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Preconcentration of Cd(II) Using Derivative Sulfonamide and Determination in Water Samples and Paraffin-Embedded Tissues from Liver Loggerhead Turtles Specimens by FAAS

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A simple and reproducible method for the rapid extraction and determination of trace amounts of Cd(II) ions using N,N'-dimethylthioureasulfonamide resin and flame atomic absorption spectrometry (FAAS) is presented. Metal determinations at low concentration levels ($\leq$ ng mL^{-1}) comprise one of most important targets in analytical chemistry. As a result, interest in preconcentration techniques still continues increasingly for trace metal determinations by flame atomic absorption spectrometry (FAAS) due to the high accuracy of this method. In this work, N,N'-dimethylthioureasulfonamide resin was synthesized, characterized and applied as a sorption material for determinations of Cd(II) ions in water samples. The method is based on the sorption of Cd(II) ions on the synthesized resin without using any complexing reagent. The optimization of experimental conditions was performed using factorial design including pH, amount of resin, contact time, first sample volume and final eluent volume. Using the experimental conditions defined in the optimization, the method was applied to the determination and preconcentration of Cd(II) at ng mL^{-1} level in natural water. Flame atomic absorption spectrometry was used for trace metal determinations. Here, the application of preconcentration techniques for trace metal determinations by FAAS for quantification of Cd in formalin-fixed paraffin-embedded (FFPE) tissues from liver loggerhead turtles is reported. This method exhibits the superiority in compare to the other adsorption reagents because of the fact that there is no necessity of any complexing reagent and optimum pH of solution presents in acidic media.

Key Words: N,N'-Dimethylthioureasulfonamide resin, Preconcentration, Cd(II), Flame atomic absorption spectrometry, Formalin-fixed paraffin-embedded, Tissues from liver loggerhead turtles.

INTRODUCTION

In the recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments),

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as well as their production from burning oil and coal and incineration of waste causes an extensive anthropogenic contamination of soil, air and water[1]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS)[2,3], inductively coupled plasma atomic emission spectrometry (ICP-AES)[4] and inductively coupled plasma mass spectrometry (ICP-MS)[5] are available for the determination of trace metals with enough sensitivity for the most applications. Despite good developments in the modern analytical instruments, which allow great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples. Sample preparation is still a bottleneck for overall throughput because the involved steps often employ large volumes of hazardous organic solvents, are time consuming and/or expensive[1]. Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrices effects. Preconcentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several procedures have been developed for the separation and preconcentration of contaminants from environmental matrices, such as: liquid-liquid extraction (LLE)[6-8], co-precipitation[9-11], solid phase extraction (SPE)[12-16].

Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes.

Cloud point extraction (CPE)[17-20], homogeneous liquid-liquid extraction (HLLE)[21,22] and single drop microextraction (SDME)[23-25] are fairly new methods of sample preparation which are used in separation and preconcentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous researches, we demonstrated a novel microextraction technique, named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs), organphosphorus pesticides (OPPs) and chlorobenzenes in water samples[26,27].

Dispersive liquid-liquid microextraction is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes forming cloudy solution. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of anlaytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

Dispersive liquid-liquid microextraction is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GFAAS is used. The applicability of the approach has been demonstrated for the determination of cadmium in water samples. This element was selected for evaluation of the procedure because cadmium is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations[28-30].

In our best of knowledge, SPE and preconcentration by Cd(II)-imprinted diazoaminobenzene-vinylpyridine copolymer packed-bed columns have not been employed for the separation and preconcentration of Cd(II) from aqueous solution. This paper reports the synthesis of Cd(II) imprinted and non-imprinted copolymers by copolymerizing cadmium chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethylene glycol dimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutryonitrile as initiator and its analytical applications for column preconcentrative separation of Cd(II) from natural water. The aim of this work is to develop a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Cd^{2+} ions from aqueous media using N,N'-dimethylthioureasulfonamide pendant resin derived from crosslinked polystyrene and FAAS determination. The optimized method was applied to Cd^{2+} determinations in different natural waters. The second aim of this study was the selection of an appropriate method for the analysis of FFPE tissue were based on present work with atomic absorption spectrophotometric determination of cadmium.

