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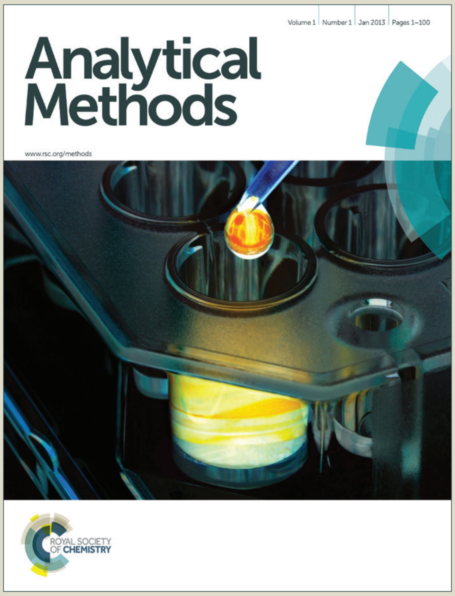

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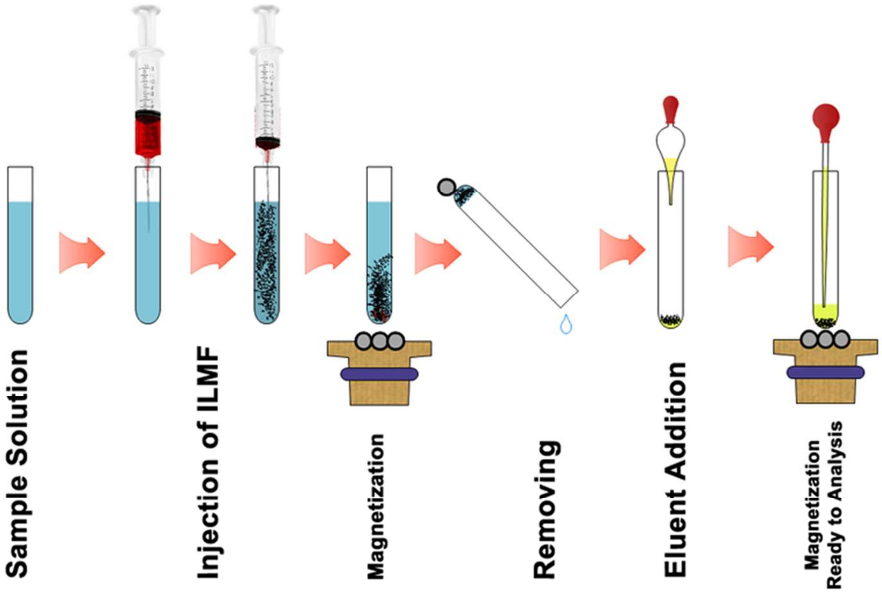

The schematic view of IL-D-SPE.
101x62mm (300 x 300 DPI)

Dispersive magnetic solid phase extraction based on ionic liquid ferrofluid

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Abstract

A novel, fast and efficient ionic liquid-based dispersive magnetic solid phase extraction (IL-D-SPE) was developed and applied for preconcentration of Cd(II) (as a model analyte) from aqueous solutions as a prior step to its determination by flame atomic absorption spectrometry (FAAS). In this methodology, after preparation of a proper ferrofluid, containing magnetic sorbent and an ionic liquid carrier, this fluid was simply injected into the sample test tube. Afterward, by reversing the tube, the extractant was wholly dispersed through the sample solution. As a result, a semi-opaque status was formed and the hydrophobic complex of analyte was adsorbed/extracted by magnetic sorbent particles. By applying a magnetic field the particles were settled and the aqueous phase was simply removed by reversing. Finally, the sorbent was eluted and concentration of the analyte was determined by FAAS. In comparison with other magnetic solid phase extraction methods, handling and performance are more facile as well as the extraction procedure is really short. In addition, this method is very useful and applicable for opaque/dark samples, in which observation and separation of extraction phase are difficult. The applicability of the technique was evaluated by determination of trace amounts of cadmium in several water and milk samples. Under the optimum conditions, relative standard deviation (for 10 ng mL^{-1} of cadmium) and the limit of detection were obtained 4.0 % and 0.11 ng mL^{-1} , respectively (n = 7). Maximum concentration factor of 200 was obtained, while the extraction time was below than five minutes.

Keywords: Ionic Liquid; Ferrofluid; Magnetic solid phase extraction; Cadmium; Water samples.

1. Introduction

Heavy metals may enter into the environment by a wide range of processes and pathways; they are naturally found on earth's crust and have been used in many different applications over decades. Generic sources of heavy metals include: mining and industrial production such as foundries, smelters, oil refineries, petrochemical plants and chemical industry, untreated sewage sludge, disperse sources such as metal piping, traffic and fossil fuel combustion. Consequently, heavy metal toxicity has emerged in modern times to become one of the most serious underlying causes of chronic diseases, and is known to increase cancer incidence, as a major threat to our health. [1]

Among toxic metals, cadmium is classified as number 7 in ATSDR's (Agency for Toxic Substances and Disease Registry, 2008) top 20 list. Cadmium, which is known to be a human carcinogen, mainly stored in bones, livers and kidneys. Regrettably, only small amounts of this element may cause kidney damage and fragile bones during a period of years.[2] Mainly, cadmium can enter the body through drinking water, diet, tobacco smoking, and inhalation from the air. Accordingly, the determination of cadmium at trace levels especially in environmental samples and biological materials not only is of considerable importance for the studies of environmental pollution and occupational exposure, but also is one of the great targets in analytical chemistry.

During the time, despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before analysis due to their frequent low concentrations in numerous environmental samples (especially in water samples). Additionally, since high levels of sundry components usually accompany analytes, a sample preparation step is often necessary. Various sample preparation techniques have been proposed for separation and preconcentration of cadmium from different matrices, including: liquid–liquid extraction (LLE) [3, 4], solid phase extraction (SPE) [5], cloud point extraction (CPE) [6], single-drop microextraction (SDME) [7], solid phase microextraction (SPME) [8], dispersive liquid-liquid microextraction (DLLME) [9] and etc.

