A novel nanomagnetic task specific ionic liquid as a selective sorbent for the trace determination of cadmium in water and fruit samples

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Abstract

A selective sorbent was prepared for the simultaneous separation and preconcentration of cadmium ion from water and fruit samples, prior to determination by flame atomic absorption spectrometry (FAAS). The sorbent was synthesized by combining of Fe3O4 magnetic nanoparticles (MNPs) and Aliquat 336 thiosalicylate, [A336][TS], a thiol-containing task specific ionic liquid (TSIL). The high affinity of TSIL toward the target compound as well as the magnetic behavior of Fe3O4 was combined to provide an efficient and simple magnetic sorbent for solid-phase extraction (SPE). The prepared nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and vibrating sample magnetometer (VSM). The important parameters influencing the extraction efficiency such as pH, sorbent dosage, extraction and desorption conditions were studied and optimized. Under the optimum conditions, the calibration curve was linear in the range of 2.5–260 ng mL⁻¹ and good linearity (R² > 0.996) was obtained. The limit of detection (LOD) and enrichment factor (EF) of the method were found to be 0.5 ng mL⁻¹ and 50, respectively. The relative standard deviations (RSDs %) were less than 3.1 (n = 6) for the target analyte. In this method, only small amounts (20 mg) of adsorbent were needed to obtain satisfactory extraction recoveries within 20 min. Finally, the proposed method was successfully applied for the trace determination of cadmium ions in fruit (apple, orange and banana) and water samples. Good spike recoveries, varied within the range of 95–105%, confirmed the good performance of the method in real sample analysis.

1. Introduction

Cadmium is well recognized as a highly toxic element to human beings because of its high accumulation capability in living organisms [1,2]. One of the main pathways that cadmium enters into the human body is through the intake of food and drinking water [3–5]. Therefore, monitoring of cadmium concentrations in food and water samples is important. Moreover, such data can provide the information about cadmium contamination in surrounding environment [3].

Flame atomic absorption spectrometry (FAAS) is one of the widely used techniques for determination of cadmium because of its advantages such as simplicity in operation and low cost of analysis [6–8]. However, this technique also has some disadvantages such as the matrix interfering effects on the analyte signal and higher limit of detection (LOD) than the usual concentrations of metal ions in real samples [6,9]. Therefore, separation and preconcentration steps are often required to achieve accurate, sensitive and reliable results by FAAS [7,10]. Among different preconcentration techniques used in for (ultra) trace analysis of metal ions, solid phase extraction (SPE) is widely used [6,11] because of its flexibility, simplicity, high enrichment factor, high recovery, rapid phase separation, low cost due to low consumption of reagents, and ability of combination with different detection techniques in on-line or off-line modes [12–14]. By selection of an appropriate sorbent, SPE performance can be improved significantly [15,16]. Various new adsorbents have been reported for preconcentration and separation of Cd (II) by SPE. For instance, Zou et al. [17] reported determination of trace Cd (II) in environmental samples using [OMIM][PF6]-modified nano-TiO2 supported on glass beads as a reusable sorbent for SPE. Latore et al. [18] also described the use of carbon nanotubes (CNTs) as SPE sorbent of metal species.

Recently, magnetic nanoparticles (MNPs) have attracted increasing attention due to their significant physical and chemical properties such as high large surface area, highly active surface sites and short diffusion routes for analytes [8,11–13]. SPE technique based on the use of these sorbents called magnetic solid-phase extraction (MSPE), and has become one of the most...
potential strategies for separation and preconcentration procedure. MSPE is a convenient method, since the magnetic sorbent can be recovered from a sample solution under an external magnetic field and does not need further centrifugation and filtration [8,19–21]. However, several unavoidable problems are associated with MNPs, such as their intrinsic instability over long periods due to their tendency to aggregate for reducing the surface energy, being easily oxidized in air and easily formation of large aggregates, which may alter their magnetic properties. Moreover, they are not target selective and suitable for the samples with complicated matrices. Therefore, they are usually modified with different functional groups or a suitable coating to overcome such limitations [12,14,19,20].

