



Anal. Bioanal. Chem. Res., Vol. 8, No. 1, 39-53, July 2020.

Evaluation of Polyvinyl Chloride Functionalized with 3-(2-Thiazolylazo)-2,6-diaminopyridines as a New Chelating Resin for On-line Pre-concentration and Determination of Traces of Cadmium in Real Samples by Flame Atomic Absorption Spectrometry

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(Received 10 October 2019 Accepted 25 August 2020)

In the present work, an on-line solid-phase extraction system is proposed for the preconcentration and accurate determination of trace amounts of cadmium(II) ions by flame atomic absorption spectrometry. The preconcentration of cadmium(II) ions was performed using polyvinyl chloride functionalized with 3-(2-thiazolylazo)-2,6-diaminopyridine in a minicolumn system. The adsorbed cadmium(II) ions were then eluted from the sorbent by the eluent. The important influencing parameters such as the sample solution pH, type and concentration of the eluent used for stripping cadmium(II) ions from the sorbent, flow rate of the sample and the eluent, and the amount of adsorbent were investigated in detail. Under the optimum experimental conditions, the linear dynamic range of the method was found to be in the range of 2.0-40.0 $\mu\text{g l}^{-1}$ (with the determination coefficient equal to 0.9987). The limit of detection and improvement factor were 0.7 $\mu\text{g l}^{-1}$ and 52.4, respectively. The inter assay precession (RSD%, $n = 7$) was in the range of 0.8-4.1% at the concentration levels of 5.00, 9.00 and 25.0 $\mu\text{g l}^{-1}$. The validated method was successfully employed for determination of cadmium(II) ions at trace levels in the spiked water and soil samples with satisfactory results.

Keywords: Cadmium(II), Solid-phase extraction, Preconcentration, Flame atomic absorption spectrometry, 3-(2-Thiazolylazo)-2,6-diamino pyridine, Polyvinyl chloride

INTRODUCTION

Heavy metals are toxic and non-biodegradable elements causing serious ecological and health risks even at low concentration levels [1,2]. Cadmium is one of these toxic elements which can cause high blood pressure, kidney damage, osteoporosis, and destruction of red blood cells [3]. Consequently, determination of trace amounts of this element is very important. One of the popular analytical techniques available for determination of metals in various matrices is flame atomic absorption spectrometry (FAAS) [4]. However, the sensitivity of this method is lower than that of the other spectral techniques [1,4]. To resolve this

problem, different separation and preconcentration techniques such as liquid-liquid microextraction [5,6], cloud-point extraction [7-9], and solid-phase extraction [10-13] have been developed. Among these methods, solid-phase extraction is commonly used because of the design simplicity, low solvent usage, low price, short extraction time, and off-line and on-line operation chance [4,14]. The strategy employed in solid-phase extraction is to use an adsorbent in order to adsorb the analyte [15]. Therefore, one of the most important aspects of a solid-phase extraction technique is the nature and properties of the sorbent [16]. Due to the important advantages of polymeric sorbents such as low price, simple preparation, high porosity, and stability in acidic or basic solutions [17], they are good choices to attain very useful systems for preconcentration and

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determination of heavy metals. By linking a chelating agent to the polymeric support, a new highly selective adsorbent can be synthesized for very low amounts of the elements [18].

Literature reviews reveal that different functionalized polymeric solid supports have been employed for the preconcentration and determination of metal ions in different samples [19-23]. In this work, for the first time, a new chelating polymeric sorbent (Fig. 1) is synthesized by the chemical functionalization of polyvinyl chloride (PVC) with 3-(2'-thiazolylazo)-2,6-diamino pyridine (TADAP). The prepared sorbent was used in an on-line system (Fig. 2) designed for a rapid preconcentration and determination of cadmium in real samples. To the best of our knowledge, there is no report on the application of this resin for the on-line preconcentration of cadmium.

EXPERIMENTAL

Instrumentations

Determination of cadmium in the samples was performed using a Shimadzu flame atomic absorption spectrophotometer, model AA-670, equipped with air-acetylene flame (acetylene flow rate: 1.8 l min⁻¹, air flow rate: 8 l min⁻¹, aspiration rate: 3.0 ml min⁻¹), and cadmium hollow cathode lamp (of wavelength 228.8 nm). An electro-multichannel peristaltic pump (model PP201V) was employed to pump the sample stream. In addition, a Teflon tube of 0.8 mm i.d., was used as an analyte and eluent transmitter. A polyethylene tube (3 mm i.d., 10 cm length), located between the selection valve and the flame atomic adsorption spectrometer, was used as a mini-column, and a six-way rotary injection valve (Rheodyne, model 5011) was used as a selection valve for selection of the sample or eluent flow through the column. Characterization of the synthesized sorbent was made by an FT-IR spectrophotometer (Brucker, model vertex 70). The CHN analyses were made using an Elementar Vario EL II elemental analyzer.

Reagents and Solutions

All the chemicals used including cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), nitric acid, hydrochloric acid, sodium nitrite, sodium hydroxide, potassium

hydrogen phthalate, sulfuric acid, citric acid, acetic acid, potassium hydrogen phosphate, potassium dihydrogen phosphate, PVC, 2,6-diaminopyridine, ethanol, and 2-aminothiazole were purchased from Merck KGaA Company (Darmstadt, Germany). All aqueous solutions were prepared using deionized water. All the plastic and glassware were cleaned by soaking in 10% (v/v) HNO₃ and rinsed three times with deionized water prior to use. A buffer solution (pH 6.0) was prepared by mixing appropriate volumes of potassium hydrogen phosphate (0.27 M) and potassium dihydrogen phosphate (0.27 M). The eluent solution hydrochloric acid was prepared by appropriate dilution of its concentrated solution. The resultant solution was standardized with sodium carbonate. The 1000 mg l⁻¹ cadmium(II) stock solution was prepared by dissolving 0.2744 g of Cd(NO₃)₂·4H₂O in a 100-ml volumetric flask. The standard and working solutions were prepared by serial dilutions of this stock solution.