EXPERIMENTAL

Determination of Cd^{2+} contents in working samples were carried out by a Varian spectra A 200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCl) according to the recommendations of the manufacturers.

Separation of sorbent was assisted using a centrifuge (centurion scientific model: K 240R, West Sussex, UK). The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

All acids were of the highest purity available from Merck and were used as received. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and copper(II) were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstat, Germany and high purity double distilled deionized water was used throughout the experiments. Working solutions were prepared by appropriate dilution of the stock solution. In the digestion procedure, concentrated HNO_3 was used for decomposition of adsorbed Cd(II) on the synthesized resin surfaces. The diluted standard solutions were prepared from stock standard metal solutions of 1000 mg L^{-1} (Merck). The buffer solutions in the range of pH: 2.0-6.0 ± 0.2 were prepared by using 0.1 mol L^{-1} citric acid plus 0.1 mol L^{-1} HCl/0.1 mol L^{-1} NaOH solutions. The newly synthesized resin was grinded and sieved by using the sieve of 320 mesh.

Chlorosulfonation of the beaded polymer: The polymer beads were chlorosulfonated using chlorosulfonic acid as described in the literature[28]. The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g) sample was added to 20 mL of 10 % NaOH (m/v) and boiled for 4 h. After filtration and neutralization with HNO_3 (5 mol L^{-1}), the chlorine content was determined by the mercuric-thiocyanate method[29]. This gave a final chlorosulfonation degree of 4.0 mmol g^{-1}.

Preparation of N,N'-dimethylthioureasulfonamide resin: The chlorosulfonated polymer (10 g) was added portion wise to a stirred solution of N,N'-dimethylthiourea of 1.453 mol L^{-1} (40 mL) in 1-methyl-2-pyrrolidone at 0 ºC in the presence of triethylamine. The mixture was shaken with a continuous shaker for 24 h at room temperature. Then, the obtained mixture was added into 600 mL of water, filtered and washed with excess of water and methanol. The modified resin was dried under vacuum at room temperature for 30 h. The obtained resin was found to be 12.4 g. To characterize the modification degree, the total nitrogen content was determined by using Kjeldehal nitrogen method and found to be 3.8 mmol g^{-1}. The reaction mechanism was given in Fig. 1.

Determination of sorption capacity: Determination of the sorption capacity of the polymeric resin was performed by the interaction of polymer samples with aqueous metal solutions as follows. The resin sample (0.04 g) was added to a metal solution of 180 mL (4.0×10^{-5} mol L^{-1} Cd^{2+}). The optimized enrichment conditions were applied to these solutions. After centrifugation, the metal concentrations in filtrate were determined by flame atomic absorption spectrometry (FAAS). Similar experiments were repeated under the same conditions with different initial metal concentrations (3×10^{-5}, 2×10^{-5} and 1×10^{-5} mol L^{-1} Cd^{2+}). The sorbtion capacities were calculated from subtracting metal amounts in filtrate than known amounts in first solution.