Similar to MNPs, ionic liquids (ILs) have also recently received a great deal of attention [22–24]. ILs are generally defined as salts that are liquid with melting points equal or below 100 °C, and are as a combination of organic cations with various anions [5,7,25,26]. Polarity, conductivity, viscosity, acidity and hydrophobicity of ILs depend on the nature and the size of their cationic and anionic species [22]. They possess unique chemical and physical properties, such as negligible vapor pressure, good thermal stability and high conductivity [5,7,25,26]. Therefore, ILs have been used as an alternative sorbent for extraction and preconcentration of heavy metals and organic pollutants. Gao and Ma [27] presented a new approach for preconcentration and speciation analysis of trace amount of mercury from water samples by dispersive liquid–liquid microextraction (DLLME) coupled to high performance liquid chromatography with diode array detection (HPLC–DAD). Mercury species were complexed with dithizone (DZ) to form the hydrophobic chelates and then extracted into the fine drops of ionic liquid [HMIM][PF6] as dispersive solvent. Zeeb et al. [28] developed a microextraction procedure based on modified ionic liquid cold-induced aggregation-DLLME for trace determination of chromium in water and food samples. A hollow fiber supported liquid-phase microextraction procedure was also developed using ionic liquid [BMMIM][PF6] as solvent for extraction, cleanup and enrichment of benzene, toluene, ethylbenzene, and o-, m- and p-xylene (BTEXs) from aqueous samples [29]. The application of solid-phase microextraction using cross-linked polymeric ionic liquid (PIL)-based sorbent coatings for the extraction of 21 polychlorinated biphenyls (PCBs) from ocean water and bovine milk samples was demonstrated [30]. However, ILs wide application is yet held back due to some limitations such as difficulty in their isolation and recovery, low rate of mass transfer, long equilibrium time and need for large amount of them which increase the analysis costs. These limitations can be overcome by immobilizing ionic liquids on solid substrates. Supported ionic liquid phase combine the advantages of ionic liquids with those of support materials. Therefore, IL-modified materials have been successfully used in the separation fields [12,20,24,31].

Task specific ionic liquids are a unique subclass of ionic liquids with functional group covalently tethered to the cationic or anionic part. The functional group has the ability to coordinate to the metal ions (preferably as a bidentate or a polydentate ligand) [22,32,33]. Hence, the synthesis of task specific ILs (TSILs) has been a focus of research, leading to tailor-made substances for desired applications such as selective extraction of analytes based on unique molecular interactions [34,35]. Typically, TSILs contain complexing groups in cationic (imidazolium-based) part that makes them relatively expensive and difficult to synthesize. An attractive alternative may be ILs which contain complexing anions, in particular tetra alkylammonium carboxylates [36]. For example Aliquat 336 (trimethylmethylammonium chloride) is a water insoluble quaternary ammonium salt that can be a relatively cheap precursor for the production of Aliquat-derived ILs by a simple replacement of the chloride anion with various anions such as thiosalicylate (a thiol-containing anion) [21,34,37]. Sulfur-containing functional groups play an important role in binding to certain metal ions. In particular, soft and borderline metals, e.g., Cd2+, exhibit high affinity to a soft sulfhydryl group based on Pearson’s theory. Furthermore, a 5- or 6-membered ring structure through concerted binding with –OH, –SH groups of thiosalicylate is expected [38]. Kogelnig et al. [34] reported that tricaprylmethyl ammonium thiosalicylate, [A336][TS], could be as potential extracting agent for cadmium because it contain carboxylic and thiol functional groups. The calculated distribution coefficients for alkali- and earth alkali metals were < 2, whereas distribution coefficient for cadmium was > 10,000 with [A336][TS], indicating an undisturbed fast metal uptake and a high affinity for cadmium under neutral conditions, even in a complex matrix.

To the best of our knowledge, this is the first report of using a hydrophobic task specific ionic liquid-coated Fe3O4 for the fast and selective preconcentration and trace determination of cadmium from real samples. In this study, we demonstrated successful synthesis of [A336][TS]-modified Fe3O4. Factors affecting the recovery of the analyte were investigated and optimized and the new sorbent was successfully applied to the determination of cadmium in fruit (apple, orange and banana) and water samples.

2. Materials and methods

2.1. Instrumentation

A Varian Spectra AA-400 atomic absorption spectrometer equipped with a deuterium background correction and an air-acetylene flame was utilized for determination of cadmium concentrations. A cadmium hollow-cathode lamp at a wavelength of 228.8 nm was used as a radiation source and operated at 4 mA with spectral bandwidth of 0.5 nm. Other operating parameters were set as recommended by the manufacturer. Morphology of sorbent was investigated on a Hitachi S-4160 Field Emission Scanning Electron Microscope. Energy-dispersive X-ray spectroscopy (EDX) analysis was obtained on EVO+ 30 Series (Carl Zeiss AG). The magnetic property of the prepared nanoparticles was analyzed using a vibration sample magnetometer (VSM) (4 in., NDKF, Kashan, Iran) operating at room temperature with applied fields up to 10 kOe. The pH values were measured with a pH-meter (Metromh 692, Switzerland) supplied with a glass-combined electrode. IR spectra were recorded by a BOMEM/MB series spectrometer. Magnetic separation was performed by a supermagnet with 1.4 T magnetic fields.