Preparation of TADAP Ligand

The ligand TADAP was prepared using a process reported in Elsevier [24]. 2-aminothiazole (10.0 mmol) was dissolved in hydrochloric acid (16.0 ml, 6.0 M) and cooled in an ice salt bath. Sodium nitrite (0.70 g) was also dissolved in a minimum amount of water. After cooling both solutions in an ice salt bath, the nitrite solution was gradually added to the 2-aminothiazole solution along with mechanical stirring at a low temperature (-5-0 °C). The diazonium salt solution obtained was added drop wise to the cooled solution of 2,6-diaminopyridine dissolved in hydrochloric acid (1.0 g in 40.0 ml of 4.0 M). The mixture was stirred in an ice salt bath for 1 h and then sodium hydroxide solution was added to the mixture until pH 6.0 was reached. The red precipitate obtained was filtered and washed with water. Finally, the air-dried product was recrystallized with a mixture of ethanol-water (3:1) to obtain the pure red needle-shaped crystals of TADAP.

Preparation of Polyvinyl Chloride-3-(2-thiazolylazo)-2,6-diaminopyridine (PVC-TADAP)

For immobilization of TADAP on the PVC polymeric bed, PVC (0.5 g), ethanol (50.0 ml), and TADAP (0.7 g) were added to a round-bottomed flask, and the resulting mixture was refluxed for 72 h. The precipitate thus obtained

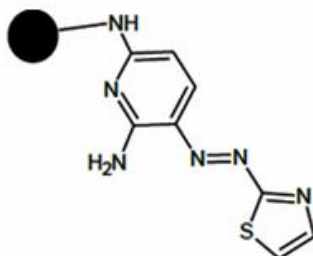


Fig. 1. Structure of the synthesized resin.

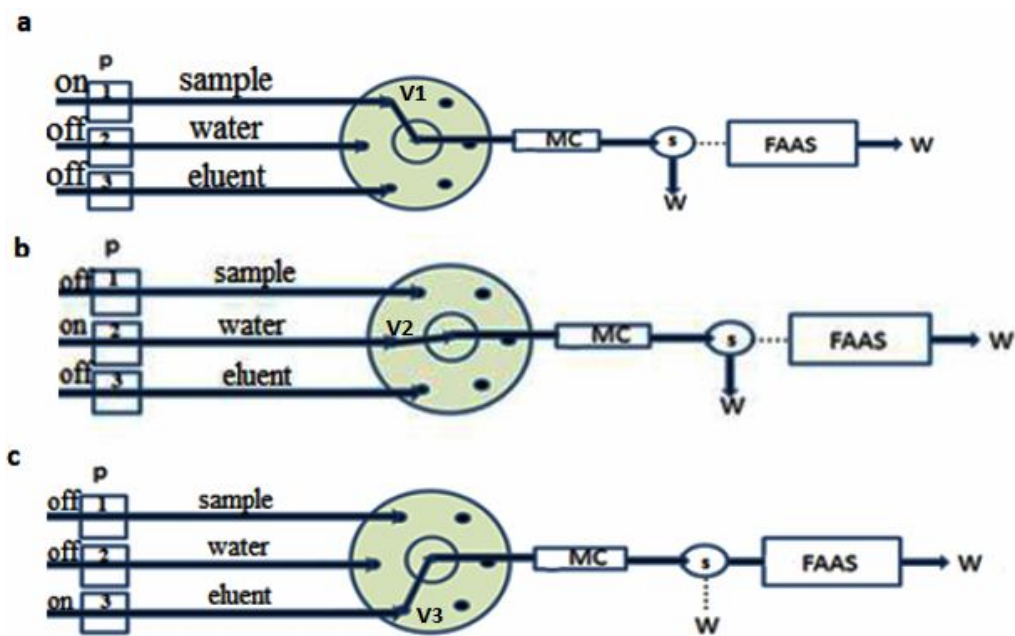
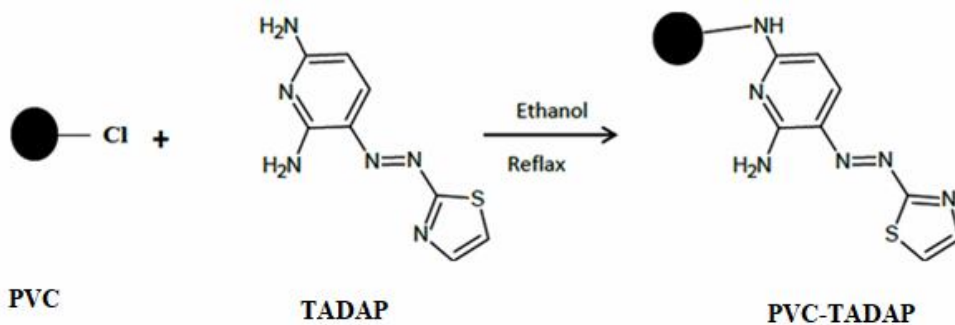


Fig. 2. Schematic diagram of the preconcentration process (a) sample adsorption, (b) washing, and (c) elution. P: peristaltic pump; MC: mini-column; s: selection valve; W: waste.