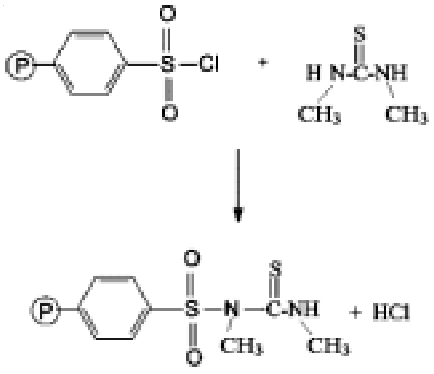

Fig. 1. Scheme of reaction mechanism

Enrichment procedure: The adsorbent resin of 30 mg was added to 60 mL of the solution of 5 ng mL^{-1} Cd^{2+} including matrix components: Ca^{2+}, Ni^{2+}, Cr^{3+}, Ag^{+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Mn^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Na^{+}, K^{+}, Zn^{2+},UO^{2+}, NO_3^{-}, NO_2^{-}, CH_3COO^{-}, $H_2PO_4^{-}$ and Hg^{2+} to represent natural water. (Table-1) This solution containing matrix components was described as model solution in the subsequent parts. After pH adjustment to desired value using diluted HCl and NaOH (optimum pH: 3.2 ± 0.3), 10 mL of buffer solution was added to this mixture. Then, the pH of this mixture was again adjusted to the studied pH, if necessary. The mixture was mechanically stirred for 25 min at room temperature and centrifuged. The residue was dried at 60 ºC in oven. After transferring of the residue to a glass beaker, conc. HNO_3 of 4 mL was added and then the mixture was evaporated to near the dryness. After cooling, 3 mL of 1.5 mol L^{-1} HNO_3 was added, mixed and centrifuged to take liberated metal to the solution. The clear solution was measured by using FAAS. The blank solutions were carried out in the same way.

Sample addition: After complete homogenization, accurate volumes of the sample solutions (60 mL portions) were transferred to the top reservoir of the adsorbent resin of 30 mg apparatus. At the same time, the solution was drawn through the adsorbent by applying a mild vacuum. Application of vacuum was continued until the adsorbent was completely dry (about 5 min).

Analysis of sample paraffin-embedded tissues from liver loggerhead turtles specimens: Selected areas from fresh frozen tissues from liver loggerhead turtles specimens were sliced in three pieces (numbered as 1, 2 and 3) of approximately 10 mm × 5 mm × 2 mm each. Sets of pieces of set 1 (controls), were placed into a vacuum chamber at 50 ºC overnight to dry (until a constant weight was obtained) and the sets 2 and 3 were subjected to the standard 10 % buffered formalin fixation and paraffin embedding[31] histological process using a tissue processor (Tissue-Tek VIP, Sakura Finetek USA Inc., Torrance, CA). After the paraffin embedding process, tissues were subsequently excised from the blocks with a titanium knife and deparaffinized in xylene at 55 ºC for 1 h in the tissue processor (the set 2), or with hexane at 20 ºC for 1 week with frequent changes of the solvent in handling-based procedure (the set 3). Xylene was of a grade routinely used for the FFPE process and hexane was of "Optima" grade (Fisher Scientific). Upon deparaffinization, the tissue samples were dried in a vacuum chamber until constant weight was obtained. Each dried sample (of the sets 1-3) was divided into three portions (5-10 mg each) to be further analyzed as triplicates.

TABLE-1
SEPARATION OF Cd^{2+} FROM BINARY MIXTURES[a]

Diverse ion	Amounts taken (mg)	Found (%)	Recovery of Cd^{2+} ion (%)
Na^{+}	50	1.25 (2.3)[b]	98.7 (1.8)
K^{+}	45.5	1.42 (2.4)	98.0 (1.9)
Mg^{2+}	5.7	0.7 (2.6)	97.1 (2.9)
Ca^{2+}	35	1.27 (2.0)	97.6 (2.1)
Sr^{2+}	3.5	2.25 (1.7)	98.2 (2.1)
Ba^{2+}	2.4	3.11 (1.8)	96.3 (1.9)
Mn^{2+}	2.8	1.55 (1.8)	96.7 (2.9)
Co^{2+}	2.9	1.80 (1.8)	97.0 (1.9)
Ni^{2+}	2.2	2.00 (1.9)	96.1 (3.1)
Zn^{2+}	2.2	1.87 (2.1)	96.8 (2.2)
Cd^{2+}	2.3	1.98 (2.1)	98.2 (3.0)
Pb^{2+}	2.2	2.22 (2.9)	96.5 (1.7)
Hg^{2+}	2.5	4.81 (2.1)	96.8 (2.8)
Ag^{+}	2.1	2.45 (1.9)	97.6 (1.9)
Cr^{3+}	2.2	2.92 (2.3)	97.0 (2.4)
UO^{2+}	2.0	1.80 (2.5)	97.5 (2.7)
NO_3^-	3.2	1.80 (2.3)	97.0 (2.4)
NO_2^-	1.8	2.50 (2.5)	96.0 (2.0)
CH_3COO^-	1.9	2.80 (2.0)	99.0 (2.3)
$H_2PO_4^-$	1.8	1.50 (2.3)	98.0 (2.1)

