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Determination of Cadmium(II) Using Cd(II)-Imprinted Nano Diazoaminobenzene-Vinylpyridine Copolymers

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Cd(II) imprinted and non-imprinted copolymers were prepared by metal ion imprinted polymer (MIIP) technique. The copolymers were obtained by copolymerizing cadmium chloride (or without it), nano diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycoldimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutyronitrile as initiator. The separation and preconcentration characteristics of the copolymers for Cd(II) were investigated by batch and column procedures. The results demonstrated that the Cd(II) imprinted copolymers had higher adsorption capacity with the value of 205 μmol g^{-1} of dry copolymer, *ca.* 3.5 times and good selectivity for Cd(II) compare to non-imprinted copolymers (58.6 μmol g^{-1} of dry copolymer). The distribution ratio (D) values of the Cd(II) imprinted copolymers increased for Cd(II) with respect to both D values of Zn(II), Cu(II), Fe(II) and non-imprinted copolymer. The relatively selective factor (α_r) values of Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Fe(II), are 36.7, 51.8, 86.7, respectively. The tolerance limit for other electrolytes such as NaCl, KBr, KI, $NaNO_3$, Na_3PO_4, Na_2SO_4 and $Mg(NO_3)_2$ is also greatly improved with the values of 10-100-fold of the non-imprinted copolymer. The Cd(II) imprinted copolymers can be used at least 20 times with recoveries no less than 96 %. Based on the packed columns with Cd(II) imprinted copolymers, a highly selective solid-phase extraction (SPE) and preconcentration method for Cd(II) from dilute aqueous solution was developed. The MIIP-SPE preconcentration procedure showed a linear calibration curve within concentration range from 0.13-25 μg L^{-1}. The detection limit and quantification limit were 0.05 and 0.13 μg L^{-1} (3σ) for graphite furnace atomic absorption spectrometry (GF AAS). The relative standard deviation of the eleven replicate determinations was 2.6 % for the determination of 1 μg of Cd(II) in 100 mL water sample. Determination of Cd(II) in certified tap water and rain water demonstrated that the column was good enough for Cd(II) determination in matrixes containing components with similar chemical property such as Cu(II), Zn(II), Fe(II).

Key Words: Solid-phase extraction, Metal ion imprinted polymer, Preconcentration, Cd(II), Graphite furnance atomic absorption spectrometry.

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), 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. Pre-concentration 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)[12-20].

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)[21-26], homogeneous liquid-liquid extraction (HLLE)[27,28] and single drop microextraction (SDME)[29-33] 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[34-36]. DLLME 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. Thereby, cloudy solution forms. 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.

DLLME 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 GF AAS 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[37,38].

Nowadays, metal ion imprinted polymers (MIIP) have been investigated as highly selective sorbents for solid phase extraction in order to concentrate and clean up samples prior to analysis. One potential application that has recently attracted widespread interest is their use for clean up and enrichment of analytes present at low concentrations in complex matrices[39-41]. In our knowledge, solid phase extraction and preconcentration by Cd(II)-imprinted nano 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), nano diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycol 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.

EXPERIMENTAL

The experiments were performed using a Shimadzu (Kyoto, Japan) atomic absorption spectrophotometer (AA 6300G) with a graphite furnace atomizer (GFA-EX7i). A cadmium hollow cathode lamp (Hamamatsu Photonics, Shizaoka, Japan), operated at a current of 8 mA and a wavelength of 228.8 nm with a spectral band pass of 0.7 nm was used. Pyrolytically coated graphite tubes (Shimadzu) were used. The sample injection volume was 20 μL in all experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table-1. The absorbances of Fe(II), Cu(II) and Zn(II) were also measured using a Perkin-Elmer AA-6800 atomic absorption spectrometer equipped with Perkin-Elmer single element hollow cathode lamps and an air-acetylene burner. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected were as follows: Cu 324.7 nm, Zn 213.9 nm and Cd 228.8 nm. The pH values were measured with a Metrohm pH-meter (Model: 691, Herisau, Switzerland) supplied with a glass-combined electrode. The flow rate of liquid through columns was controlled using a model BT00-600M peristaltic pump (Baoding Laonger Precision Pump Co. Ltd.).