Scheme 1. Synthesis of PVC-TADAP resin

was washed thoroughly with ethanol and dried in 90 °C for 2 h to obtain dry PVC-TADAP resin. A representation of this process is given in Scheme 1.

Preparation of Mini-column

To prepare the mini-column, about 349.4 mg of the PVC-TADAP sorbent prepared was packed inside a laboratory-made polyethylene column (10.0 cm length and 3.00 mm i.d.), and the two ends of the column were closed with glass wool to hinder the loss of adsorbent during the preconcentration process. Before use, the packed mini-column was washed with HCl (1.0 M) and water, respectively. Due to the unlimited lifetime of the packing material, re-packing of the column was not necessary.

General Procedure

In the designed flow system (Fig. 2), the preconcentration and quantitative determination of cadmium were performed in a three-step process: step 1 (preconcentration): by rotation of valve V1, the sample (10.0 ml, pH 6.0) with a flow rate of 4.0 ml min⁻¹ was loaded into the mini-column and the cadmium ions were retained on the PVC-TADAP adsorbent; step 2 (washing): by turn off the first pump and turn on the second pump (while the valve was switched to another position), distilled water (2.5 ml, flow rate of 2.5 ml min⁻¹) was conducted into the packed column to eliminate the impurities weakly held on the adsorbent; step 3 (elution): by rotation of the valve and turn off the second pump and turn on the third pump, HCl (1.0 M) stream (3.8 ml) was sent to the column at a flow rate of 3.8 ml min⁻¹ to elute cadmium held by adsorbent and then continuously transported to the flame atomic adsorption spectrometer to monitor the analyte signal. While 10 ml of distilled water (pH 6.0) was passed through the mini-column instead of the 10 ml of the sample, the blank signal was measured. The difference of sample signal and blank signal was considered as an analytical signal. The average absorbance value at the three replicate experiments was considered as an analytical signal.

RESULTS AND DISCUSSION

Characterization of TADAP and PVC-TADAP

The functional groups and purity of the synthesized

ligand TADAP were investigated by the FT-IR spectra and melting point. The spectral data for TADAP displayed distinctive absorption bands in wave number (cm⁻¹), relating to the following functional groups: N-H (3335 and 3217), C-H (3082), C=N (1660), and N=N (1454), C-N (1292), and C-S (1159). The melting point of the ligand was in the range of 226-227 °C.

After immobilization of the this ligand on the PVC polymeric bed (Fig. 3a), the new peak in 1637 cm⁻¹ exists in the spectrum for PVC-TADAP (Fig. 3b), which is related to the stretching vibration of carbon-carbon double bond (C=C) [25] and/or carbon-nitrogen double bond (C=N) [26] inside the aromatic ring. The IR spectrum for PVC-TADAP also shows the characteristic absorption of the stretching vibration amino (N-H) groups at 3434 cm⁻¹ [25,27]. These peaks confirm that TADAP binds on the polymeric bed. Also the nitrogen percentage (3.26%) obtained in elemental analysis confirmed the immobilization of the ligand.

Optimization of Preconcentration Column Conditions

The experimental studies showed that the analytical signal for bare PVC was about one-fifth of the analytical signal for PVC-TADAP. Therefore, TADAP improves the adsorption capacity and sensitivity.

In order to obtain the best performance for the on-line designed system, different parameters affecting the process (such as pH of sample solution, type and concentration of eluent solution, flow rate of sample solution and eluent solution, length of column, and volume of sample solution) were optimized using the one-variable-at-a-time optimization method.

Effect of pH and Buffer Composition

Among the chemical parameters involved, sample solution acidity, stated as its pH, is the most important factor for an effective retention of the metal complexes onto the sorbent [28]. In this regard, 10 mL of cadmium(II) solutions (5.0 µg l⁻¹) buffered in the pH range of 4.0-8.0 (phosphate buffers) were passed through the PVC-TADAP packed column at a flow rate of 3.3 ml min⁻¹. The up-taken cadmium(II) ions were desorbed by introducing HCl (1.0 M), and the related analytical signals were registered. According to the results obtained (Fig. 4), at pH values