a: Initial samples contained the adsorbent resin of 30 mg was added to 60 mL of the solution of 5 ng mL^{-1} Cd^{2+}. b: Values in parentheses are RSDs based on five individual replicate analysis.

RESULTS AND DISCUSSION

Characterization of new polymeric resin: The major disadvantage of using polymeric resins to remove or preconcentrate the toxic metals is their hydrolysis by acid and bases in the regeneration step. Sulfonamides have chemical properties differently from carboxylic acid amides in that they have reasonable stability towards acid and base hydrolysis[32]. Therefore, there is no such disadvantage in the synthesized resin in this study because of the sulfonamide group in the resin has had resistance to hydrolysis by acid and bases. Thiourea functions have been incorporated into cross-linked polystyrene resin beads (420-560 µm) according to the reaction in Fig. 1 for the preparation of a polymeric sorbent. The polymer with a 4 mmol g^{-1} chlorosulfonation degree (determined by chloride analysis): when reacted with an excess of N,N'-dimethylthiourea in 1-methyl-2-pyrrolidone solvent, gives rise to the corresponding polymer with N,N'-dimethylthiourea sulfonamide functions. Total nitrogen content of the product was found as 3.8 mmol g^{-1} by using the Kjeldahl nitrogen analysis.

The chemical transformation in each experimental step was followed by FT-IR spectra. As seen in Fig. 2a, sulfon, $-SO_2-$, stretching vibration of chlorosulfone groups appear at 1366 cm^{-1} (asymmetric stretch) and 1168 cm^{-1} (symmetric stretch). Fig. 2b shows the FT-IR spectrum of the sulfonamide product. The band at 1366 cm^{-1} shifts to lower frequencies due to amide resonance at 1164 cm^{-1}. The bands at 1475 and 1450 cm^{-1} are assigned to -CS-NH- vibration. The shoulder band is assigned to the C-S stretch. A broad band also observed at about 3410 cm^{-1} belongs to N-H stretching vibration. This is clear-cut evidence of the transformation. As a result, the synthesized resin can be examined its usage to remediation of contaminated environmental matrices such as soil and water. The parameters that are thought to affect the enrichment and measurement steps in the analytical scheme were examined. These parameters were investigated by using the model metal solutions. The effect of each parameter was repeated three times.

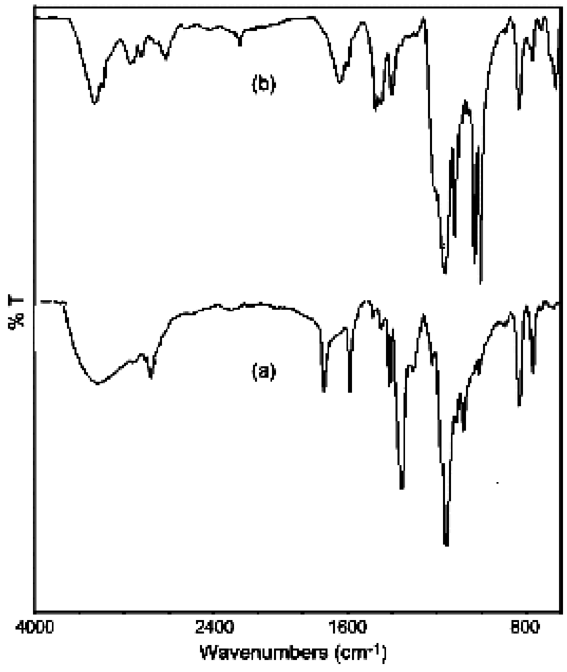

Fig. 2. FT-IR spectra of (a) chlorosulfonated PS and (b) N,N'- dimethylthioureasulfonamide resin

