

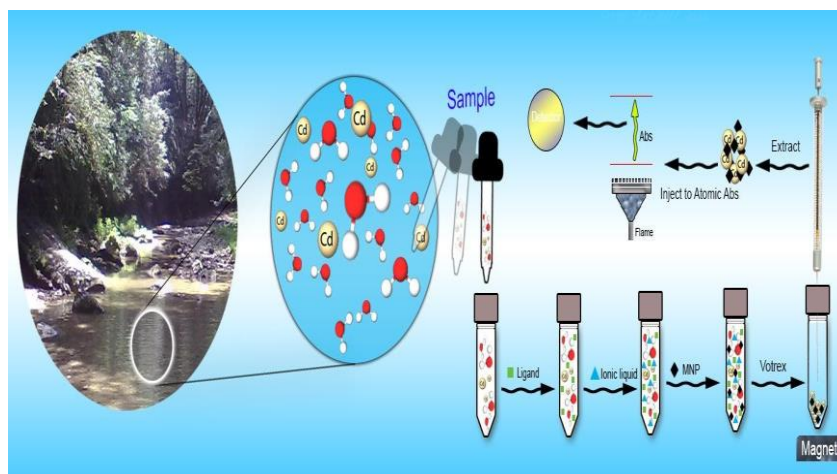
SciRad SCIENTIAE RADICES

Use of magnetic nanoparticles in an Ionic liquid (BMIM-PF6) based vortex-assisted dispersive liquid–liquid microextraction (VSLLME) for measuring the traces amounts of cadmium in environmental, biological and nutritional samples

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Abstract: In the present project, the magnetic nanoparticles were used in a type of an ionic liquid based micro-extraction to measure trace amounts of cadmium in different real samples containing environmental water samples, saliva and human hair. In the optimum condition, the recovery percentages for the real sample were about 94.5% to 101.3%, showing the designed method is suitable to be used for analyzing the real environmental and biological samples. The main parameters were evaluated and optimized as follows: pH was 2.5, the volume of ionic liquid was 150

μl , the amount of Fe_3O_4 magnetic nanoparticles was 50mg, the volume of the complexing agent was 12 μl , and the vortex time was 1 min and 2 min for ionic liquid, and magnetic nanoparticle distribution steps, respectively. Also, the volume of the medium was 10 to 20 ml.

Keywords: VSLLME, Cadmium, Vortex-assisted, Heavy metal, real sample

Received: 2023.12.06

Accepted: 2023.12.26

Published: 2023.12.29

DOI: 10.58332/scirad2023v2i4a05

Introduction

In the recent decades, due to the wholesale changes in the natural order of our planet, concerns related to the environmental issues have attracted the attention of a great number of researchers all around the world [1]. Releasing wastes, gases, and other unnatural species in to the earth, and atmosphere which sometimes have catalyzing activities, cloud play the main role in changing the ecosystem (as the environmental pollutions) [2]. Since, those directly effect on a wide range of living species, the chemical and biological pollutants are of the most important agents which are dealing with natural environment of earth. That is, many researches in this area have been made [3-11]. These researches were performed by different experimental as well as theoretical approaches [12-15]. Somehow, even in the production of organic molecules especially in drug synthesis, scientists made attempt to develop green, catalyst-free or ecofriendly methods [16-23]. For example, the researches showed that existence of high dosages of some heavy metal ions like mercury, or cadmium, and lead [24] in drinking water or food could lead to metabolic syndrome or even damage in organs. Especially, the International Agency for Cancer Research has identified cadmium as a human carcinogen [25], with a high carcinogenic potential even in very low concentrations, destroying body tissues such as the liver, kidneys and lungs [26]. In addition, the world health organization (WHO) has expressed that the maximum tolerable amount of cadmium in food sources daily 1 to 1.2 $\mu\text{g kg}^{-1}$, indicating the importance of the toxicity of this element [27]. Also, the US Environmental Protection Agency (EPA) has announced that the limit of cadmium in drinking water is 5 $\mu\text{g l}^{-1}$ [28]. Therefore, designing sensitive and accurate analytical methods for measuring the trace amounts of cadmium in environmental, biological, and nutritional samples seems to be crucial. In this regard, a number of analytical methods for detection of cadmium in various samples have been reported, such as flame-Atomic Absorption Spectroscopy (AAS) [29], Graphite furnace-AAS [30], Inductively coupled plasma atomic emission spectroscopy (ICP-OES) [31], Inductively coupled plasma mass spectrometry (ICP-MS) [32], active Neutron making, anodic free voltammetry, differential pulse free voltammetry,