LLE is a classical sample preparation method. It presents some disadvantages like large volumes of solvents, which are expensive and toxic, high operation costs, possible formation of emulsions, large equipment and high residence time. The continuous quest for novel sample preparation procedures led to the development of new methods, whose main advantages are speed and negligible use of solvents. Watanabe and co-workers [10] introduced CPE, a new separation and extraction technique, as an alternative to LLE.[11] Despite many benefits when using CPE, in the rather high content of salt, the background is increased since the enrichment phase is composed of a little aqueous sample. Also in the presence of more than 3% of water-miscible organic solvents, such as acetone, phase separation does not occur and the extraction system is destroyed.[12] In SDME, since very small amount of the solvent is used, there is minimal exposure to toxic organic solvents.[13] However it is time-consuming, as well, at the fast stirring conditions, organic drop would be broken down. SPME, which is a solvent free process, was developed by Arthur and Pawliszyn.[14] This technique is fast, portable, easy to use, and has been applied for determination of heavy metals.[8] However, SPME suffers from some drawbacks, too: its fiber is fragile and has limited lifetime and desorption temperature, and also sample carry-over is a problem.[15] Along with the others, DLLME is simple, fast and inexpensive. However, it still has some drawbacks, including the difficulty to automate and the necessity of using a third component (disperser solvent) that usually decreases the partition coefficient of the analytes into the extractant solvent. Furthermore, the extractant and disperser solvent used in DLLME are often volatile organic compounds. Among the mentioned methods, SPE is the very popular technique due to its availability, selectivity and rapidity. It reduces solvent usage and exposure, disposal costs and extraction time. [16] In addition, its versatility allows use of this method for many purposes, such as purification, trace enrichment, desalting, derivatisation and so more. In these fields, the most frequently used groups of sorbents are: chemically modified silica gel [17], polymeric sorbents [18] and porous carbon [19]. Unfortunately, these traditional SPE methods are usually tedious and time-consuming.

In recent years, many alternative sorbents have been explored and suggested to substitute the traditional phases for improving the enrichment performance and reducing extraction time in SPE processes. Among them, magnetic particles (MP) are the most commonly used materials in separation techniques due to their paramagnetic properties, which ease the isolation of analytes in solution by attracting them and settling with the aid of an external magnetic field. The method used for synthesis of MP, determines their compatibility with and suitability for a given separation method, mainly by the controlling of sorbent composition and morphology.

Magnetic solids were first used to isolate biomolecules.[20] However, in recent years, the use of magnetic solids bearing different functional groups, has been extended to the pre-concentration of organic and inorganic compounds such as: heavy metals [21], anti-inflammatory drugs [22], antibiotics [23], analgesics [24], insecticides [25], pesticides [26], dyes [27], surfactants [28], carcinogens [29] and phenolic compounds.[30] Easy and fast isolation/extraction (even from large-volume samples) would be allowed due to the paramagnetic properties of such particles. Unfortunately, most of these magnetic solid phase extraction (MSPE) techniques, were found to have some limitations, such as difficulty in handling of the magnetic particles (especially in the weighing and addition steps), impracticality of magnetic stirrers and steel-made devices during the process, as well as the long equilibrium time needed for complete extraction.

We suppose that some of the mentioned drawbacks would be improvable by applying a fluid state of MP instead of the solid form. As stated in the previous work, by using remarkable properties of dispersive-solid phase extraction (D-SPE) and applying a suitable suspension of magnetic particles, the extraction time was greatly shortened and the operation/handling get clearly facile.[31] Ferrofluids (FF), which are stable colloidal suspensions of single-domain magnetic particles dispersed in a liquid carrier [32, 33], have both magnetic and fluid properties, characteristically.[34-36] Unique properties of such fluids make them useful for many technological [37], biological and medical purposes [38], as well as an assist in materials science [39] and engineering research.[40] Generally, in these materials, magnetic particles have to be covered with a proper coating, due to avoiding agglomeration/aggregation by van der Waals forces or magnetostatic interactions. Consequently, FF are classified into two main groups according to the coating native: surfacted ferrofluids (SFF), if a surfactant covers the particles, and ionic ferrofluids (IFF), if the shell consists of electric layer(s). The stability of the magnetic colloid depends on the thermal contribution and balance between attractive (van der Waals and dipole-dipole) and repulsive (steric and electrostatic) interactions, while the carrier can be a polar or nonpolar liquid.[41]

In the recent years, many efforts have been focused on the preparation of new FF with favorable modern properties, by changing the carrier fluid.[42, 43] In this regard, ionic liquid (IL) have attracted considerable interest as promising candidates to replace conventional organic carriers.[44] Reasons for this interest in ILs are related to their unique physicochemical properties. Unlike conventional carriers, the properties of ILs (e.g., viscosity, solubility, electric conductivity, melting point, etc.) can be tuned by varying the composition of their ions. Furthermore, they are considered to be very stable and “environmentally friendly” compounds owing to their negligible vapor pressure, negligible flammability, and liquid state in a broad temperature range.[45-47] Nowadays, hundreds more ILs are commercially available (and a considerable number of new ILs can be readily synthesized) [45], covering a wide range of properties. Owing to these characteristics, it is thought that the use of ILs as carriers of FF may expand and/or improve their applications in different areas of science and engineering. The first IL-based ferrofluid (ILFF), which consisted of bare maghemite and cobalt ferrite nanoparticles dispersed in 1-n-butyl-3-methylimidazolium tetrafluoroborate, has been reported by Oliveira.[43] However, it has been proposed that the electrostatic repulsion which may exist among particles dispersed in ILs would not be enough [48] and steric repulsion is needed too for making long-term stability.[49]

The aim of this work is to develop a fast, simple and efficient D-SPE method based on ILFF, for the extraction of Cd(II) and its determination by FAAS. For this purpose, an appropriate amount of ILFF was injected rapidly into the aqueous sample solution with a syringe. The hydrophobic complex of the analyte was extracted by the magnetic sorbent, which was wholly dispersed into the aqueous solution. Because of the large contact surface between the sample and the sorbent, mass transfer processes speed up and extraction would be achieved within a few seconds. The developed procedure was applied for preconcentration of the analyte form various water and milk samples.