Influence of pH on recovery: The model solutions were preconcentrated as described in enrichment procedure using various pH values in the range of 2-6 because of the fact that preconcentration yield depends on pH. The obtained recoveries were given in Fig. 3. From Fig. 3, it is seen that the maximum recoveries (up to 90 %) were found in the pH range of 2-4. Therefore, the pH of solution was chosen as 3.2 ± 0.3 in all subsequent studies.

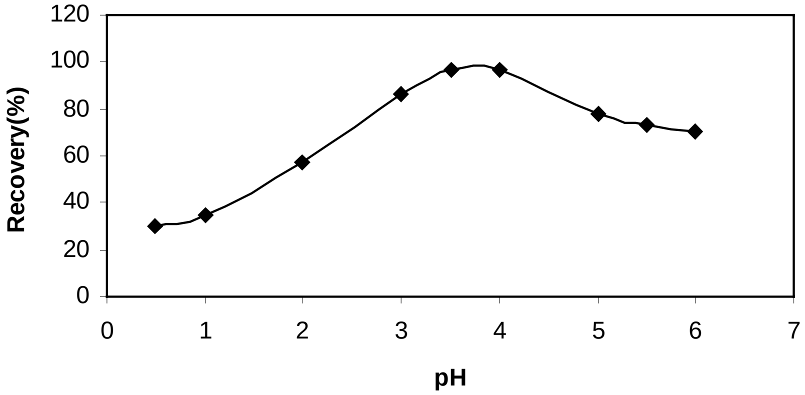

Fig. 3. Effect of pH on the recovery

Effect of the contact time on recovery: The enrichment procedure was applied to the model solutions by using different stirring times at the other optimum conditions. Fig. 4 showed that the stirring time of 25 min was sufficient for maximum recovery (up to 95 %). The obtained contact time is relatively shorter except some studies[33], because the rather long contact time as long as 36 h was reported in the literature for maximum recovery[34]. So, 25 min was selected as optimum contact time and applied during all studies.

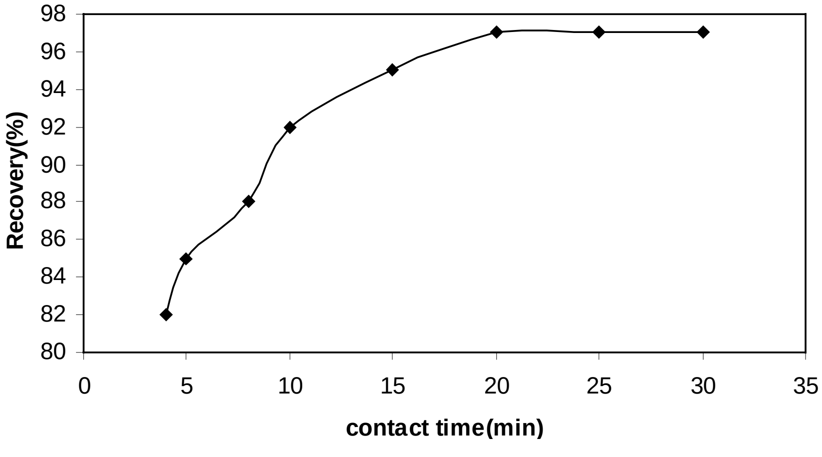

Fig. 4. Effect of contact time on the recovery

Effect of buffer solution: The influence of buffer solution was carried out by using model metal solutions where the other experimental variables found remained constant. The results have shown that more than 10 mL of buffer solution added in 60 mL of solution, no obvious variation took place in the extraction yield (Fig. 5). A 10 mL aliquot of buffer solution was added in all subsequent experiments and this volume was increased with the sample volume, proportionally.