2.2. Reagents and solutions

Aliquat 336 (trimethylmethylammonium chloride) and hydrogen peroxide (H2O2, 30%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Thiosalicylic acid, ethanol, sodium hydroxide, nitric acid (HNO3, 65%), iron (III) chloride hexahydrate (FeCl3·6H2O), iron (II) chloride tetrahydrate (FeCl2·4H2O), ammonia and dichloromethane (CH2Cl2) with analytical grade were purchased from Merck Chemicals (Darmstadt, Germany). The Cd (II) working solution was prepared daily from its stock standard solution (1000 mg L−1) (Merck, Germany).

2.3. Preparation of real samples

The tap water sample (50 mL) was collected from the laboratory (Tehran, Iran). Three types of fruits including apple, orange and banana were chosen for the analysis. These samples were purchased from a local supermarket (Tehran, Iran). The dried and ground fruit samples (5 g) were transferred into the separate
vessels, then 20 mL HNO₃ (65%) and 5 mL H₂O₂ (30%) were added and the vessels were heated on a hot plate at 80 °C for 2–3 h, till the clear transparent digests were obtained. After cooling down the resulting solutions to room temperature, they diluted to 50 mL with distilled water. The prepared water and fruit samples were analyzed according to the described procedure in Section 2.6.

2.4. Synthesis of magnetic iron oxide nanoparticles (Fe₃O₄)

Fe₃O₄ nanoparticles were synthesized by a simple ultrasonic chemical co-precipitation method according to the previously reported procedure with a little modification [39]. Briefly, FeCl₂·6H₂O and FeCl₃·4H₂O with the molar ratio of 2.5:1 were dissolved in distilled water. Under ultrasonic agitation, ammonia solution was added while increasing the temperature up to 80 °C. After reaction, the black precipitates (Fe₃O₄ NPs) were separated using a magnet and washed three times with distilled water.

2.5. Synthesis of [A336][TS]

Aliquat™336 (tricaprylmethyl ammoniumchloride) thiosalicylate, [A336][TS], was prepared according to the literature protocol [40]. Briefly, Aliquat™336 was transferred to a round-bottom flask and purged with argon. An equimolar amount of thiosalicylic acid was dissolved in a mixture of water/ethanol (1:1, v/v) and subsequently deprotonated with equivalent amount of NaOH. Thiosalicylate solution was added to Aliquat™336, and the dispersion was vigorously stirred under an inert atmosphere for 4 h at 45 °C. The IL was separated from the aqueous phase in a separation funnel. Due to the high viscosity of the IL and avoiding its loss during washing step, it was dissolved in dichloromethane, and then washed with small amounts of ice-cold water several times. Finally, the solvent was evaporated by a rotary evaporator at 40 °C for 2 h, and the resulting IL was dried for 24 h under vacuum at 40 °C. The yield of resulting greenish-yellow viscous IL was about 97%.

2.6. Synthesis of [A336][TS]-modified Fe₃O₄

Freshly prepared Fe₃O₄ nanoparticles (0.5 g) were suspended in distilled water that its pH was adjusted to 10, and then the resulted suspension was shaken mechanically for 15 min. It was followed by addition of 0.5% [A336][TS] solution in ethanol and the shaking was continued for 4 h at room temperature. The modified Fe₃O₄ nanoparticles were magnetically separated and washed several times with distilled water and then dried in an oven for 2 h.

The point of zero charge (PZC) for Fe₃O₄ nanoparticles is about 6.5, as reported previously [41,42]. When the pH is adjusted above the PZC, the MNPs surface charge will be negative. Therefore, at pH higher than 6.5, the MNPs surface has negative charge because of the formation of –MO⁻ sites on the surface of nanoparticles. Since the modification of nanoparticles occurred at pH = 10, the mechanism of ionic-liquid bonding onto Fe₃O₄ nanoparticles must be due to a strong cumbic attraction between negatively-charged Fe₃O₄ nanoparticles and the cationic constituent of the IL [41].

2.7. TSIL-based MSPE procedure

Extraction of Cd (II) from aqueous solutions was carried out in batch mode based on the following steps. A 50 mL volume of standard solution with 100 ng mL⁻¹ initial concentration was placed in a 50 mL screw-cap conical-bottom tube. Its pH value was adjusted to 7.0 and then 20 mg [A336][TS]-modified Fe₃O₄ was added. The mixture was placed in a shaker for 15 min and vigorously shook to completely suspend the prepared MNPs and facilitate the extraction process of Cd (II). Afterwards, a strong magnet (1.4 T) was used to collect them at the bottom of the tube, and the supernatant was decanted. Finally, the analytes were eluted from the sorbent by 0.1 mol L⁻¹ HNO₃ (1 mL) with shaking for 5 min, and then the concentration of Cd (II) were determined in the supernatant by FAAS. All tests were performed in duplicate at room temperature.

