adsorbed on the sorbent at pH = 8.0. Addition of 1–6 mL of buffer did not have any effect on the adsorption. Therefore, 2 mL of 0.1 mol L\(^{-1}\) aqueous solution (pH = 8.0) was used in all subsequent experiments.

Effect of the adsorbent amount

The amount of adsorbent is another important parameter to obtain quantitative recovery. In order to study the effect of the adsorbent amount, 10–100 mg of the MBT-SDS-MNPs was added to the sample solution. The obtained results showed that by increasing the sorbent amounts from 10 up to 70 mg, due to the increasing of accessible sites, extraction recovery slowly increased and then remained constant (Figure S2, SM, available with the online version of this paper). Therefore, 70 mg of MNPs was used in all subsequent experiments.
Effect of contact time

Effects of contact time on the adsorption of cadmium by MBT-SDS-MNPs were studied in the range of 1–10 min. The results showed that the recovery percent increased sharply to 5 min and remained constant (Figure S3, SM, available with the online version of this paper). Therefore, ultrasonication time of 5 min was selected for subsequent experiments.

Effect of ionic strength

Different volumes of 10% (w/v) NaCl, from 0.0 to 2 mL, were chosen to investigate their effect on cadmium adsorptions onto MBT-SDS-MNPs (Figure S4, SM, available with the online version of this paper). The results showed that the extraction efficiency was increased as ionic strength increased to 0.75 mL and then was decreased in the range of 0.75–1.5 mL. Therefore, 0.75 mL of 10% (w/v) NaCl was used in all further experiments.

Type, volume, and concentration of the eluent

Another important factor which affects the preconcentration procedure is the type, volume, and concentration of the eluent used for the removal of the cadmium ions from the sorbent. For selection of the best eluent, HCl in water, HCl in methanol, HNO₃ in water, and HNO₃ in methanol (10 mL of 1.0 mol L⁻¹) were used as eluent solution. Quantitative recovery for cadmium ions was obtained with HNO₃ in methanol (Table S1, SM), and therefore it was selected as an eluent for subsequent experiments. After the findings above, experiments were carried out for selecting the concentration of nitric acid solution in methanol. HNO₃ solutions in methanol at the concentrations between 0.30 and 4.0 mol L⁻¹ were studied for this purpose. The results are given in (Figure S5, SM), and show that the recovery percent increased, with an increasing concentration of HNO₃ solutions in methanol up to 1.0 mol L⁻¹, and then remained constant. Therefore, 10 mL of HNO₃ 1.0 mol L⁻¹ solution was selected for subsequent experiments. The influence of the volume (2–10 mL) of 1.0 mol L⁻¹ HNO₃ in methanol was also examined (Figure S6, SM). The optimum eluent volume was specified as 5 mL for the subsequent studies. (Table S1 and Figures S5 and S6, SM, are available with the online version of this paper.)

Breakthrough volume

For this purpose, 100.0–800.0 mL of an aqueous solution containing 10.0 μg of cadmium ions was processed according to the extraction procedure. The results (Figure S7, SM, available with the online version of this paper) showed that quantitative recoveries of studied metal ions were obtained when sample volume was less than 400 mL. With respect to eluent volume (5.0 mL), an 80 preconcentration factor (the ratio of the highest sample volume to the lowest eluent volume) for the analyte ions was obtained.

Finally optimal analytical conditions were found to be pH = 8.0, 70 mg of MNPs as adsorbent, ultrasonication time of 5 min, 0.75 mL of 10% (w/v) NaCl as suitable ionic strength and 5 mL of 1.0 mol L⁻¹ HNO₃ in methanol as eluent.

Isotherms

The relationships between adsorbent and adsorbate described by adsorption isotherms, usually the ratio between quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium, can be described by adsorption isotherms. The Langmuir and Freundlich models (Baker & Khalili 2004; Nuhoglu & Malkoc 2009) are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of cadmium ions adsorbed and its equilibrium concentration in solution at room temperature.