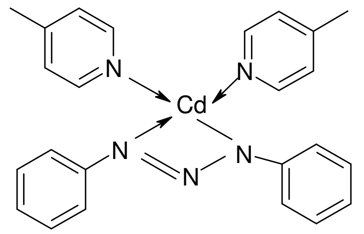
TABLE-1
GRAPHITE FURNACE TEMPERATURE PROGRAM FOR CADMIUM(II) DETERMINATION

Argonflow rate (mLmin^{-1})	Temp. (°C)	Ramp time(s)	Hold time(s)	Step
250	70	1	20	Drying
250	200	5	10	Pyrolysis
0	2200	0	4	Atomization
1000	2400	0	2	Cleaning

Unless otherwise stated, all water is 18 MΩcm pure water purified with a Milli-Q system (Millipore, USA) and all reagents used were of analytical grade and all solutions were prepared with pure water. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with pure water, according to a published procedure[42].

Stock solutions (containing 1000 mg Cd/L) of cadmium(II) chloride in water were purchased from Aldrich. The prepared cadmium standard solutions were stored in brown glass bottles with TFE-lined closures at 4 ºC in a dark environment. The reference and working solutions were diluted daily from stock metal solutions. Other metal stock solutions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of nitrate in 1.0 % (v/v) HNO_3 and further diluted daily prior to use. The pH was adjusted with the following buffer solutions: $H_2C_2O_4$/$NaHC_2O_4$ for pH 2.0 and 3.0; $NaCH_3COO/CH_3COOH$ for pH 4.0-6.0. Na_2HPO_4/NaH_2PO_4 for pH 7.0; $Na_2B_4O_7$/NaOH for pH 8.0-11; NaOH for pH 12-14. Nano diazoaminobenzene (DAAB) was procured from Aldrich (Milwaukee,USA). Azobisisobutyronitrile (AIBN) and thylene glycoldimethacrylate (EGDMA) were obtained from Fluka (Switzerland). 4-Vinyl pyridine was purchased from Merck (Darmstadt, Germany).

Preparation of Cd(II) imprinted and non-imprinted copolymers: Nano diazoaminobenzene (DAAB) (10 mmol) and 10 mmol cadmium chloride was dissolved in 50 mL of methanol and stood for 2 h, then 40 mmol 4-vinylpyridine (VP), 200 mmol ethyleneglycoldimethacrylate (EGDMA) and 0.4 g azobisisobutyronitrile (AIBN) were added and dissolved in a ultrasonic water bath for 15 min. The polymerization mixture was flushed by bubbling N_2 for 10 min, sealed and heated at *ca.* 60 ºC with stirring for 30 h. The solid formed was ground in a mortar and dried in constant temperature vacuum oven at 70 ºC for 2 h. The resulting copolymers were grinded and screened, of which the 30-54 µm size were selected as experimental sorbents. The selected particles were treated with 1:4 (v/v) methanol/water for 10 h and then the mixed solution of 0.1 mol L^{-1} HCl and 0.5 mol L^{-1} thiourea till to remove all of Cd(II) linked to the copolymer. Cd(II) imprinted copolymer was cleaned with pure water and then dried in a vacuum oven at 65 ºC for 48 h. In the same way, non-imprinted copolymers were also prepared without cadmium chloride added. The repeated unit of Cd(II) imprinted copolymers complex with Cd(II) are shown in **Scheme-I**.



Scheme-I: Repeated unit of Cd(II) imprinted copolymers complex with Cd(II)

Batch procedure: In 100 mL polyethylene bottles, previously cleaned with detergent, pure water, dilute nitric acid and pure water in sequence, added 5mL pH 8.0 buffer solution except for pH effect test with pH 1.0-12.0 buffer and 45 mL 2.0×10^{-7} mol L^{-1} metal ion solution except for sorption capacity measurement with the metal ion concentration of 0.05-5.0 × 10^{-5} mol L^{-1} and immersed 50 mg Cd(II) imprinted copolymer with shaking at 25 ºC. At pre- fixed time, an aliquot of the supernatant was separated and the metal ions were determined by FAAS or GFAAS. The adsorbed copolymer was eluted with 0.1 mol L^{-1} of HCl + thiourea and the desorbed Cd(II) was measured with complex titration or GFAAS. The adsorption capacity, the distribution ratio, the selectivity factor of Cd(II) with respect to Cu(II), Zn(II), Fe(II) and the relative selectivity factor were calculated as the following equations:

$$Q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$E = \frac{C_0 - C_e}{C_e} \quad (2)$$

$$D = \frac{Q}{C_e} \quad (3)$$

$$\alpha = \frac{D_{Cd}}{D_M} \quad (4)$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \quad (5)$$

where Q represents the adsorption capacity (µmol g^{-1}), C_0 and C_e are the initial and equilibrium concentration of Cd(II) (µmol L^{-1}), respectively,W is the mass of copolymers (g) and V is the volume of metal ion solution (L), E is the extraction percentage (%), D is the distribution ratio (mL g^{-1}), α is the selectivity factor, D_{Cd} and D_M represent the distribution ratios of Cd(II) and Cu(II), Zn(II) or Fe(II), α_r is the relative selectivity factor, α_i and α_n represent the selectivity factor of imprinted copolymer and non-imprinted one.