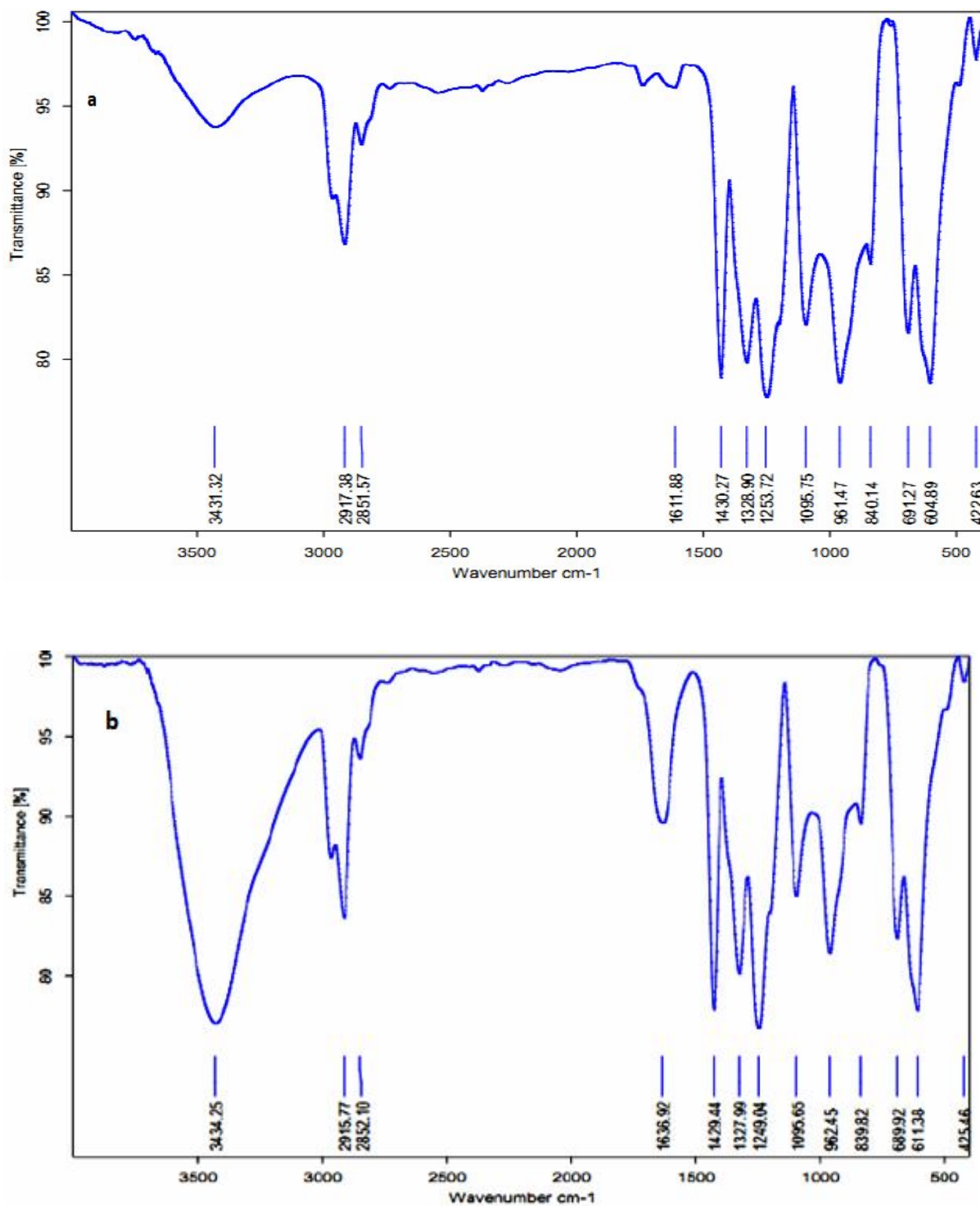


Fig. 3. IR spectra for (a) PVC, and (b) PVC-TADAP.

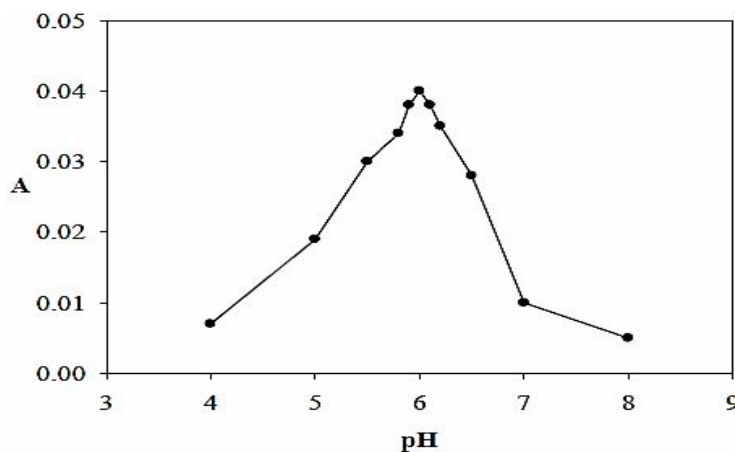


Fig. 4. Effect of solution pH on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) with flow rate of 3.3 ml min^{-1} on a 5.0 cm mini-column, desorption with HCl (1 M) at flow rate of 3.3 ml min^{-1} .

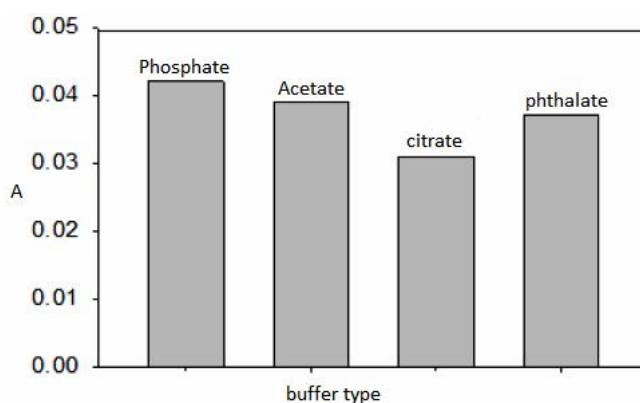


Fig. 5. Effect of buffer type on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) with flow rate of 3.3 ml min^{-1} on a 5.0 cm mini-column, desorption with HCl (1 M) at a flow rate of 3.3 ml min^{-1} .

lower than 6, due to the protonation of electron-donor groups present in the TADAP ligand, recovery decreased and at pH values higher than 6, competition between the hydroxyl or phosphate ions and TADAP for reaction or formation of complex with cadmium may be responsible for reduction of the analytical signal. Thus to achieve a higher signal for all the subsequent experiments, the solution pH values were adjusted to 6.0 using a phosphate buffer solution with a final concentration of 0.014 M. The effect of buffer type on the analytical signal was also studied using the phosphate, acetate, citrate, and phthalate buffer solutions at pH 6.0, and the corresponding results were demonstrated

in Fig. 5. The higher reduction of the analytical signal at the citrate buffer solution can be attributed to the formation of cadmium(II)-citrate complexes [29]. On the other hand, the presence of cadmium (as impurity) in the acetate and phthalate buffer solutions increased the blank signal. Based on the results obtained, the phosphate buffer solution was selected.