2. Experimental

2.1. Apparatus

A field emission scanning electron microscope (FE-SEM, Hitachi, S-4160, and Japan) was used for preparation of SEM images. A Varian model AA-400 atomic absorption spectrometer (http://www.varianinc.com), equipped with an air-acetylene burner and with cadmium hollow cathode lamp was used as the radiation source. The lamp was operated at 4 mA, using the wavelength at 228.8 nm and slit of 0.5 nm, and the flow rates of air and acetylene were set as recommended by the manufacturer. Background correction has been used with a deuterium lamp. All measurements were carried out in peak height mode. A pH-meter Model 692 from Metrohm (http://www.metrohm-ag.com, Herisau, Switzerland) equipped with a glass combination electrode was used for the pH measurements. For sonication processes an ultrasonic bath (Elmasonic, model S 40 H) and for magnetic separations a few strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnets (1.31 T) were used.

2.2. Reagents and solutions

1-(2-Pyridylazo)-2-naphthol (PAN), acetone, ethanol, acetic acid, nitric acid, sodium hydroxide, sodium chloride, ammoniac, ammonium hydroxide, potassium hydrogen phthalate, hydrogen peroxide, tetraethyl orthosilicate (TEOS) and all used salts were obtained from Merck (Darmstadt, Germany), all of them were of analytical grade or even better. Doubly distilled water was used throughout the experiment.

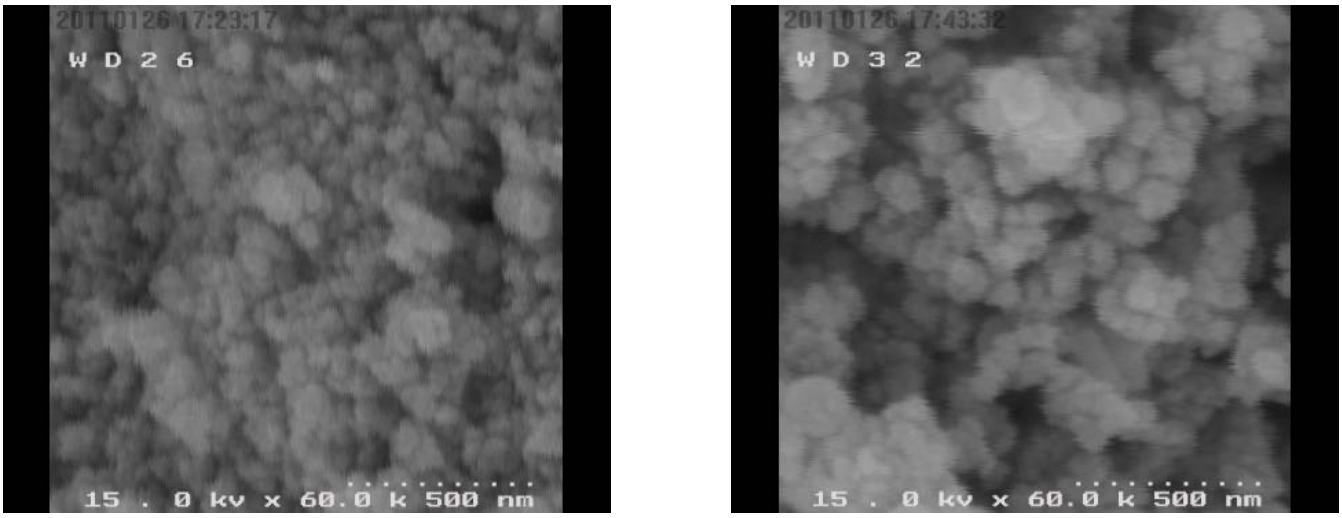
1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([Bmim][Tf_2N]), 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([Emim][Tf_2N]), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]), 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) were purchased from Merck.

A 1.0×10^{-2} mol L^{-1} solution of PAN was prepared by dissolving the required amount in pure ethanol. Buffer solution (pH = 5.5) was prepared by dissolving proper amounts of potassium hydrogen phthalate (KHP) and sodium hydroxide in water.

2.3. Preparation of silica-coated magnetite nanoparticles

Although for ILFF, the electrostatic repulsion was intensified, and it resists against bare-particles agglomeration, but actually this is not such enough to obtain the long-term stabilization. Consequently, strong steric repulsion is required for such IL-based suspensions [49]. Therefore, a suitable coating, which properly covers the particles and interacts with IL carrier, seems to be essential. Meanwhile such cover plays protective role and enhances selectivity of adsorption for particles [50]. In the recent report, silica was selected as covering material for magnetite nanoparticles.

Fe_3O_4 nanoparticles was firstly synthesized according to the previous method [51]. Then, silica coated particles (Fe_3O_4/SiO_2) were synthesized according to the previous reports by some modifications [52]. In Brief, the prepared Fe_3O_4 nanoparticles (4.0 g) were suspended in ethanol (250 mL) under sonication for one hour. Concentrated ammonia (80 mL), deionized water (50 mL) and TEOS (2 mL) were added in sequence to the suspension. In order to reach suitable thickness of silica layer, the mixture was sonicated for 2 h followed by vortex mixing for 12 h. The silica-coated nanoparticles (SCNPs) were collected by applying magnetic field and were thoroughly washed with deionized water three times, and finally dried at 100 °C for at least 24 h. Fig. 1 (b) shows the SEM image of the modified nanoparticles.



(a) **(b)**

Fig.1. The SEM images of a) Fe_3O_4 NPs, b) silica-coated Fe_3O_4 NPs.