ion chromatography, electrochemiluminescence and molecular absorption spectrophotometry [33-36]. Also, the X-Ray Fluorescence (XRF), Electrochemical Methods (Potentiometry, Coulometry), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Mass Spectrometry Techniques (Laser Ablation ICP-MS - LA-ICP-MS), Capillary Electrophoresis (CE) are of the suitable methods for cadmium detection in various samples [37-38].

Usually, at first steps, analytical methods are designed for investigating the laboratory samples which are prepared via dissolving certain amounts of standards; while, as could be predicted, works on real samples face researchers to some problems like successful and high percentage extractions, high consumption of time and cost, and also, difficulties in separation of the selected required species from a wide range of unwanted chemical compounds. Due to these, in the present project, we have made attempts to design a suitable method based on Ionic liquid based vortex-assisted dispersive liquid-liquid microextraction (VSLLME) [39] for detection of trace amounts of cadmium in real samples containing environmental, biological and nutritional ones.

Results and discussion

In the following study, the optimized method was applied for environmental aqueous samples (including drinking water, river water and groundwater), biological aqueous samples (including Oral saliva and human hair) and salt aqueous solution (NaCl). Also, to evaluate the matrix effects, the above samples were spiked with cadmium standard solutions with concentrations of 20 and 40 ng.mL⁻¹. The recovery factor ranged from 94.5 to 101.3%. The vortex eliminated the organic solvent of the dispersant and also improved the extraction efficiency by good distribution in the solution. The ionic liquid (BMIM-PF6) was extracted as a green environment, replacing organic solvents in the system. The APDC was stable in acidic medium, facilitating pre-concentration and sample separation, and the Fe₃O₄ magnetic nanoparticles were completely environmentally friendly. Therefore, the method was simple, fast, efficient and with robust preparation technique.

Effects of pH

Due to considerable effects of pH on the formation of the metal-ligand complex, it seems that the separation process of metal ions is significantly depended on the formation of the cadmium complex. It is notable that in one hand, ammonium pyrrolidine dithiocarbamate (APDC) which is used here, forms a stable complex with some transition-metals and semi-metals in acidic medium but it does not react with alkali metals, and it could be considered as an advantage due to its hydrolysis resistance [40]. On the other hand, sample

solutions were stored in the acidic medium which need to deal with a low pH-stable ligand. Therefore, the effect of pH of the sample was investigated in the pH range of 1 to 9. As shown in Figure 1, the cadmium extraction process was increased in the range of pH 1 to 2.5; while, it decreased in 2.5 to 9. Thus, it could be concluded that at lower pH, the cations tend to be less sedimentary, so the study was adjusted to pH of the 2.5.