3. Result and discussion

3.1. Characterization of the synthesized [A336][TS]-modified Fe₃O₄

Fig. 1 represents the FTIR spectrum of magnetic [A336][TS] to identify the functional groups and the chemical bonding of the sorbent. The absorption bands at 561–417 cm⁻¹ are usually attributed to the Fe–O stretches and the broad absorption band at 3241 cm⁻¹ indicates the presence of surface hydroxyl groups (O–H stretching). The long hydrocarbon chains in [A336] give significantly strong peaks in the ranges of 2916–2847 and 1459–1363 cm⁻¹. The observed peak at 1035 cm⁻¹ can be assigned to C–N stretches. The absorption band at 1581 cm⁻¹ is related to the C=O stretches. Interestingly, an expected absorption band of the thiol group near 2500 cm⁻¹ could not be observed for the prepared magnetic [A336][TS]. This may be attributed to the generally considered low intensity of this band.

Fig. 2 shows the SEM image of the Fe₃O₄ and [A336][TS]-modified Fe₃O₄. As it can be concluded from the SEM image, the Fe₃O₄ nanoparticles were coated successfully with TSIL, since size of the nanoparticles has been changed from below 30 nm (before coating) to the range of 65–99 nm after coating. Also, most of the particles are quasi-spherical in shape. These observations confirm that [A336][TS] is successfully coated on the surface of Fe₃O₄.

The composition of the sorbent was also determined using EDX analysis as shown in Fig. 3. The corresponding EDX spectrum confirmed the presence of TSIL on the surface of Fe₃O₄ as the sulfur, nitrogen and carbon peaks were observed.

Sufficient magnetic properties are required for applications of the magnetic materials in aqueous solution. Fig. 4 shows VSM curves of Fe₃O₄ (a) and [A336][TS]-modified Fe₃O₄ (b) at room temperature. The maximum saturation magnetization was 61.96 and 54.45 emu g⁻¹ for Fe₃O₄ and [A336][TS]-modified Fe₃O₄, respectively. Therefore, the magnetic property of the prepared sorbent did not reduce significantly after coating with ILs. Once the external magnetic field is taken away, the sorbent could re-disperse rapidly.

![Fig. 1. FTIR spectrum of [A336][TS]-modified Fe₃O₄.](image-url)
3.2. Optimization of the MSPE procedure

3.2.1. Effect of pH
To assess the impact of pH on extraction efficiency, the pH of working solutions (10 mL) containing 100 ng mL\(^{-1}\) Cd (II) were adjusted to different values in the range of 2–8. Higher pH values were neglected due to the interference of OH\(^{-}\) ions and formation of hydroxyl complexes with cadmium ions [22]. The samples were mechanically shaken with 20 mg portions of [A336][TS]-modified Fe\(_{2}\)O\(_{4}\) for 30 min. Then, the sorbent was separated magnetically and later the adsorbed Cd (II) ions were eluted with 0.1 mol L\(^{-1}\) HNO\(_{3}\) (2 mL) for 5 min. As shown in Fig. 5, the highest recovery of metal ions as function of pH was obtained between pH 7 and 8; therefore, pH 7 was selected for further experiments. Considering the fact that –COOH groups can be protonated under the acidic conditions and as the oxidation of –SH groups can be occurred under the same condition, recoveries were decreased at lower pH values.

3.2.2. Effect of sorbent amount
To obtain a high extraction efficiency, different doses of [A336][TS]-modified Fe\(_{2}\)O\(_{4}\) ranging from 5 to 100 mg were tested. The results showed that the highest extraction recovery was achieved by 20 mg sorbent. For higher amounts of modified magnetic NPs, the extraction efficiency was almost constant.

3.2.3. Effect of contact time
Since, insufficient time reduces the recovery of metal ion extraction and extra time causes wasting time [43], shaking time was investigated in the range of 5–60 min. The optimum pH of 7 and amount of MNPs of 20 mg were considered with initial concentration of 100 ng mL\(^{-1}\) of Cd (II) and 0.1 mol L\(^{-1}\) HNO\(_{3}\) (2 mL) as eluent for this investigation. As evident from Fig. 6, 15 min was sufficient for achieving quantitative recovery.