2.4. Sample preparation

"NIST-SRM-1643e" (trace elements in water) standard reference material (SRM) was employed for testing the accuracy of the proposed method. In addition, different real samples were analyzed, such as: Fatless ultra-high temperature treated cows' liquid milk (Teen-Damdaran, Iran), "Lactomil 1" milk powder (Pegah infant formula Co., Iran) and water samples (mineral, tap and sea water). Details of the sample preparation are as follows.

Milk samples were digested according to "Wet digestion in an open vessel" procedures, with a little modification [53]. Briefly, for liquid sample 3.0 mL and for powder sample about 5 g (accurately weighted) was poured into a 100 ml conical flask; 10.0 mL nitric acid (67 %) was added and the flask was covered with a watch glass. The sample was allowed to stand overnight at room temperature in order to reduce the amount of gas produced during the subsequent heating cycle. Then the watch glass was replaced by a glass funnel (5 cm i.d.) inserted into the flask and the sample was heated on a hot-plate at 140 ° C for about one hour to gently boil off the nitric acid. After cooling down to room temperature the funnel was taken away, 3.0 mL perchloric acid (72%) were added and heating prolonged at 210 ° C until the liquid turned brown. After cooling down to the room temperature, 3.0 mL hydrogen peroxide (60 %) were added to the sample solution drop by drop and the content reheated until the liquid turned brown again. The addition of hydrogen peroxide was repeated four times until a colorless solution was obtained and white fumes of perchloric acid were generated. The solution was evaporated to near one milliliter and after cooling was transferred into a 50 mL volumetric flask, adjusted to pH = 5.5, and made up to the mark with doubly distilled water. This solution was used in both the IL-based extraction method and direct determination by ETAAS.

Tap water sample was freshly collected from our laboratory (University of Tehran, Tehran, Iran). Other samples were collected from the north of Iran (Caspian Sea and Damavand Mountain). All of them were analyzed by the proposed methodology as a prior step to its determination by FAAS. Only the seawater sample was filtered through a 0.45 μm membrane filter immediately after sampling. Finally, 50 mL of each water sample was transferred to a tube, then pH of the solutions was adjusted to pH 5.5 with the buffer solution. Then, the separation/preconcentration method was applied.

2.5. Extraction procedures

2.5.1. Preparation of the ferrofluid

Before mixing IL carriers and SCNPs, these nanoparticles should be activated by an acid solution. It would provide positive charges on the silica surface [54], thus more effective interactions between anion of ionic liquid and the particles would be appeared.[43, 55] According to preliminary experiments, acetic acid has been used as a surface activating agent. For this purpose, 15 mg of dried SCNPs and 100 μL of glacial acetic acid were mixed in a plastic vial and the mixture was heated at 90 °C under continuous stirring for 45 min to allow acetic acid adsorption. Afterward excess acid was removed by vacuum. For preparation of each ferrofluids, acetic acid-activated magnetite nanoparticles were dispersed in the proper amount of IL carriers, individually and these suspensions were sonicated for at least 30 min. The resulting suspension had a magnetite fraction of 9.3%.

2.5.2. IL-D-SPE Extraction

A schematic view of IL-D-SPE experimental setup is shown in Fig. 2. The sample or standard solution containing Cd(II) in the range of up to 50 ng mL^{-1} and PAN (5.5×10^{-5} mol L^{-1}) was poured into a 50 mL Falcon plastic tube. By adding an appropriate amount of KHP/NaOH buffer solution, the pH was adjusted to 5.5, and then the total volume was adjusted with doubly distilled water. Afterward, the extractant ferrofluid suspension, containing proper amounts of SCNPs and the ionic liquid carrier, was injected rapidly into the sample solution by means of a 1.0 mL syringe (equipped with a proper needle). Thereupon, by reversing the test tube, ferrofluid was dispersed thoroughly in the solution, a semi-opaque state was obtained and the hydrophobic complex of Cd-PAN was extracted by magnetic particles. Subsequently, some tiny strong magnets were placed at the bottom of the tube to let the extractant settle. After about 2 min, the solution became limpid and the supernatant was discarded simply by decanting it. Thereafter, the magnets were removed and 0.75 mL of HNO_3 solution (1.0 mol L^{-1}) was added to desorb the Cd(II) complex by sonication. Finally, the obtained mixture was exposed to the magnets again, and the clear solution of eluent, containing the eluted analyte ions, was transferred to another tube. The analyte in the eluted phase was determined by FAAS.