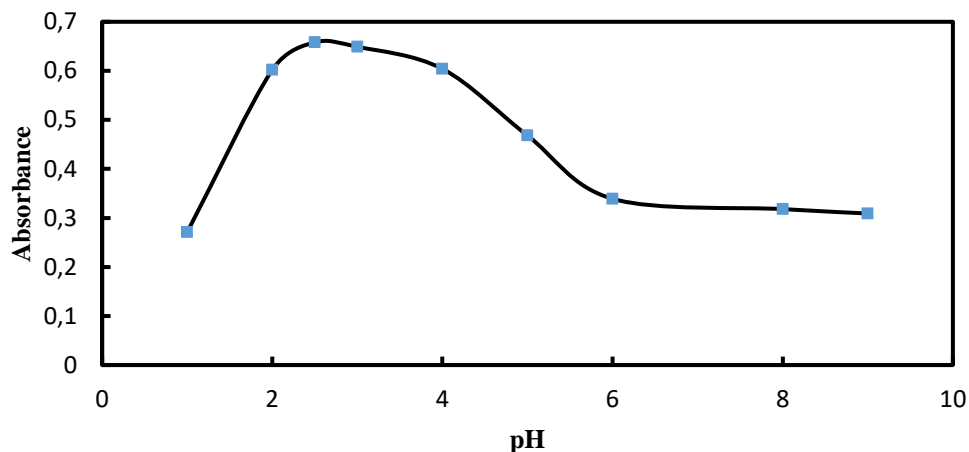


Fig 1. the effect of pH on extraction of Cd²⁺ ions, the condition involved 10 ml sample solution, 50 ppb cadmium, 150µL ionic liquid; 12µL APDC, 50mg Fe₃O₄)

Effect of ionic liquid volume (extraction solvent)

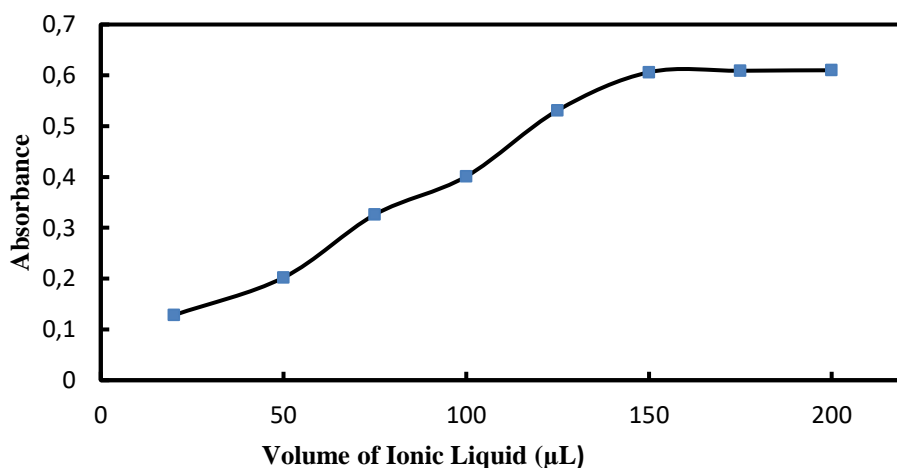


Fig 2. Effect of ionic liquid volume on Cd²⁺ extraction (10 ml sample solution, 50 ppb cadmium, pH was 2.5, 12µL APDC, 50mg Fe₃O₄)

The effect of ionic liquid volume on extraction efficiency was studied by dissolving (20–200 µL) of ionic liquid in the sample solution containing cadmium ions. As shown in Figure 2,

the extraction efficiency was increased by increasing the volume of the ionic liquid in the range of 20 - 150 μL and then it kept constant. As in the case of the volume, the best extraction efficiency was 150 μL , the optimum ionic liquid volume of 150 μL was selected for further research.

The effect of the amount of the used magnetic nanoparticles

The magnetic nanoparticles (MNPs) have often shown a higher extraction capacity, faster extraction dynamics and higher extraction efficiency compared to the other nano and micro sorbents [41]. Due to the fact that the amount of MNPs (as the sorbent) could play an efficient role on the extraction behavior of cadmium (II) ions, in this project, the effect of this parameter on the extraction efficiency was investigated in the range of 0 to 100 mg. As shown in Figure 3, the recovery factor for cadmium (II) ions was about 42% without the addition of Fe_3O_4 (as magnetic nanoparticles), while it increased after the addition of 25 mg of Fe_3O_4 . This increase could be due to the adsorption of Cd-APDC complex on the surface of MNPs. According to the results, 50 mg Fe_3O_4 was chosen as the optimum amount for further studies.