Column procedure: The stopcock of the glass column (100 mm in length and 10 mm in diameter) was covered with a fritted glass disc. A total of 500 mg of copolymers was slurred in water and then poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the copolymer beads during sample loading. It was treated successively with 1 mol L^{-1} HCl and pure water. The column was preconditioned by passing a blank solution and then a solution containing 1 µg of Cd(II) in a volume of 100 mL was passed through the column at a flow rate of 0.5 mL min^{-1} (controlled by a peristaltic pump) after adjusting pH 8. The column was washed with 15 mL pure water and the adsorbed Cd(II) was eluted with 8 mL of 0.1 mol L^{-1} of HCl + thiourea and 2 mL pure water and 100 µL eluent were injected to determine by GFAAS.

Sample preparation: The certified tap water and rain water sample were prepared according to the previous procedure[18]. The surface tap water and rain water samples, collected from dirty region of Varamin in 2006. The Caspian sea water samples were collected from Mhmoodabad. To oxidize organic matter such as humic acid, the tap water and rain water and sea water samples were digested by an oxidizing UV photolysis in the presence of 1 % H_2O_2 using a low pressure Cd-lamp which was integrated into a closed quartz vessel[28,29].

A 100 mL of the above samples were percolated through the column packed with 500 mg of copolymers. The adsorbed analytes were eluted and analyzed according to the column procedure.

RESULTS AND DISCUSSION

Evaluation of the role of the Cd(II) imprinted copolymer: Some preliminary experiments were performed for investigation of absence or presence of Cd(II) imprinted copolymer on the quantitative extraction of Cd(II). It was concluded that the without imprinting itself does not show any tendency for the retention of Cd(II), but introduction of 100 mL portions of aqueous Cd(II) samples containing $C_{Cd(II)}$ 5.0 × 10^{-7} mol L^{-1} Cd(II)and 500 mg of 30-54 µm Cd(II) imprinted copolymers leads to satisfactory its retention Table-2. The latter case is most probably attributed to the existence of a considerable interaction between Cd(II)and the Cd(II) imprinted copolymer. It should be mentioned that formation of stable complexes between Cd(II) and Cd(II) imprinted copolymer at pH = 8 is probably due to an ion pair formation mechanism.

TABLE-2
EFFECT OF PRESENCE OF Cd(II) IMPRINTED COPOLYMER ON EXTRACTION PERCENT OF Cd(II)[a]

Cd(II) imprinted copolymer	Extraction per cent of Cd(II)
Absence	0.09(5.7)[b]
Presence	95.7(2.7)

[a]Other conditions, 500 mg of 30-54 µm Cd(II) imprinted copolymers; $C_{Cd(II)}$ 5.0 × 10^{-7} mol L^{-1}; V 100 mL; pH 8.0; temperature 25 ºC. [b]Values in parentheses are RSD_S based on five individual replicate analyses.

Adsorption capacity of copolymers for Cd(II): Adsorption of Cd(II) from aqueous solution was investigated in batch experiments with shaking for 24 h. As can be seen in Fig. 1, the amount of Cd(II) adsorbed per unit mass of poly-Cd(II)-DAAB-VP increased with the initial concentration of Cd(II) increase. In order to reach the "saturation", the initial Cd(II) concentrations were increased till the plateau values (adsorption capacity values) were obtained. The average maximum adsorption capacity of Cd(II) imprinted copolymer (205 µmol g^{-1} dry copolymer) was about 3.5 times of non-imprinted one (58.6 µmol g^{-1} dry copolymer) for three replicate measurements.