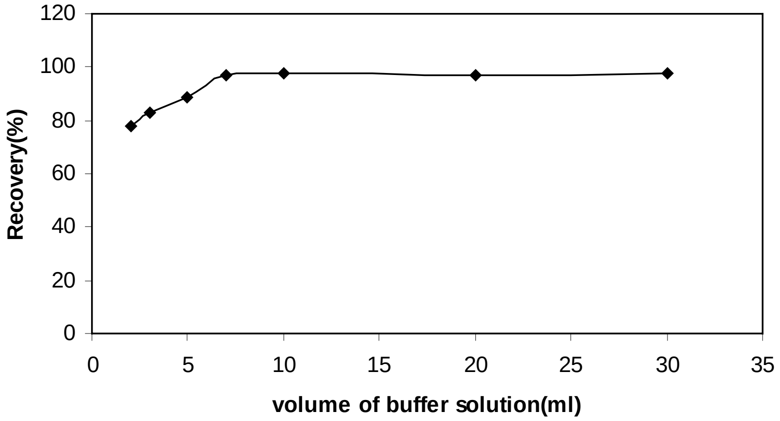

Fig. 5. Effect of the volume of buffer solution on the recovery

Effect of the elution volume on recovery: In the preliminary studies, it was found that higher recoveries were observed by using 1.5 mol L^{-1} HNO_3 in compared to 0.5 and 1.0 mol L^{-1} HNO_3. The efficiency of the eluent volume of 1.5 mol L^{-1} HNO_3 was examined by taking its different volumes (1-7 mL). From Fig. 6, it was found that 3 mL of 1.5 mol L^{-1} HNO_3 was sufficient for maximum recovery (95 %) of Cd^{2+}. Therefore, 3.0 mL of 1.5 mol L^{-1} HNO_3 was used for complete desorption of the adsorbed metals. Furthermore, after using concentrated HCl instead of HNO_3 in the desorption step, 3.0 mL of 1.5 mol L^{-1} HCl was also examined to elution procedure. The recoveries were observed to be 85 % for Cd^{2+}. As a result, HNO_3 was chosen for elution procedure.

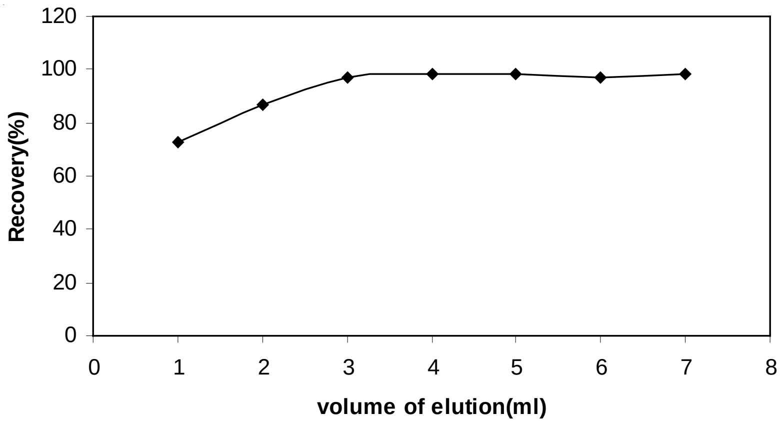

Fig. 6. Effect of final elution volume on the recovery

Analytical performance: To investigate the effect of solution volume on recovery in enrichment step, recoveries of Cd^{2+} was examined by using 180 mL of model solutions. The recoveries more than 95 % were observed for Cd^{2+}. The calibration curves were also obtained in the concentration range of 0.07-1.00 ng mL^{-1} Cd^{2+} by taking of 180 mL solution to final volume of 3 mL. Therefore, the enrichment factor of 60 times was achieved by using the developed enrichment method. The obtained graphs were linear in the concentration ranges described above and the equations of the curves were as follows: $Y = 136.4X + 0.08$, $R^2 = 0.9998$, for Cd^{2+} (0.07-1.00 ng mL^{-1} after preconcentration FAAS) As a result, limit of quantitations (LOQs) were found to be 0.07 ng mL^{-1} for Cd^{2+}. The levels of Cd^{2+} in blank samples were found to be 0.3 ng mL^{-1} with the standard deviation values of 0.05 ng mL^{-1}, by preconcentrating 180 mL of blank solution to a final volume of 3.0 mL and using FAAS in measurement step. Limit of detection (LOD) were calculated as 3σ of the reagent blank.