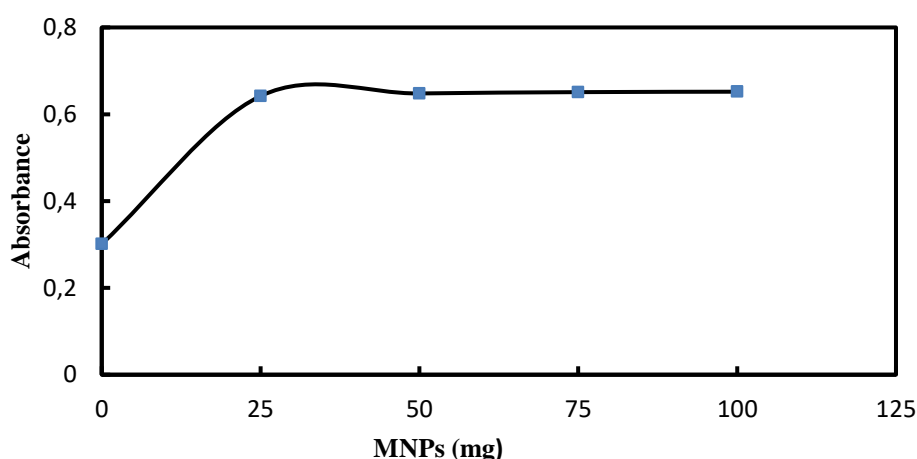


Fig 3. Effect of amount of magnetic nanoparticles applied (10 ml sample solution, 50 ppb cadmium, pH was 2.5, 12 μL APDC, 150 μL ionic liquid)

Effect of complexing reagent concentration

In this section, the effect of ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent was studied and the results are shown in Figure 4. As could be observed, by increasing the reagent up to about 0.01%, the absorbance was increased, while after the mentioned concentration, not significant changed was observed. After completing the process, the absorbance was fixed at values above 12 μM .

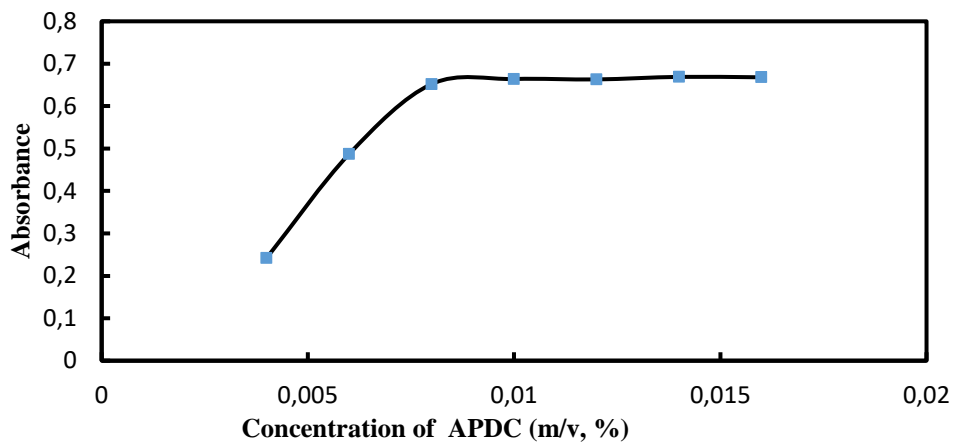


Fig 4. Effect of complexing reagent concentration (10 ml sample solution, 50 ppb cadmium, pH was 2.5, 50mg Fe₃O₄)

Effect of Vortex time

The vortex process is an effective method to increase the mass transfer from the aqueous phase to the extraction phase [42, 43]. Therefore, in each extraction process, the vortex time must be optimized to give the highest efficiency in the lowest possible time. Due to this, in the present project, we have also optimized the vortex time as an important parameter. The results showed that the 1 and 2 minutes vortex were suitable for the ionic liquid distribution phase and the magnetic nanoparticle stage, respectively.