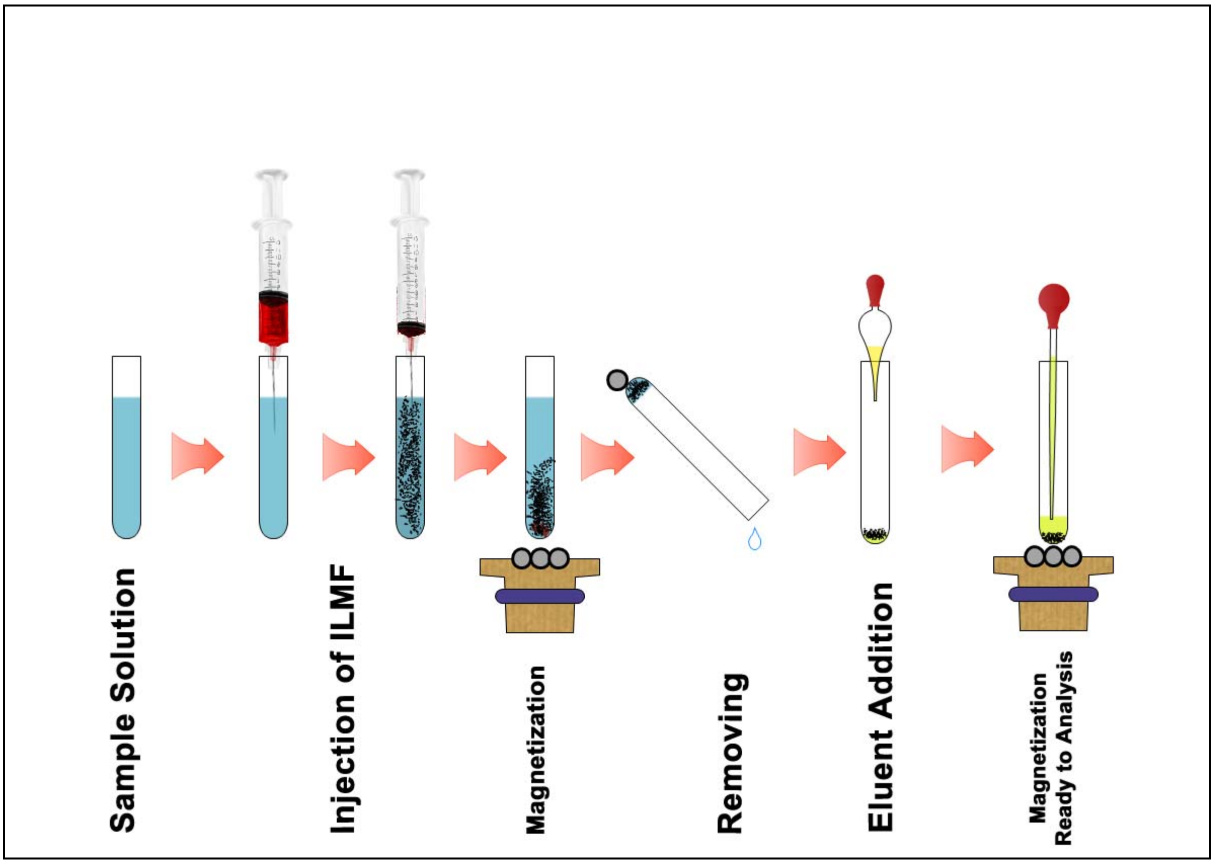


Fig.2. The schematic view of IL-D-SPE experimental setup.

3. Results and discussion

3.1. Preliminary studies

According to preliminary studies and experiments, concerning about 50 mL sample solution, 50 mg of SCNPs was used for analyte extraction and 1.0 mL of HNO_3 solution (2.0 mol L^{-1}) was applied at the elution step, while the concentration of PAN was chosen 5.0×10^{-5} mol L^{-1}.

3.2. Selection of ionic liquid carrier: type and volume

Generally, in this work, to achieve a satisfactory ferrofluid, some criteria for selecting the IL carrier phase should be met. Firstly, selected IL must have proper sterical interactions with SCNPs to achieve stable ferrofluid. Secondly; it has to be miscible in the sample solution to improve the distribution efficiency of the extractant. Additionally, it should have an acceptable capacity for containing the magnetic extractant.

In this work some ILs containing an imidazolium cation like [Bmim][Tf_2N], [Emim][Tf_2N], [Bmim][PF_6], [Emim][PF_6], [Bmim][BF_4] as well as [Emim][BF_4] were examined to choose the proportionate carrier for the extractant ferrofluid. The stability of each IL suspensions was checked by qualitative observations while time was recorded. Before this test, all the samples were redispersed by ultrasound in order to ensure equal initial conditions. Results indicate that all IL carriers provide stable ferrofluid over 8 hr, while both suspensions of [BF_4] remain entirely stable. As it has been reported, we believe that the size of the anions is an important parameter affecting the stabilization of the nanoparticles in the IL carriers [43]. Moreover, both [Bmim][BF_4] and [Emim][BF_4] are hydrophilic ionic liquids and suitable for this work. However, the first was competent to contain higher concentration of magnetic particles (up to 25 % (w/v)). In accordance with all these results, [Bmim][BF_4] was selected as the carrier fluid in this work.

In the next step, the minimum volume of IL carrier for extraction of Cd(II) was determined in the range of 100–400 µL. Accordingly, 200 µL [Bmim][BF_4] of was enough to preconcentrate the metal ions quantitatively, at the studied concentrations, using 50 mL of sample in the presence of 30 mg of modified magnetic particles. Meanwhile, for higher volumes of this carrier, the extraction efficiency was almost constant.

3.3. Effect of pH and KHP/sodium hydroxide buffer concentration

Two major factors affecting the extraction of metal ions are complex formation and chemical stability of the formed complex. Both of them are influenced by pH of the aqueous phase as an exclusive parameter. Moreover, pH controls charge of the sorbent surface, as well as its interaction tendency.

Effect of pH on the extraction of Cd(II) was investigated in the range of pH 2.0–9.0 by adding proper amounts of hydrochloric acid or sodium hydroxide solutions into aqueous samples, the results are shown in Fig. 3. The illustrated results reveal that by increasing the pH, the efficiency of extraction was increased slowly and formed a plateau approximately in the range of pH from 5.0 to 9.0. This increase is due to two parameters, the first is the growth in the tendency of Cd ions to form stable complex with PAN [56], and the second is the rise in adsorption affinity of SCNPs. For the subsequent works, a pH of 5.5 was selected. Hence buffer solution 5.5 (containing KHP and sodium hydroxide) was chosen for pH adjustment. In addition, extraction efficiency as a function of the buffer concentration was studied up to 0.05 mol L^{-1}. The efficiency increased until a buffer concentration of 3×10^{-3} mol L^{-1} and then it stayed approximately constant. A buffer concentration of 4×10^{-3} mol L^{-1} was selected for subsequent experiments.