In order to investigate the selective separation and determination of Cd^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions containing Cd^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table-1. The results show that the Cd^{2+} ions in binary mixtures are retained almost completely by the adsorbent, even in the presence of various ions. Meanwhile, retention of other cations by the disk is very low and they can separate effectively from the Cd^{2+} ion. Additionally, the counter anions influence on the extraction and subsequent clean-up and recovery of Cd^{2+} has been summarized in Table-1. The limit of detection (LOD) of the method for the determination of Cd(II) was studied under the optimal experimental conditions. Therefore, the LODs defined as three times of the standard deviations of the reagent blanks were found to be 0.03 ng mL^{-1} for Cd^{2+}. To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cd from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), Snow water (Saveh , 6 February, 2007) and sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table-2).

TABLE-2
RECOVERY OF CADMIUM ADDED TO DIFFERENT WATER SAMPLES (CONTANING 0.1 M ACETATE AT pH = 3.2)

Sample	Cd^{2+} added (μg)	Cd^{2+} determined (ng mL^{-1})
Tap water	0.0	1.86 (1.8)[a]
	10.0	12.22 (1.9)
Snow water	0.0	4.86 (2.8)
	10.0	14.98 (2.9)
Rain water	0.0	2.55 (2.3)
	10.0	12.72 (1.8)
Sea Water	0.0	13.50 (1.9)
	10.0	23.95 (2.0)
Development of a methodology for the determination of Cd in FFPE tissue	0.0	–
	10.0	10.07 (0.9)

a: Values in parentheses are RSDs based on five individual replicate analysis.

These recoveries are not contradictory with the given recoveries (95 %) in the optimization steps because the calibration graphs obtained by recoveries of 95 % were used. Using 180 mL solution of 4×10^{-5} mol L^{-1} Cd^{2+}, adsorption capacity was found to be 29.670 µg g^{-1} for Cd^{2+}. As a result, total adsorption capacity for the synthesized sorbent was calculated to be 72.300 µg g^{-1}. The observed high adsorption capacity may be explained by the sorption of both cadmium and lead ions to per each monomer in polymer chain.

Applications: To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cd from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), Snow water (Saveh , 6 February, 2007) and sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table-2).

The studied water samples were taken from the Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), Snow water (Saveh, 6 February, 2007) and sea water (taken from Caspian sea, near the Mahmoud-Abad shore). Depending on the concentrations of Cd^{2+} ions in the studied samples, a 180 mL of water samples was transferred into a 400 mL beaker. The optimized enrichment method was applied to the determination of Cd^{2+} in these samples. The obtained results were given in Table-2. The values given are the mean values of three different portions of the same sample. The Cd^{2+} concentrations were found to be in the range of 1.89-23.9 ng mL^{-1}.

Development of a methodology for the determination of cadmium in FFPE tissue was performed in a number of steps to optimize the major factors affecting the precision of the analysis (Table-2).

Conclusion

The developed method is simple, reliable and precise for determining cadmium in water. The proposed method is also free of interference compared to conventional procedures to determine cadmium[35-37]. The method can be successfully applied to the separation and determination of cadmium in binary mixtures. An adsorbing reagent was synthesized, characterized and applied to determine cadmium levels in water samples. The optimized method has high sensitivity, selectivity and reliability. The sensitivity of FAAS was increased up to 60 times by using the optimized enrichment method. In comparing to most of the reported adsorption reagents in the literature, the other important advantage of the synthesized polymeric sorbent is that there is no need to use ligand in the enrichment step because ligand can be imprinted to sorbent reagent in the days ago.

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