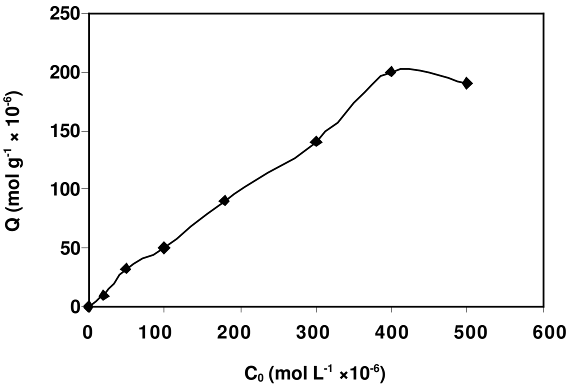


Fig. 1. Effect of Cd(II) initial concentration on the adsorption quantity of Cd(II) imprinted copolymers. Other conditions, 50 mg of Cd(II) imprinted copolymers; Vol. 50 mL; pH 8.0; shaking time 24 h; temperature 25 ºC

Effect of pH: The effect of varying pH values on Cd(II) uptake was investigated using the batch procedure with shaking for 1 h. The sorption experiments were triplicates. It can be seen from Fig. 2, the sorption quantity of Cd(II) increases with the increase of pH values. The sorption quantity is very low owing to the protonation of Cd(II) imprinted copolymers below pH 3, but the sorption capacity is increasing rapidly; after pH 5, the increasing rate is relatively very slow, the sorption capacity is near the maximum capacity at pH 8.0. So, pH 8 is chosen for this experiment.

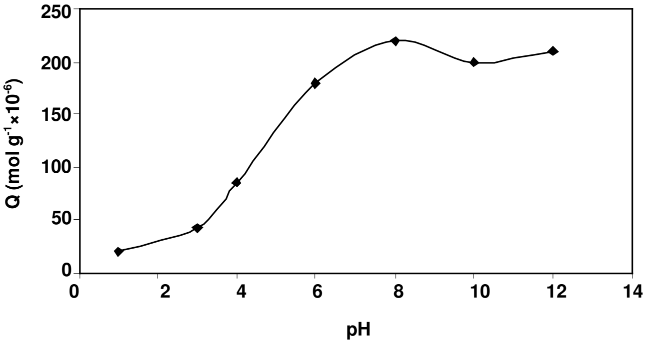


Fig. 2. Effect of pH on sorption of Cd(II) on Cd(II) imprinted copolymers. Other conditions, 50 mg of Cd(II) imprinted copolymers; $C_{Cd(II)}$ 2.0 × 10^{-7} mol L^{-1}; Vol. 50 mL; shaking time 2 h; temperature 25 ºC

Kinetics of Cd(II) sorption: To determine the rate of loading Cd(II) on the copolymers, batch experiments were carried out. The Cd(II) concentration in suspensions was analyzed in 5 min interval. Fig. 3 shows that an equilibration time of *ca.* 1 h was required for 96 % sorption. Although the time ($t_{1/2}$) of 50 % sorption was less than 20 min, but it was longer than that obtained with the ordinary resins such as the modified Amberlite XAD series[17-19] this is derived from the high degrees of crosslinking.

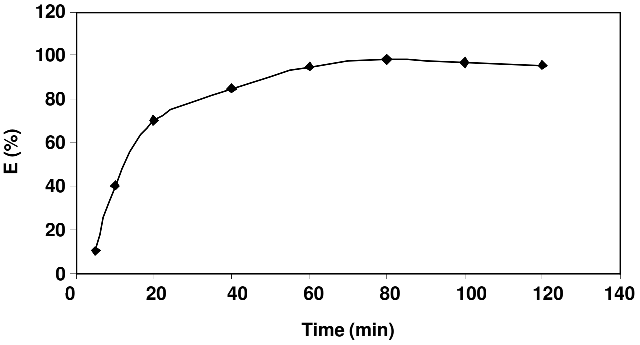


Fig. 3. Kinetics of Cd(II) sorption on Cd(II) imprinted copolymers. Other conditions, 50 mg of Cd(II) imprinted copolymers; $C_{Cd(II)}$ 2.0 × 10^{-7} mol L^{-1}; Vol. 50 mL; pH 8.0; temperature 25 ºC

Effect of temperature: The temperature effect experiments were carried out in the range of 10-50 ºC in consideration of the evaporation of cadmium species in real analysis. The results showed that the adsorption of Cd(II) with the imprinted copolymer was slightly dependent on temperature with the adsorption capacity decreased 14 % due to the adsorption process were exothermal and the elution time was shortened 16 %. In this experiment, temperature 25 ºC were chosen for easy control.