Langmuir isotherm

The Langmuir equation may be written as (Hameed et al. 2008):

\[
q_e = \frac{QbC_e}{1 + bC_e}
\]

non-linear form

\[
\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}
\]

linear form

where \(q_e\) (\(q_e = V (C_0 - C_e)/m\)) is the amount of adsorbed cadmium per unit weight of adsorbent (mg g⁻¹), \(V\) is the volume of aqueous phase (mL), \(C_0\) is initial concentration solution of cadmium (mg L⁻¹) and \(C_e\) is the concentration of cadmium in the solution at equilibrium (mg L⁻¹); \(Q\) is the monolayer adsorption capacity (mg g⁻¹). Based on the linearized form of the adsorption isotherm derived from plots of \(C_e/q_e\) versus \(C_e\), the constant \(Q\) values were calculated from the slope of the graph (Figure 3). The parameter \(b\) is the constant related to the free energy of adsorption \((b = e^\Delta G/RT, \text{where } \Delta G \text{ is free energy of adsorption (kJ)})\), \(R\) is standard gas constant (kJ K⁻¹ mol⁻¹) and \(T\) is absolute temperature (K)). The constants of the Langmuir isotherm are obtained by plotting \(C_e/q_e\) versus \(C_e\).
Freundlich isotherm

The Freundlich isotherm may be written as (Hameed et al. 2008):

\[ q_e = K_f C_e^{1/n} \text{ non-linear form} \]

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \text{ linear form} \]

where \( K_f \) is the constant indicative of the relative adsorption capacity of the adsorbent (mg g\(^{-1}\)) and \( 1/n \) is the constant indicative of the intensity of the adsorption. The constants of the Freundlich isotherm are obtained by plotting \( \log q_e \) versus \( \log C_e \) (Figure 4). Freundlich and Langmuir constants are given in Table 1; as can be seen in this table, the higher correlation coefficient (0.989) showed that the Langmuir model was more suitable than the Freundlich model for describing the adsorption equilibrium of cadmium.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Freundlich and Langmuir constants</th>
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<tr>
<td>Model</td>
<td>( K_f ) (mg(^{-1}) L(^{1/n}) g(^{-1}))</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>6.07</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>–</td>
</tr>
</tbody>
</table>

Calibration, precision and detection limit

Under the optimum conditions described above, the figures of merit of the proposed method were investigated. The dynamic linear range was obtained for the studied cadmium ions in the concentrations ranging from 10.0 to 5000.0 \( \mu \)g L\(^{-1}\) with good correlation coefficients (\( R^2 = 0.9990 \)). The detection limit (DL) was obtained from \( DL = kS_b/m \), where \( k = 3 \), \( S_b \) is the standard deviation of seven replicate blank measurements, and \( m \) is the slope of the calibration curve (Figure S8, SM). The DL of the proposed method for determination of cadmium ions under the optimum conditions was 0.009 \( \mu \)g L\(^{-1}\). Relative standard deviation of the method for determination of the cadmium ions was 2.2\% (seven replicate measurements at 2 \( \mu \)gmL\(^{-1}\) cadmium. The analytical characteristics of the extraction procedure are given in (Table S2, SM). (Figure S8 and Table S2, SM, are available with the online version of this paper.)

Application to real samples

The proposed method was applied to the determination of cadmium ions in tap water, fountain water, and rice and macaroni samples. The cadmium ions were quantitatively recovered from the all samples, by the proposed procedure. The obtained results are shown in Table 2. These results

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Determination of cadmium ions in real samples</th>
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<tbody>
<tr>
<td>Sample</td>
<td>Cadmium added (( \mu )g)</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Tap water of Ilam city</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Bahman Abad fountain water</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Macaroni</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Rice</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
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<td></td>
<td>4</td>
</tr>
</tbody>
</table>
The effects of interference on the recovery of cadmium(II) are given in Table 3. According to the results, the proposed method is selective and can be used for determination of cadmium ions in real samples.

**CONCLUSIONS**

The results demonstrated that the method is very suitable for the rapid extraction of cadmium ions from water and food samples at ppm levels, besides having both good accuracy and precision. Also, it can be concluded from the results that MBT-SDS-MNPs are an effective sorbent for separation and preconcentration of trace amounts of cadmium from various samples. These modified magnetic nanoparticles carrying the target metal could be easily separated from the aqueous solution simply by applying an external magnetic field; no filtration or centrifugation was necessary. The size of the produced modified magnetic nanoparticles was determined by XRD analysis and SEM. Also, the proposed method can be a guideline for the extraction of other metal ions from environmental samples.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


Mashhadi, M. S. & Karami, Z. 2011 Solid phase extraction of trace amounts of Ag, Cd, Cu, and Zn in environmental samples using magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propantiol and modified with 2-amino-5-mercaptop-1,3,4-thiadiazole and their determination by ICP-OES. *Journal of Hazardous Materials* **190**, 1023–1029.