Effects of Type and Concentration of Eluent

The nature of the eluent solution has an important role in the elution (desorption) procedure. In this work, mineral acids were used as the eluent since their protons interact

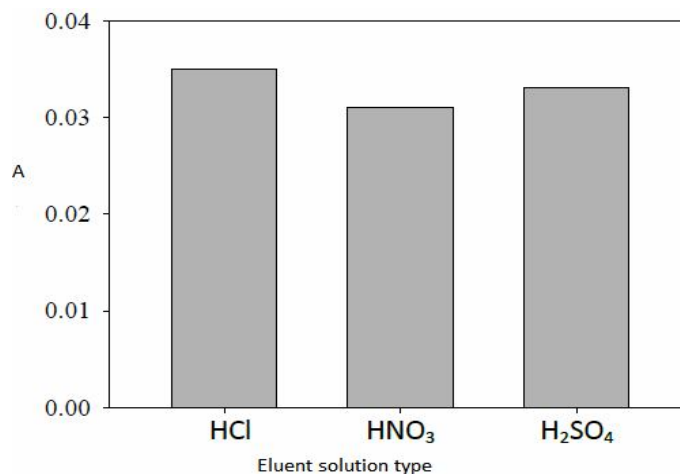


Fig. 6. Effect of eluent solution type on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) buffered at pH 6.0 with a flow rate of 3.3 ml min^{-1} on a 5.0 cm mini-column, desorption at a flow rate of 3.3 ml min^{-1} .

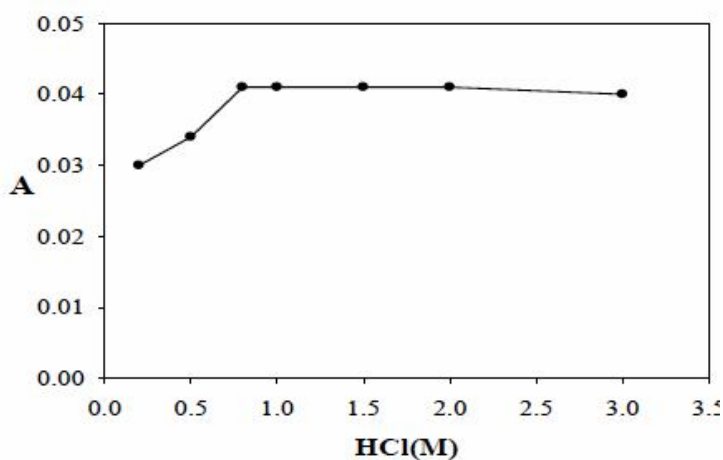


Fig. 7. Effect of eluent concentration on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) buffered at pH 6.0 with a flow rate of 3.3 ml min^{-1} on a 5.0 cm mini-column, desorption with HCl at a flow rate of 3.3 ml min^{-1} .

with the electron pairs in the ligand, breaking the metal-chelate bonds, and release cations from the solid bed [19]. In order to select the best acidic eluent (desorption solvent), different solvents including hydrochloric acid, nitric acid, and sulfuric acid were studied. The results obtained (Fig. 6) imply that there is no significant difference between the selected solvents. However, since hydrochloric acid has a less corrosive effect than nitric acid and the chloride ions

has less interaction with the analyte, hydrochloric acid was selected as the eluent. Then, the effect of the eluent concentration was investigated in the range of 0.25-3.0 M. As it can be seen in Fig. 7, the analytical signal increases with increase in the concentration of hydrochloric acid up to 0.8 M, and then it is almost constant. To ensure the complete elution of cadmium, the hydrochloric acid concentration of 1.00 M was chosen.

Effects of Flow Rates of Sample Solution and Eluent Solution

The amount of analyte retained in the column directly depends on the flow rate of the sample solution passed through the column. This parameter must be optimized to achieve the highest amount of retained analyte in the shortest time. In this regard, 10 ml of the sample solution ($5 \mu\text{g l}^{-1}$, pH 6) was sent through the column with the flow rate in the range of 2.0-7.0 ml min^{-1} . As it can be seen in Fig. 8a, at flow rates greater than 4.0 ml min^{-1} , because of the decrease in the cadmium adsorbed on the solid phase, the adsorption signal slowly decreased. Also at flow rates lower than 4.0 ml min^{-1} , the sampling frequency reduces. For this reason, the flow rate of 4.0 ml min^{-1} was selected as the optimum one.

In order to optimize the flow rate of the eluent solution, at pH 6 and a flow rate of 4.0 ml min^{-1} , 10 ml of cadmium solution ($5 \mu\text{g l}^{-1}$) was sent through a 5 cm packed column. The flow rate of the eluent solution was tested in the range of 2.0-6.0 ml min^{-1} . According to Fig. 8b, the amount of extracted analyte was increased by raising the flow rate of the eluent from 2.0 to 3.8 ml min^{-1} . In addition, because of the insufficient time for a complete elution of the adsorbed cadmium, the analytical signal was decreased. Thus, the flow rate of 3.8 ml min^{-1} was selected as the optimum one.