The effect of sample volume

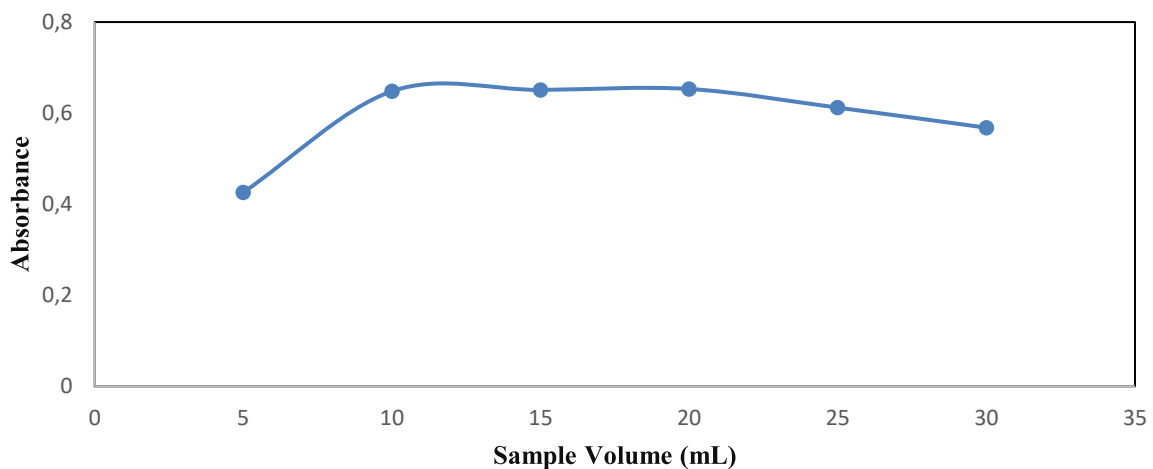


Fig 5. The effect of sample size (50 ppb cadmium, pH was 2.5, 50mg Fe₃O₄, 12µL APDC, 150µL ionic liquid)

The sample volume is important because cadmium is trace in real samples [44-46]. For this reason, a series of 5, 10, 15, 20, 25 and 30 ml volumes was prepared, and examined. As shown in Figure 5, the analyte recovery factor was not significantly different when the sample volume was 10 to 20 ml, while, that parameter decreased with further increase of sample volume. It seems that the reason of this decrease was that in higher volumes, the extraction phase could not be completely separated from the aqueous phase. Therefore, because the recovery factor and enrichment factor were higher, the sample volume was chosen to be 10 to 20 ml.

The effect of obtrusive ions

The effect of the obtrusive ions was investigated to evaluate the selectivity of the method for detection of cadmium ions in presence of other obtrusive ions. In this experiments, 10 ml of a solution containing 50ng ml⁻¹ of cadmium ions was introduced to different concentrations of other obtrusive ions (If the absorbance was changed up to about 5%, that ion would be considered as an obtrusive). As shown in Table 1, cadmium extraction was possible in the presence of obtrusive ions.

Table 1. Effect of obtrusive ions (150 mL of cadmium in real samples)

obtrusive ions	Concentration ratio of obtrusive ion to cadmium
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , F ⁻ , CO ₃ ²⁻ , I ⁻	50000
Li ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , CH ₃ COO ⁻	10000
Al ³⁺ , Ba ²⁺ , Ag ⁺ , Hg ²⁺	5000
Cr(VI), Mn(II), Cr(III), Zn(II)	500
V(V), Co(II), Ni(II)	100
Pb(II), Fe(II), Fe(III), Cu(II)	50

The figure of merits

Repeatability

Table 2. Results from 5 time preconcentration (solution containing 50 ng.ml⁻¹ cadmium)

Average of Absorbance	Standard Deviation	RSD %
0.661	0.064	0.97

As the repeatability cloud show the accuracy of the method and the experimental results, we have also investigated the repeatability of the designed method for cadmium ions. Repeatability was evaluated using 5 solutions containing cadmium (50 ppb) prepared by a

medium in a pH of 2.5. As the results given in Table 2 show, the RSD percentage for five points is about 0.97% which show the method is suitably repeatable.

LOD and LOQ

Determination of the limit of detection (LOD) and the limit of quantification (LOQ) are of the most important parameters which must be calculated by drawing the calibration curve for a certain range of concentrations. To obtain the LOD and LOQ, in this work, the calibration curve was plotted at 5 points (0 to 300 ppb). As the calibration curve shown in Figure 6, the coefficient of determination was 0.9997 (Table 3).