Cd(II) imprinted copolymers stability tests: To test the copolymers stability, it was subjected to several loading and elution batch operations. The elution operations were carried out by shaking the copolymers with 25 mL of 0.1 mol L^{-1} of HCl + thiourea for 1 h to ensure complete equilibration. The operating capacity was calculated from the loading and elution tests. The results from both tests agreed within 2-5 % difference up to 20 cycles of repeated experiments. The Cd(II) imprinted copolymers show good reusability and stability towards Cd(II).

Effect of flow rate: The flow rate of the Cd(II) solution through the packedbed column is a very important parameter for the time controls of adsorption and analysis. Using the column procedure, the effect of flow rate on sorption of Cd(II) was investigated. The results show that the flow rate has more influence on the sorption of Cd(II). Cd(II) can be adsorbed quantitatively by Cd(II) imprinted copolymers at a flow rate below 1 mL min^{-1}. Above 1 mL min^{-1}, the recovery was less than 96 %, as shown in Fig. 4, it need longer time using Cd(II) imprinted copolymers than using the ordinary copolymers to get equilibrium with the copolymers bed, owing to the reason mentioned in effect of pH. So, the flow rate of 0.5 mL min^{-1} was chosen for column procedures.

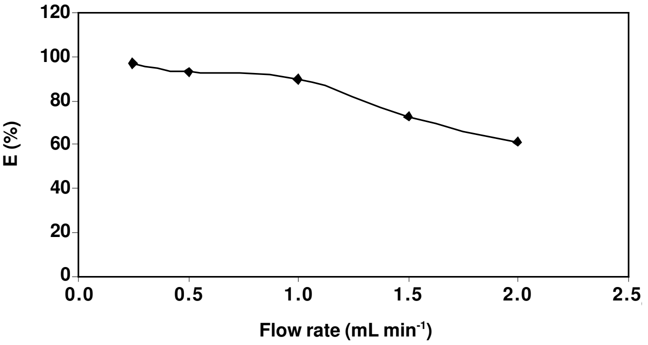


Fig. 4. Effect of flow rate on the adsorption of Cd(II). Other conditions, 500 mg of 30-54 μm Cd(II) imprinted copolymers; $C_{Cd(II)}$ 5 × 10^{-7} mol L^{-1}; Vol. 100 mL; pH 8; temperature 25 ºC

Maximum sample volume, enrichment factor and elution breakthrough volume: The enrichment factor was studied by recommended column procedure using increasing volume of Cd(II) solution and keeping the total amount of Cd(II) loaded constant to 1 μg. The maximum sample volume can be up to 2000 mL with 96 % recovery. The eluent type was also studied in column procedure. The results show that 6 h was needed using 2 mol L^{-1} HCl or HNO_3 for 96 % recovery, whereas, 0.5 h was sufficient using 0.1 mol L^{-1} of HCl + thiourea. So, 8.0 mL 0.1 mol L^{-1} of HCl + thiourea and 2 mL pure water was used as eluent in all further experiments. Therefore, the highest enrichment factor of 200 can be obtained.

Selectivity of copolymers for matrix ions: The effect of the electrolytes commonly coexisted with Cd(II), such as NaCl, KBr, KI, $NaNO_3$, Na_3PO_4, Na_2SO_4, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ on the sorption of Cd(II) was studied using the batch procedure with shaking 1 h. The results show in Table-3 that the selectivity of Cd(II) imprinted copolymers for Cd(II) over the investigated electrolytes was greatly improved with the tolerance limits 10-100-fold of the non-imprinted ones, indicating that the Cd(II) imprinted copolymers can be suitably used as sorbent for Cd(II) in high concentration of electrolytes. The reported tolerance limit is defined as the ion concentration causing a relative error < ± 5 %.

Competitive adsorption of Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Fe(II), from their binary mixture was also investigated in batch procedure. The D values of Cd(II) imprinted copolymers show increase for Cd(II), while decreasing significantly for Zn(II), Cu(II), Cd(II), (Table-4). The α_r values for Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Fe(II), are 36.7, 51.8, 86.7, respectively. This means that Cd(II) can be determined even in the presence of Cu(II), Zn(II), Fe(II). In order to further check the selectivity of the method for Cu(II), Zn(II), Fe(II) solution containing Cd(II) and other metal ions were prepared and analyzed by the proposed procedure. Studies with 1.0 μg L^{-1} of Cd(II) showed that the concentration of 25 μg L^{-1} Zn(II), Cu(II), Fe(II), did not interfere with Cd(II) determination after the MIIP-SPE and preconcentration procedure.