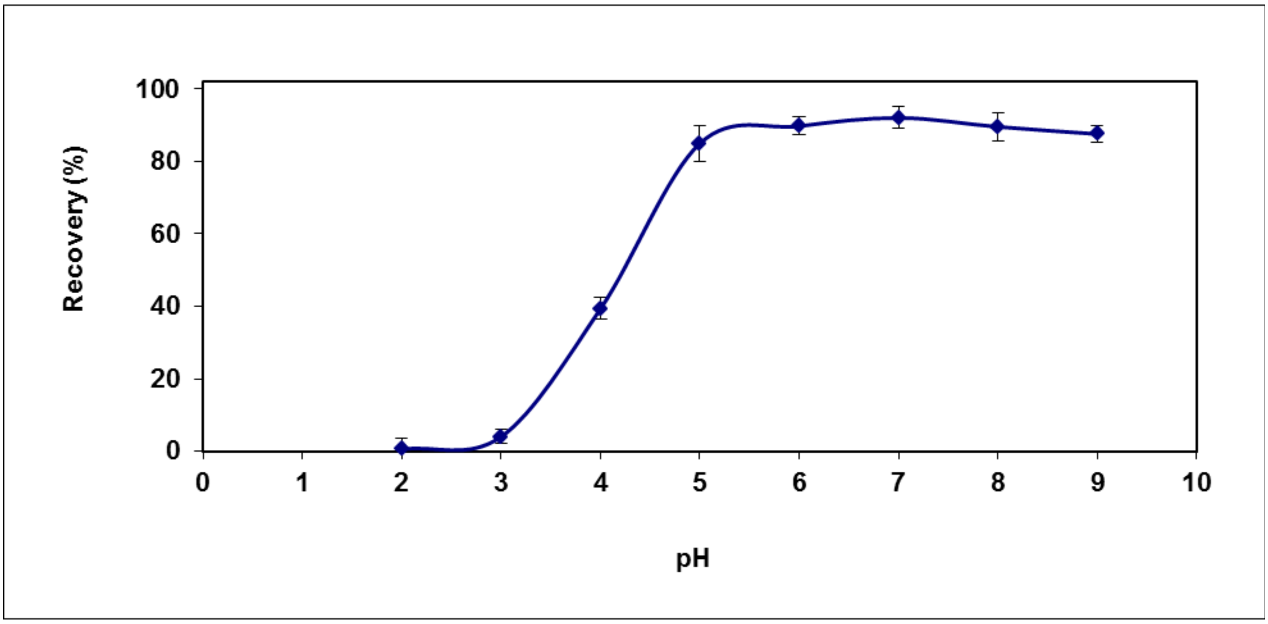


Fig.3. Effect of pH on the extraction recovery of Cd(II). Sample volume, 50 mL; Pd(II), 30 ng mL^{-1}; concentration of PAN , 5.0 × 10^{-5} mol L^{-1}; IL volume, 300 µL (n=3).

3.4. Choice of the eluent: type, concentration and volume

In order to choose the most effective eluent for the quantitative recovery of the cadmium ions, a variety of acidic eluents was selected and tested. Although, according to these facts; at low pH the adsorption of Cd ions was almost negligible, as well as most metal-PAN complexes are dissociable in such media [56]. Hence, various acidic eluents were prepared in the range of 0.5 - 3.0 mol L^{-1} by proper dilution of HCl or HNO_3 in water or ethanol, afterwards 1.0 mL of each solution was utilized for the extractant elution. According to the recovery results of the metallic complex, for both aqueous and alcoholic HNO_3 solutions, results were similar, and they seemed to be more effective for the quantitative recovery. However, the aqueous solution was preferred to the alcoholic one.

Further results showed that by increasing concentration of HNO_3 up to 1.0 mol L^{-1}, elution recoveries gradually increased and then stay approximately constant. Consequently, a concentration of 1.0 mol L^{-1} of this acid was selected as the optimum for the subsequent work. Moreover, for the estimation of the minimum required volume of the selected eluent, various volumes in the range of 0.25 to 1.50 mL were applied. Results indicated that volumes larger than 0.7 mL are proper for the complete elution. Thus, for achieving the highest enrichment, a volume of 0.75 mL of this eluent was selected for the following experiments.

Moreover, for effective desorption, sonication times were evaluated up to 10 min. The results showed that one minute is sufficient time for quantitative desorption by 0.75 mL of HNO_3 aqueous solution (1.0 mol L^{-1}).

3.5. Effect of amount of the sorbent

For quantitative extraction with maximum uptake, the optimum amount of the sorbent was determined in the range of 5-70 mg. At the studied concentrations, 25 mg of SCNPs was enough to preconcentrate the metal ions quantitatively, while 50 mL sample solutions were examined. Meanwhile for greater amounts of modified magnetic sorbent, the extraction efficiency was almost constant.

3.6. Effect of PAN concentration

The influence of PAN concentration on the adsorption of the analyte complex was investigated in the range from 2.5×10^{-5} to 9.0×10^{-5} mol L^{-1}, while Cd(II) concentration was 30 μg L^{-1}. The results are shown in Fig. 4. As it was well expected, the adsorption efficiency of the metal ion increased by increasing PAN concentration up to about 5.0×10^{-5} mol L^{-1} and then remained approximately constant. In order to achieve high efficiency of adsorption, a concentration of 5.5×10^{-5} mol L^{-1} of this ligand was used in the following experiments.