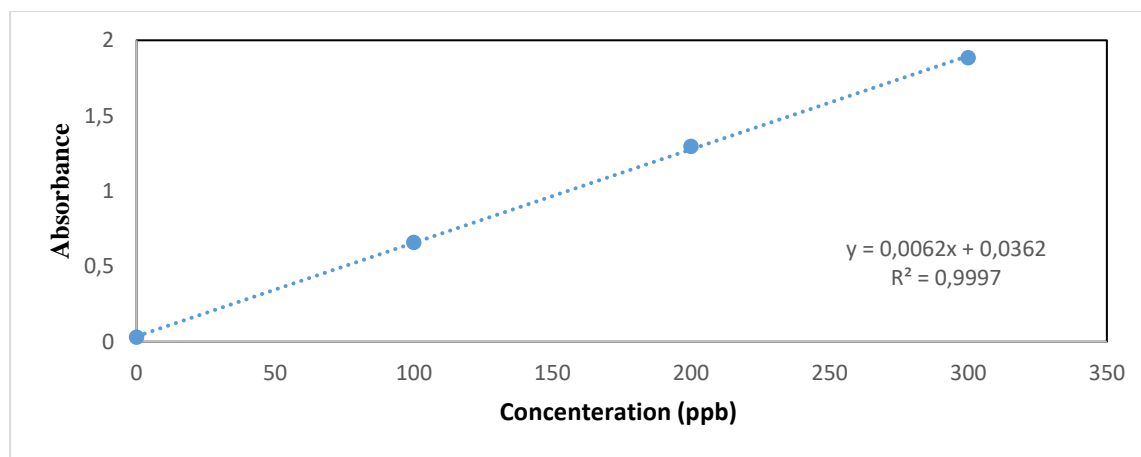


Figure 6. Calibration Curve of Cd²⁺ (10 ml sample solution, pH was 2.5, 50mg Fe₃O₄, 12μL APDC, 150μL ionic liquid)

The results presented in Table 4, show that the LOD, and LOQ for the designed method are 0.58 ng L⁻¹, and 1.92 ng L⁻¹, respectively, indicating the sensitivity of the method.

Table 3. The figure of merits of Cd²⁺

LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	R ² (n=5)	EF
0.58	1.92	0.9997	96

Analysis of real samples

In order to assess the efficiency of the designed method for investigation of the real samples, some experiments were designed for analysis of environmental water sample (containing drinking water, river water, and groundwater), the food samples (sodium chloride), and biological samples (salivary and human hair). Also, the samples were introduced to cadmium standards with concentrations of 20, and 40 ng.ml⁻¹ to probe the matrix effect. The results presented in Table 4 shows that the recovery percentages for the polluted samples were about 94.5% to 101.3%.

Table 4. Results of cadmium measurements in real samples

Sample	Spike Concentration (ng.L ⁻¹)	Result (ng.L ⁻¹)	Recovery ¹
drinking water	0	Less than LOD	---
	20	19.92±0.02	99.6
	40	40.04±0.03	100.1
river water	0	5.8±0.02	---
	20	25.00±0.03	96.9
	40	44.97±0.04	98.2
groundwater	0	6.30±0.04	---
	20	25.56±0.05	97.2
	40	45.55±0.06	98.4
Oral saliva	0	Less than LOD	---
	20	20.10±0.10	100.5
	40	40.52±0.10	101.4
human hair	0	Less than LOD	---
	20	18.90±0.02	94.3
	40	39.32±0.04	98.3
Salt aqueous (NaCl)	0	7.8±0.20	---
	20	27.49±0.30	98.9
	40	47.36±0.30	99.1

¹ The average value ± standard deviation (n=3)

Comparison with other methods

As given before, due to important of the issue of cadmium pollution in the environment and its toxicity, a number of methods based on different extraction approaches were designed for detection of this hazard ion in the real samples.