Effect of Column Length (Amount of Sorbent)

To investigate the effect of column length (amount of sorbent) on the analytical signal, mini-columns with different lengths (in the range of 3-11.0 cm) were prepared and their performance in the preconcentration procedure of (10 ml cadmium sample of $5.0 \mu\text{g l}^{-1}$) was studied. While the other variables were regulated in the optimized conditions, the results obtained (Fig. 9) demonstrated that the absorbance signal augmented with increase in the column length up to 7.0 cm, and then it was nearly constant. The increase in the signal can be attributed to the increase in the amount of adsorbent. In columns with a length more than 7.0 cm, the amount of adsorbent and consequently the amount of adsorbed cadmium was increased. On the other hand, the amount of longitudinal diffusion of the analyte in the column increased. Therefore, these two factors neutralize each other and cause the analytical signal to remain nearly constant. Considering that with increase in

the amount of adsorbent, the analyte inhibitory capacity increased, and in order to prevent the fast blocking of the column, an 8.0 cm length (349.4 mg of adsorbent) was ideal for the adsorption of different concentrations of the analyte.

Effect of Sample Volume

The effect of sample volume (loading time) on the absorbance signal was studied from 5.0 to 50.0 ml of $5.0 \mu\text{g l}^{-1}$ cadmium solution (75-750 s loading time). The results obtained (Fig. 10) demonstrated that with increase in the sample volume up to 40 ml, the analytical signal increased linearly. This observation implied that the retention efficiency was constant at the studied interval time. It was found that the recoveries were constant when up to 40 ml of the sample solution was used. At volumes higher than 40 ml, the recoveries for the analytes were decreased. According to the eluting flow rate of 3.8 ml min^{-1} and the 3 s time for elution of the retained Cd(II) up to the full observation of signal, the volume of the eluent consumed was calculated to be 0.19 ml. The preconcentration factor was calculated using the ratio of the sample volume and the eluent volume [30-33]. These results show that the preconcentration factor was obtained to be 210.5 (maximum) and 52.6 when 40 ml and 10 ml of the sample were used. However, for compatibility between sensitivity and sampling frequency, 10 ml was chosen as the sample volume. Of course, it is important to note that for a low concentration, a higher sample volume (a longer loading time) can be applied.

Effect of Ionic Strength

To investigate the effect of ionic strength (salt effect) in the optimum conditions, 10 ml of cadmium solutions ($5.0 \mu\text{g ml}^{-1}$) containing different concentrations of potassium nitrate (in the range of 0.00-0.20 M) were subjected to the preconcentration procedure, and the related analytical signals were monitored. The results obtained (Fig. 11) imply that the salt concentration (even at a high concentration) does not have a substantial effect on the analytical signal.

Figures of Merit

The linear regression equation for the calibration curve without preconcentration is $A = 0.17 \times 10^{-3} C_{\text{Cd(II)}} + 0.0023$

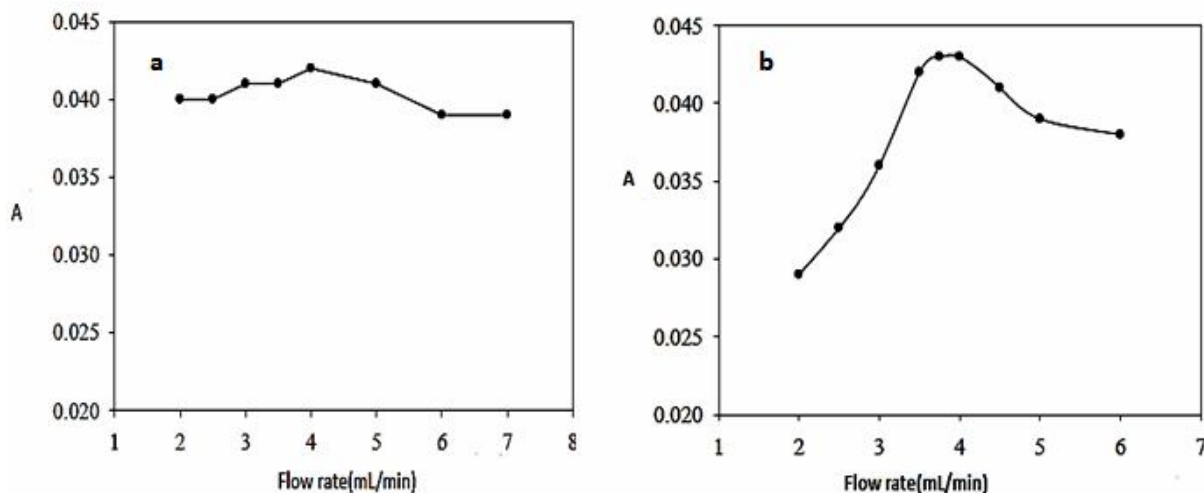


Fig. 8. Effects of (a) flow rate of sample solution and (b) flow rate of eluent solution on the absorbance signal. Conditions: 10.0 ml of $5.0 \mu\text{g l}^{-1}$ cadmium buffered solution at pH 6.0 on a 5.0 cm mini-column and elution with HCl.