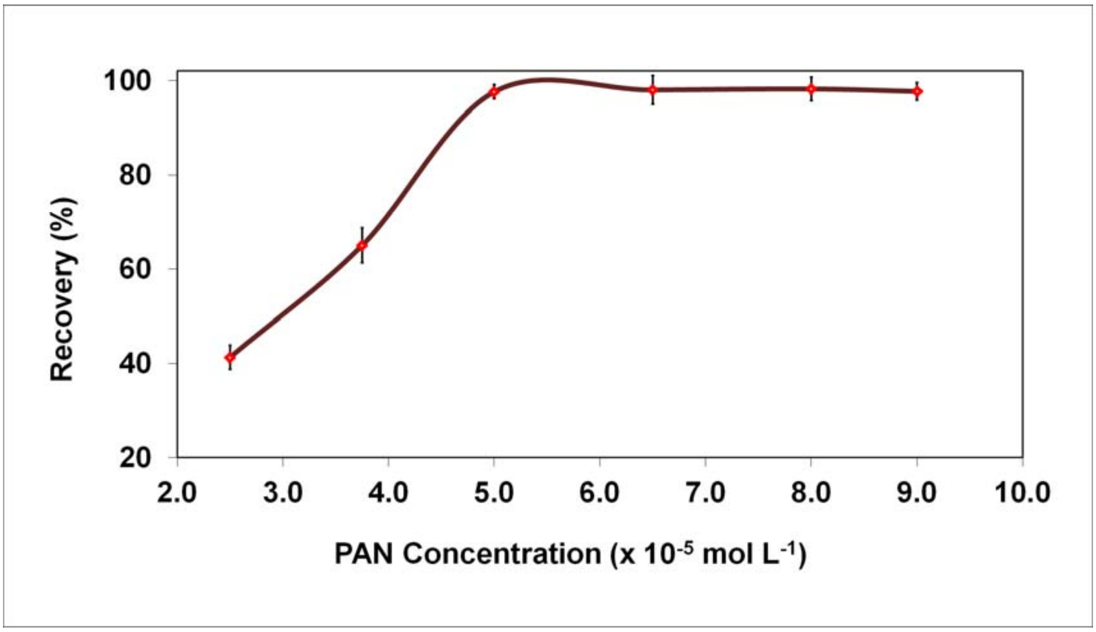


Fig.4. Effect of PAN concentration on the extraction recovery of Cd(II). Sample volume, 50 mL; pH of sample solution, 5.5; Cd(II), 30 ng mL^{-1}; amount of sorbent, 50 mg; IL volume, 300 µL (n=3).

3.7. Effect of sample volume

Concentration of trace metals in real samples, is usually so low that the determination would be intricate and almost impossible without a high enrichment factor. Generally, applying more sample volume leads to considerably higher enrichment factors at the same time. Thus, the measurement of breakthrough volume (the sample volume, which can be preconcentrated without any loss of analyte) is inevitable. For this reason, various volumes (in the range of 25 - 200 mL) of sample solutions containing 1.5 µg of Cd was processed according to the recommended procedure to investigate effects of the volume of aqueous phase on the retention of the Cd-PAN complex. The recoveries are almost quantitative up to 150 mL; however, the extraction efficiency would slightly decrease when the sample volumes were larger than this volume, hence 150 mL was chosen as the largest running volume of sample. As a result, a maximum concentration factor (CF) of about 200 could be attained for quantitative recoveries when the sample and eluent volume were 150 and 0.75 mL, respectively.

3.8. Adsorption capacity

In order to evaluate the adsorptive capacity of SCNPs for the extraction, 50.0 mL sample solutions containing 0.5 mg Cd ions were processed according to the recommended procedure. After adsorption, the supernatant solutions were analyzed by FAAS to determine the residue amount of the metal ion. Results showed that the adsorption capacity for cadmium ions was found to be 9.1 mg per gram of SCNPs sorbent.

3.9. Effect of salt concentration and coexisting ions

In order to investigate the effect of ionic strength on D-SPE based on the ionic liquid, in the presence of NaCl (as one of the most common electrolytes present in environmental samples [57]), the extraction recoveries of the analyte were studied, while the salt concentration was varied up to 1 % (w/v). Also to investigate robustness of the method against rather salty solutions, various solutions of NaCl in the range of 1- 5 % (w/v) were examined. Results indicated that recoveries of the metallic complex were approximately constant in the both ranges and there is no considerable effect on extraction efficiency even up to 5% (w/v) of NaCl.

Also, the effect of common coexisting ions on the sorption and determination of Cd(II) was studied. For this purpose, solutions containing 30 µg L^{-1} of Cd as well as excessive amounts of PAN and various amounts of interfering ions were treated according to the extraction procedure. A given species was considered to be interfering if it resulted in a ± 5 % variation of the recovery of the metal ions. The obtained results evidenced that the presence of major coexisting ions had no significant influence on the preconcentration and determination of the analyte. For example, the alkali and alkaline earth metal ions at the concentration of up to 10,000 times, Mg(II) , As(III) , Bi(III) , Cr(III) and Zn(II) at the concentration of up to 1500 times, Al(III) , Fe(III) , Fe(II) , Pd(II) and Hg(II) at the concentration of up to 500 times and Co(II) , Ni(II) and Cu(II) at the concentration of up to 50 times higher than the concentration of the analyte, did not interfere. Moreover, some anions like PO_4^{3-}, SO_4^{2-}, Cl^-, CN^- and SCN^-, did not show any interferences at the concentrations of up to 500 times higher than the analyte concentration.

3.10. Analytical Figures of merit

Under the optimal experimental conditions, calibration curves were obtained for analyte ion before and after the pre-concentrating of 50.0 mL of the sample solution. Linearity was observed over the range of 0.4-50 ng mL^{-1} with a good correlation coefficient (R^2) of 0.9932. The precision of the method was evaluated by analyzing standard solution at 10 ng mL^{-1} of Cd for seven times in continuous, and the relative standard deviation (RSD) was 4.0 %. The limit of detection (LOD = 0.11 ng mL^{-1}) was calculated as 3 S_b/m (S_b: standard deviation of seven replicates of blank signals; m: slope of the calibration curve after preconcentration). Meanwhile, maximum applicable concentration factor (CF) of about 200 would be obtained as the ratio between 150.0 mL (maximum sample solution volume) and the final volume obtained after the elution step.

3.11. Validation of the method

In order to verify accuracy and validate precision of the proposed procedure, the IL-D-SPE method was applied to determine the amount of Cd in the SRM (NIST-SRM-1643e, trace elements in water) after proper treatment. In brief, after neutralization of 25 mL of SRM acidic solution, PAN was added and pH was adjusted to 5.5. Finally, the volume was made up to 50 mL with doubly distilled water and then the general extraction procedure was applied. Results of the analyte determination indicate that there are good agreements between the certified value (6.568 ± 0.073 μg L^{-1}, n = 6) and the obtained value (6.653 ± 0.221 μg L^{-1}, n = 6), and it can be concluded that the proposed method is accurate and free from systematic errors.