Table 5 [53] shows the difference between the effect of the extraction methods on the LOD, RSD, and EF. The comparison results show that in some methods containing ultrasound-assisted liquid phase microextraction, and ultrasound-assisted emulsification–microextraction, the LOD amounts are 0.91 µg L⁻¹, and 0.66 µg L⁻¹, respectively, which is better than VALLME Using [Omim][PF6] (0.58 µg L⁻¹). On the other hand, VALLME method would be more operative than other approaches mentioned above, due to rapidness, simplicity, low cost, low toxicity, and relatively high enrichment factor. In the present project, we have used the 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]-[PF6]) as the ionic liquid agent for VALLME method and the results showed that the merit parameters like LOD (0.58 µg L⁻¹), and EF (96) would be more satisfactory than some other valuable previous VALLME work.

Table 5. Comparison of the LOD, RSD, and EF for the extraction methods targeting the cadmium ions.

Method	LOD ($\mu\text{g L}^{-1}$) ^a	RSD (%) ^b	Enhancement factor (EF)	Calibration range ($\mu\text{g L}^{-1}$)	Refs.
Solid phase extraction	1.44	≤ 3	-	216–3000	[47]
Solid phase extraction	5.50	2.3	-	5–150	[48]
Hollow fiber membrane	1.5	4	107	5–30	[49]
		Liquid phase Microextraction			
Ultrasound-assisted	0.91	1.62–2.56	13.4	10–600	[50]
		emulsification–microextraction			
Ultrasound-Assisted	0.66	2.42–3.34	15	10–450	[51]
		emulsification solidified-microextraction			
Dispersive liquid–liquid	1.16	1.8	48.1	4–200	[52]
		Microextraction (VALLME)			
Using [OMIM][PF ₆]	2.9	4.1	35	10–250	[53]
Using [BMIM][PF ₆]	0.58	0.99	96	0-300	The present work

a) 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF₆])

b) 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]-[PF₆])

Material and methods

Instrumentation

A Varian Atomic Absorption Spectrometer Model AA-220 - Australia, with GTA-100 Graphics Furnace and Deuterium Lamp for background absorption correction was used for the analysis. All of the measurements were carried out in an air/acetylene flame. A long slot-burner heads with a length of 10 cm, and a cadmium hollow cathode lamp was used as the radiation source at a wave length of 228.8 nm, and all of the process were carried out with deuterium background correction. A micro-syringe (France) for injection of ionic liquid into a glass test tube containing water-soluble cadmium, as well as a micro-syringe of 10 μL (Hamilton - Sweden) for injection of sample solution containing analyte into atomic absorption spectroscopy apparatus were used, respectively. The pH meter was Model 691 Metrom (Switzerland), the Vortex was VWR (Germany). Also, the centrifuge model was UNIVERSAL 320 R (UK), and the Balance model was Mettler Ae 206 (Switzerland) with accuracy of 0.0001 gram.

Reagents

The standard cadmium stock solution at a concentration of 1000 mg.L^{-1} , was prepared by dissolving of 2.745 g of cadmium nitrate $4.H_2O$ (Merck - German) in 5% nitric acid (V/V), and then diluted with deionized water. Cadmium working standard solutions was freshly obtained by diluting cadmium standard stock solution in 0.2% nitric acid (V/V). 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) (the ionic liquid as the extraction solvent), acetone, hydrochloric acid (37%), nitric acid (70%), sulfuric acid 98% and hydrogen peroxide 30% (for washing and digesting hair samples), as well as 5% (V/W) ammonium pyrrolidine dithiocarbamate (APDC) complexing agent (Dissolve 0.1 g of APDC in 2 ml of ethanol) were obtained from Merck chemicals (German). The pH was adjusted by hydrochloric acid (for acidifying the pH) and sodium hydroxide solution (for alkalization of the pH). A pure deionized water was used to make aqueous solutions. All solutions were stored in the refrigerator at $\pm 4 \text{ }^\circ\text{C}$. All of the glassware were immersed in 10% nitric acid for 12 hours, thoroughly washed with deionized water and then used.

5.2 grams of $FeCl_3.6H_2O$ and 2.0 grams of $FeCl_2.4H_2O$ were dissolved in 50 ml of deionized water to synthesize Fe_3O_4 nanoparticles [54]. The sample solution was exposed to argon for 15 min at $80 \text{ }^\circ\text{C}$. Then 10 ml of concentrated ammonia was added slowly and dropwise to the solution. After 15 minutes the solid black precipitate was separated using a magnet and washed three times with 50 ml of 0.1 M NaCl solution. Finally, the precipitate was washed once with acetone, and dried in the oven at $80 \text{ }^\circ\text{C}$.