TABLE-4
SELECTIVITY PARAMETERS OF COPOLYMERS FOR Cd(II)

Metal ions	D_1	D_n	< i	< ν	<.
Hg(I)	1578	389	–	–	–
Cu(II)	34	156	70	2.68	36.7
Zn(II)	28	233	87	1.89	51.8
Fe(II)	35	406	79	1.05	86.7

Accuracy and precision of the MIIP-SPE and preconcentration method: The proposed method was calibrated with a series of Cd(II) standards having concentrations up to 25 μg L^{-1}. Calibration graphs obeyed the equation $A = 3.02 \times 10^{-2} C + 3.51 \times 10^{-3}$ (r = 0.999), where A is the absorbance integrated area and C is the cadmium concentration in μg L^{-1}. The linear calibration curve within concentration range from 0.13-25 μg L^{-1}. The detection limit (3σ) and the quantification limit (10σ), defined as by IUPAC[43,44] were found to be 0.05 and 0.13 μg L^{-1} for 100 mL samples, respectively, which lower than the published methods[45,46]. The relative standard deviation of the 11 replicate determinations was 2.6 % for the determination of 1.0 μg of Cd(II) in 100 mL water sample. The developed column preconcentration method was validated by ICP analysis (Table-5).

Application of the method: The proposed method was then applied for the determination of Cd(II) in tap water, rain water and sea water samples. Meanwhile, the standard addition method was applied to check the selectivity of the imprinted copolymers for Cd(II) against matrix elements. The recoveries were in the range of 94-105 %, demonstrating that the interference species in the matrix were eliminated after the MIIP-SPE and preconcentration procedure. The results listed in Table-5 indicate the suitability of the present Cd(II) imprinted

TABLE-3
TOLERANCE LIMITS OF ELECTROLYTES (n = 3)

Copolymers	Electrolytes (mol L^{-1})							
	$MgSO_4$	$CaSO_4$	Na_2SO_4	Na_3PO_4	$NaNO_3$	KI	KBr	NaCl
0.05	0.05	0.005	0.001	0.01	0.005	0.01	0.01	Non-imprinted
1.0	1.0	0.05	0.050	1.00	0.01	0.05	0.05	Imprinted

TABLE-5
DETERMINATION OF Cd(II) IN TAP, SEA AND RAIN WATER SAMPLES AND RELATIVE RECOVERY OF SPIKED Cd(II) IN TAP, SEA AND RAIN WATER SAMPLES

Sample	Concentration of Cd(II) mean ± SD[a] (µg)	Added Cd(II) (µg)	Found Cd(II) mean ± SD[a] (µg)	ICP-AES (µg)	Relative recovery (%)
Tap water1[b]	15.1 ± 0.4	5.0	20.6 ± 0.4	20.2 ± 1.2	99
Sea water[c]	6.9 ± 0.6	5.0	11.5 ± 0.7	11.3 ± 1.3	94
Rain water[d]	7.1 ± 0.8	5.0	11.3 ± 0.7	11.7 ± 1.4	97
Tap water 2[e]	n.d.f	10.0	9.8 ± 0.9	9.7 ± 1.5	96

aStandard deviation (n = 3). [b]From drinking water system of Tehran, Iran. [c]Caspian sea water, Iran. [d]Rain water(Tehran, 26 January, 2006). [e]Tap water (Varamin, taken after 10 min operation of the tap). [f]Not detected.

copolymers for preconcentration of Cd(II) from natural water samples.

Conclusion

The Cd(II) imprinted and non-imprinted copolymers were prepared by thermal copolymerization with cadmium chloride (or without it), nano diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycoldimethacrylate (EGDMA) as cross-linker in the presence of 2,2'-azobisisobutyronitrile as initiator. Quantitative enrichment of cadmium(II) from very dilute aqueous solutions containing sub-microgram cadmium was achieved with Cd(II) imprinted copolymers packed columns. The most important characteristic of the Cd(II) imprinted copolymers is its excellent selectivity towards Cd(II) over Cu(II), Zn(II), Fe(II), in spite of their similar chemical properties with Cd(II) and other alkali and alkali earth metals which normally coexist with Cd(II) in natural water compare to non-imprinted copolymers. But the Cd(II) imprinted copolymers have some drawbacks such as long equilibration and elution time in comparison to the ordinary resins. This may make it difficult to be put into practical use and should be a subject of further investigations.

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