3.12. Analytical applications

The proposed methodology was applied for extraction and FAAS determination of the investigated toxic metal ion in different real samples with different matrices containing varying amounts of diverse ions. The results of water samples were summarized in Table 1. To examine the reliability and accuracy of the method, different amounts of the investigated metal ions were spiked into 50 mL of the water samples at optimum conditions. The results indicated that the proposed method can be reliably used for the determination of Cd(II) with good recoveries in the range of 97.5 and 103.3 %.

Table 1- Determination of Cd (II) in real water samples.

Sample	**Spiked Cd (ng mL^{-1})**	**Found Cd (ng mL^{-1})^a**	**Recovery (%)**
Mineral water [b]	-	ND[c]	-
	10	9.76 ± 0.42	97.6
	15	14.62 ± 0.35	97.5
Tap water [d]	-	ND[c]	-
	10	10.33 ± 0.33	103.3
	15	15.45 ± 0.24	103.0
Sea water [e]	-	2.21 ± 0.36	-
	10	12.17 ± 0.24	99.6
	15	17.28 ± 0.22	100.5

[a] Mean ± SD (n = 6).
[b] Damavand mineral water, Iran.
[c] Not detected.
[d] From drinking water system of Tehran, Iran.
[e] Caspian sea water.

The method was also applied for determination of Cd(II) in milk and milk powder to evaluate and prove the applicability of IL-D-SPE. Accuracy was assessed by comparing results with those obtained by using electrothermal atomic absorption spectrometry (ETAAS). The data obtained with the proposed and ETAAS methods for milk samples were summarized in Table 2. By applying paired *t*-test, no significant difference at 95 % confidence level was observed and it signified that the proposed method can be reliably used for the determination of Cd(II) in different matrices.

Table 2- Determination of Cd (II) in milk samples.

Sample	**Found Cd by IL-D-SPE** [a]	**Found Cd by ET-AAS** [a]
Lactomil 1 milk powder [b]	7.2 ± 0.3 (ng g^{-1})	7.5 ± 0.2 (ng g^{-1})
Liquid milk [c]	19.4 ± 1.3 (ng mL^{-1})	18.9 ± 0.6 (ng mL^{-1})

[a] Mean ± SD (n = 4).

[b] Obtained from the local pharmacy (Pegah infant formula Co., Iran).

[c] Obtained from the local supermarket (Teen-Damdaran, Iran).

3.13. Comparison of IL-D-SPE with other methods

A comparison of the represented IL-D-SPE method with other reported cadmium preconcentration methods is given in Table 3. In comparison with others, this method has a low LOD (0.11 ng mL^{-1}), high concentration factor (200) and short extraction procedure (less than 5 min). In fact, extraction can be achieved very fast, and no centrifugation/filtration is required for phase separation. This feature would assemble on-site extraction of various analytes (specially, unstable species). In addition, this method is very useful and applicable for opaque/dark samples, in which observation and separation of extraction phase are difficult. These significant features of IL-D-SPE are of key interest for routine trace laboratory analysis.

Table 3- Comparison of the previous preconcentration methods for Cd with the proposed method.

Method	**CF**	**LOD** (ng mL^{-1})	**RSD** (%)	**Linear range** (ng mL^{-1})	**Sorption capacity** (mg g^{-1})	**Time** (min)	**Max Volume** (mL)	**Ref**
Coprecipitation-	200	100	2.20	10-50000	10.60	> 5	1000	[5]
LLE-FAAS	80	0.3 [b]	2.6 - 5.6	0.98–40 [b]	------	> 5	250	[4]
SPE-FI-FAAS	117	0.11	2.9	1–10	0.48	> 2.5	16	[58]
SPE- FI- ICP-AES	60	1.1	1.1	5-100	------	> 1.5	------	[59]
IL-SPE- FAAS	75	0.60	3.7	1-800	13.3	> 85	150	[60]
IL-SPE- FAAS	200	0.122	2.87	0.3 to 20	9.2	> 5	50	[61]
CPE-FAAS	52	0.31	2.4	1–100	------	> 25	10	[62]
CPE-FAAS	15[a]	0.15	2.4	To 128	------	> 25	50	[6]
CPE-FAAS	62	4.0 [c]	3.1	0.08-25	------	> 25	10	[63]
LSE [d]-FAAS	50	76	<10	To 5000	9.89	> 40	500	[64]
LPME-GFAAS	390	0.0065	5.8	0.01–1	------	> 15	2	[65]
D-SPE–FAAS	200	0.11	4.0	0.4-50	9.1	> 5	150	This work

[a] preconcentration factor
[b] ng g^{-1}
[c] µg kg^{-1}
[d] liquid–solid extraction by a natural sorbent

4. Conclusions

In this study, an ionic liquid-based dispersive magnetic solid phase extraction method (IL-D-SPE) was developed for the preconcentration of cadmium ions (as a test analyte) from water and milk samples as a prior step to its determination by FAAS. After preparation of a proper ferrofluid, containing modified magnetic sorbent and an ionic liquid carrier ([Bmim][BF_4]), this fluid was simply injected into the sample solution. In comparison with solid phase methods, it is much faster, because the sorbent is highly dispersed in the aqueous phase and no centrifugation/filtration is required for phase separation. Unlike other magnetic solid phase extraction, handling and performance are more facile and faster. Furthermore, IL-D-SPE has a low toxicity since only very small amounts of an IL as an "environmentally benign fluid" is used as a carrier instead of common organic fluids. The represented system is considered in favor of further potential chemical applications of ILs. Additionally, this method is simple, low cost and suitable for opaque/dark samples, in which observation and recognition of phase separation are difficult. The precision and accuracy of the method were satisfactory, while a maximum concentration factor of 200 for a 150 mL sample volume was accessible. Taking advantage of the mentioned properties, the IL-D-SPE methodology could be expected to be widely used in complex matrix sample preparation.

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