Sampling

Environmental aqueous samples

In this study, the environmental water samples including drinking water, groundwater (from East Azarbaijan province, Iran), and river water (from a river in northwestern Iran called Sufichay River) were collected to be analyzed by the planned method. All samples were filtered with $0.45 \mu\text{m}$ and then, those pHs were acidified with hydrochloric acid and stored in a brown glass container at $4 \text{ }^\circ\text{C}$ and out of the light.

Oral saliva samples

Oral saliva samples were collected from 25 to 35-year-old volunteers (male and female) in East Azarbaijan Province, Iran. The volunteers were asked to rinse their mouth with deionized water, three times daily for one month. The samples were centrifuged for 10 min at 2500 rpm then diluted with deionized water to 5 ml.

Human hair samples

Hair samples were collected from the back of the neck (approximately 2 to 5 cm), from men and women (25 to 35 year-old) from East Azarbaijan Province, Iran. The samples were immersed in acetone and washed with deionized water for a certain time. The process was done twice. It was finally dried in the oven at 90 °C [55-57]. Samples were stored in plastic bags (bags were washed with 5% nitric acid) at room temperature.

Procedure of ionic liquid technique based on vortex-assisted and magnetization dispersive liquid–liquid microextraction

The sample or standard solution containing 50 µg.L⁻¹ cadmium at pH 2.5, was mixed with a 2.5% chelating reagent (volumetric) in a 10 ml conical test tube. Then, 150 µL of ionic liquid (as extraction solvent) was rapidly injected into the sample solution by micro-syringe, and subsequently, the extraction solvent was completely dissolved and mixed with aqueous solution. At this stage, the cadmium neutral complex was transferred from aqueous solution to the ionic liquid phase. Then, 50 mg iron oxide (III) magnetic nanoparticle was added to the test tube and vortexed for 2 minutes. The ionic liquid phase and the Cd-APDC complex were extracted into the iron oxide magnetic nanoparticles (MNP) phase. Then, the magnet was used to collect the nanoparticles. The aqueous phase was then overflowed, and the residue was diluted with concentrated HNO₃ to a volume of 250 µl and the solution was vortexed for 30 seconds. Finally, the nanoparticles were separated from the solution by a magnet, and 40 µL of the solution containing the extract was injected into the electrothermal atomic absorption spectroscopy with a micro-syringe.

Conclusions

In the present project, an ionic liquid based vortex-assisted dispersive liquid–liquid microextraction method was developed in order to measure the traces amounts of cadmium in environmental, biological and nutritional samples. Then, the method was optimized for higher efficiency, better detection limits, higher resolution, and lower cost and time. The results showed that the designed procedure is suitable to be used for analyzing the environmental aqueous samples (including drinking water, river water and groundwater), as well as biological aqueous samples (including Oral saliva and human hair) and Salt aqueous solution (NaCl). In order to evaluate the effect of matrix on the real samples, the laboratory standards were prepared and spiked with cadmium at concentration levels of 20 and 40 ng.mL⁻¹, and the results showed that the recovery factor ranged from 94.5 to 101.3%. Also, the

experiments indicated that the vortex eliminates the organic solvent of the dispersant and it improves the extraction efficiency by good distribution in the solution. Moreover, the ionic liquid (BMIM-PF6) was extracted as a green environment, replacing organic solvents in the system. On the other hand, the APDC showed to be stable in acidic medium, facilitating the pre-concentration and sample separation, and also, the Fe₃O₄ magnetic nanoparticles are completely environmentally friendly. Therefore, this method is simple, fast, and an efficient and robust preparation technique.

Finally, the result revealed that the designed method was cheap, easy to perform, and fast, due to elimination of filtration step, reducing the solvent volume, replacing the organic solvents, and simplifying the pre-concentration step. Also, this procedure is able to detect very trace amounts of cadmium in real samples.

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