3.2.4. Effect of eluent concentration and volume
An appropriate eluent for effective desorption of metal ions from a sorbent should be cheap, effective, and non-polluting [44]. Since the extraction recovery of Cd (II) on modified nanoparticles at pH < 2 was found to be negligible, elution will be favored in acidic solution. Therefore it is not surprising the desorption ability of the nitric acid. To determine best condition for the elution procedure, different concentrations (0.1–1 mol L\(^{-1}\)) and volumes (1–4 mL) of nitric acid solutions were investigated. For these experiments, 5 min desorption time was selected. From the results, 1 mL HNO\(_{3}\) (0.1 mol L\(^{-1}\)) solution provided higher recovery efficiency.

3.2.5. Effect of sample volume
The influence of sample volume on the recovery of Cd (II) was also investigated. Sample volume is a main parameter for obtaining high enrichment factor [44]. So, in order to obtain a higher
enrichment factor, a larger volume of sample solution is required. The experiments were performed by sample volumes in the range of 10–50 mL and 50 mL was selected for calibration curve and LOD experiments.

3.2.6. Evaluation of interfering ions

In view of the fact that FAAS provides high selectivity, the only interference may be attributed to the preconcentration step of Cd (II) in real samples which contain various kinds of species [14]. Thus, selectivity of the proposed method was evaluated by the extraction recovery of the analyte in the presence of interfering and/or co-existing ions. To perform this study, 50 mL solution containing 100 ng mL$^{-1}$ of Cd (II) and each of interfering ions in different ratios was subjected to the proposed procedure. The tolerance limit was defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of Cd (II) in the presence of these interfering. The results were shown in Table 1. According to Pearson’s hard and soft acid-base concept, common metal ions contained in water or food samples, such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, Al$^{3+}$, and K$^+$ which are classified as hard acids, interact only weakly with sulfur-containing ligands, which are soft bases, and consequently would not interfere in the determination of Cd$^{2+}$ [1]. Therefore, excess amount of such cations and common anions e.g. Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and PO$_4^{3-}$ did not affect the extraction process. The tolerable limit was found to be 1 mg L$^{-1}$ (10-fold) for Pb$^{2+}$, Hg$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$. From these results, the developed sorbent is quite suitable to analyze real samples containing diverse ions level since it remained selective and capable to extract Cd$^{2+}$ ions in the presence of the interfering ions.

3.3. Analytical figures of merit

To evaluate the proposed method, further experiments with regard to the linearity, limit of detection (LOD) and repeatability of the method were performed at the optimized working conditions. The calibration curve was created by plotting the peak area versus the concentration. The analyte exhibited good linearity 2.5–260 ng mL$^{-1}$ with correlation coefficient of $R^2 > 0.996$ in the studied range. The limit of detection (LOD, 0.5 ng mL$^{-1}$), defined as 3S/m, where S is the standard deviation of three replicates of blank signals and m is the slope of the calibration curve after preconcentration. The precision of the method was evaluated by repeated analysis of Cd (II) during the course of experimentation on the same day and on different days under the optimized experimental conditions. The inter-day and intra-day relative standard deviations (RSD) for six replicate determinations of Cd$^{2+}$ (100 ng mL$^{-1}$) were 2.3% and 3.1%, respectively. The enrichment factor, defined as the ratio of the volume of sample to the volume of eluent, was 50. Accordingly, the proposed method showed a good sensitivity, high enrichment factor and low detection limits at short times, which can be attributed to the large surface area, rapid dynamics of extraction, and high extraction efficiencies of the [A336][TS]-modified Fe$_3$O$_4$.

3.4. Analysis of real samples

The developed method was used for the determination of cadmium in water and fruit samples. The results, along with the recovery for the spiked samples, are given in Table 2. The recoveries for the addition of different concentrations of cadmium to water and fruit samples were in the range of 95–109%.

4. Conclusions

In this work, the synthesized [A336][TS]-modified Fe$_3$O$_4$ nanoparticles were successfully applied to the fast, easy and efficient determination of trace amounts of Cd$^{2+}$ in water and fruit samples. Magnetic separation, used in the proposed MSPE procedure, greatly reduced the analysis time and the high efficient interactions of TSIL with the analyte help the separation and pre-concentration of it. Furthermore LOD, RSD, recovery and precision

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<th>Interference ion</th>
<th>Tolerance limit (ng mL$^{-1}$)</th>
<th>Cd$^{2+}$ Recovery (%)</th>
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<tr>
<td>Na$^+$</td>
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<tr>
<td>K$^+$</td>
<td>15,000</td>
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<td>97.3</td>
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of the method revealed that the prepared sorbent has potential of being a useful sorbent for MSPE.

References