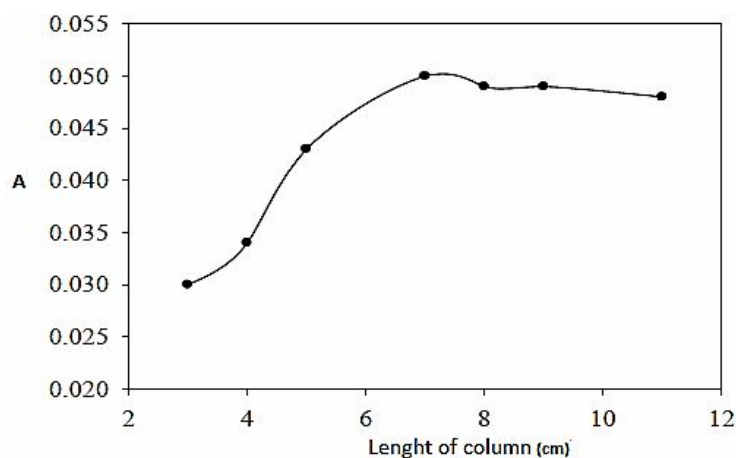


Fig. 9. Effect of column length on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) buffered at pH 6.0 with a flow rate of 4.0 ml min^{-1} , desorption with HCl (1 M) at a flow rate of 3.8 ml min^{-1} .

($r = 0.9989$, $n = 7$) over the Cd(II) concentration range of $80.0\text{-}2000 \mu\text{g l}^{-1}$.

In optimum experimental conditions (pH 6.0, sample flow rate of 4.0 ml min^{-1} , and elution with 1.0 M HCl solution at a flow rate of 3.8 ml min^{-1}), various analytical factors were calculated. For a 10 ml sample volume of, the calibration curve exhibited a linear behavior over the Cd(II) concentration range of $2.0\text{-}40 \mu\text{g l}^{-1}$. The resultant linear

regression equation for this curve is $A = 8.9 \times 10^{-3} C_{\text{Cd(II)}} + 0.0065$ ($r = 0.9989$, $n = 8$), where A is the absorbance and $C_{\text{Cd(II)}}$ is the concentration of cadmium ($\mu\text{g l}^{-1}$).

The limit of detection (LOD) is defined by the following equation:

$$\text{LOD} = 3S_b/m \quad (1)$$

where S_b is the standard deviation for the measured signal

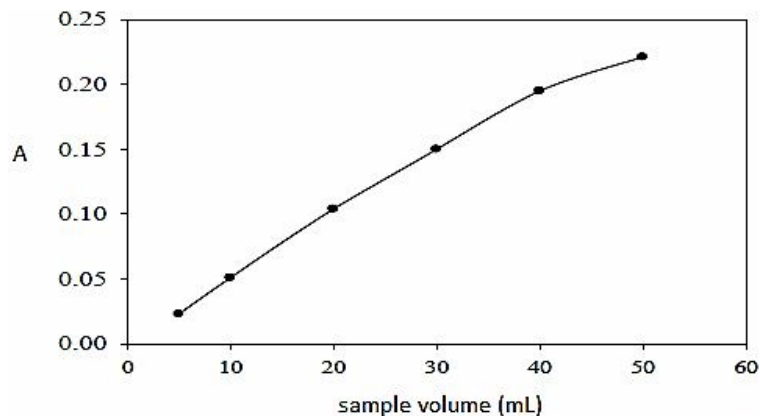


Fig. 10. Effect of sample volume on the absorbance signal. Conditions: cadmium solution ($5.0 \mu\text{g l}^{-1}$) buffered at pH 6.0 with a flow rate of 4.0 ml min^{-1} on an 8 cm mini-column, desorption with HCl (1 M) at a flow rate of 3.8 ml min^{-1} .

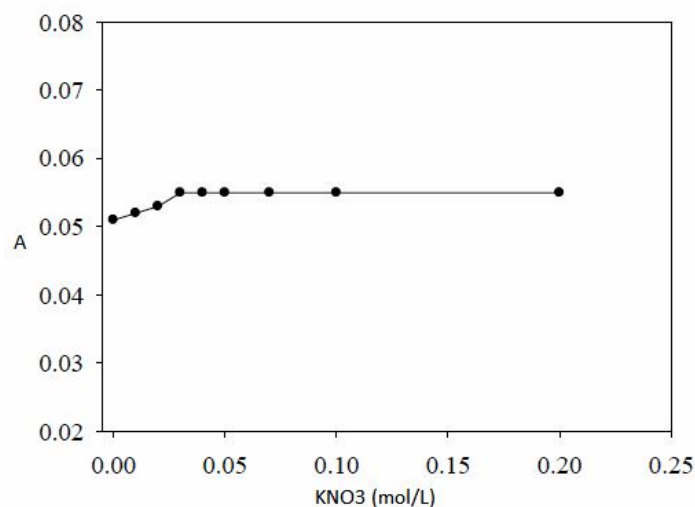


Fig. 11. Effect of ionic strength on the absorbance signal. Conditions: 10.0 ml of cadmium solution ($5.0 \mu\text{g l}^{-1}$) with a flow rate of 4.0 ml min^{-1} on an 8 cm mini-column, desorption with HCl (1 M) at a flow rate of 3.8 ml min^{-1} .

of the blank solution (a mixture of buffer and distilled water) and m is the calibration sensitivity. Considering ten replicate measurements of blank solution, a detection limit of $0.7 \mu\text{g l}^{-1}$ was acquired.

To assess the precision of the proposed method, the relative standard deviations of seven replicate measurements of Cd(II) at concentration levels of 5.0 , 9.0 and $25 \mu\text{g l}^{-1}$ were calculated. These values were 4.1%, 3.3% and 0.8%, respectively.

The improvement factor, defined as the ratio of the slopes of the calibration graphs with and without preconcentration [30-33], was 52.4 for a sample volume of 10 ml. The consumptive index (defined as the consumed sample volume (ml) per unit of improvement factor) was also calculated [34]; its value was 0.19 ml. The low value for this parameter specifies the appropriate efficiency of the method.

The percent extraction recovery (ER%) for the on-line

preconcentration system was calculated by the following equation [35]:

$$\text{ER (\%)} = \text{PF}(\text{VE}/\text{VS}) \times 100\% \quad (2)$$

where ER, PF, VE and VS are the recovery percentage, preconcentration factor, volume of eluent, and volume of sample solution, respectively. Considering that the time required for the complete elution of the adsorbed analyte in the column (with a flow rate of 3.8 ml min^{-1}) was 3 s, the calculated VE value was $190 \mu\text{l}$, and thus the resulting ER (%) was 95%.

The maximum capacity of the sorbent was determined in the batch method. For this purpose, 100 mg of this resin was mixed with 100 ml of $150 \mu\text{g l}^{-1}$ of cadmium solution (pH 6.0) and stirred for 1 h. Then, the remaining amount of cadmium in the solution was measured by direct nebulization to FAAS. Finally, the difference between the initial and remaining amounts of cadmium concentration was used for calculation of the maximum capacity. The resin had a maximum capacity of 310 mg g^{-1} of dry sorbent.

The experimental studies on the lifetime of the PVC-TADAP packed mini-column showed that from the 1000 retention and elution cycles, the synthesized resin did not show any loss or gain in the analytical signal, and therefore, the packed column did not require re-packing.

Effect of Co-existing Ions

In order to detect the potential interferences of various ions present in the matrix of real samples with the determination of cadmium, synthetic mixtures of solutions containing cadmium ($5.0 \mu\text{g l}^{-1}$) and various amounts of diverse ions were analyzed using the proposed method. The tolerance limit was considered as the concentration of foreign ions that caused an error not more than $\pm 5\%$ in the absorbance [36]. Based on the results obtained (Table 1), it was found that a large number of cations and anions examined did not interfere with this method, and only Cu^{2+} and Hg^{2+} ions had serious interferences. Cu(II) and Hg(II) interfere with the adsorption on the PVC-TADAP adsorbent, reducing the adsorption of Cd(II) ions on the adsorbent, and consequently, reducing the analytical signal for Cd(II) . The interference of these ions is non-spectral. Additional studies demonstrated that the interference effect

could be reduced to 60-fold and 100-fold for Cu^{2+} and Hg^{2+} ions, respectively, using 5.0 mg l^{-1} of SCN^- (as the masking agent), respectively.

Analysis of Well Water

The developed technique was employed for the quantitative determination of cadmium in well water, collected from 10 different locations in the city of Shahrood, Iran. The well water was first filtered, and then 40 ml of it was transferred to a 50 ml volumetric flask. To this solution was added 2.5 ml of the buffer solution at pH 6, and the volume of the flask was made to the mark using distilled water. In order to evaluate the accuracy of the preconcentration procedure, the recovery experiments were performed with spiked water samples using the standard addition method. The results of the measurements are summarized in Table 2. According to the recovery values (in the range of 97-98.7%) and the calculated t values (less than $t_{\text{critical, df}=3} = 3.18$), one can conclude the accuracy of the proposed method. Therefore, the proposed method can be used to determine Cd(II) in the well water samples without a systematic error.

Analysis of Soil Samples

The soil samples were randomly collected from several points of an agriculture located in Shahrood. For the digestion process, 10.0 g of a soil sample was mixed with 15.0 ml of aqua regia (mixture of nitric acid and hydrochloric acid with a volume ratio of 1:3) and stirred at $70 \text{ }^\circ\text{C}$ for 12 h. Afterwards, 15 ml of aqua regia was added again and stirred for 6 h under the previous conditions. Then, 50 ml of distilled water was added to the sample, and the resulting mixture was filtered using a Whatman filter paper and neutralized with a concentrated sodium hydroxide solution up to pH 4. The resulting solution was transferred to a 250 ml volumetric flask and marked to volume with distilled water. 40.0 ml of the prepared solution was transferred to a 50 ml balloon, and after adding 2.5 ml of a phosphate buffer with pH 6, it was diluted with distilled water. Finally, the cadmium concentrations in 10.0 ml of the prepared solution were analyzed by the proposed preconcentration process using the standard addition method. The t -test and recovery results (Table 3) confirmed that there were no significant statistical differences between

Table 1. Tolerance Limits for Interferences in the Determination of Cadmium ions ($5.0 \mu\text{g l}^{-1}$)

Foreign species	Tolerated ratio ($W_{\text{species}}/w_{\text{Cadmium}}$)
Na^+	10000
Cr(VI) , IO_4^- , CH_3COO^-	6000
Pb^{2+} , Cr^{3+} , NH_4^+ , As^{3+} , Br^- , $\text{C}_2\text{O}_4^{2-}$	5000
F^- , $\text{C}_6\text{H}_5\text{O}_7^{3-}$ (citrate)	2000
Mn^{2+} , SO_4^{2-}	1200
Al^{3+} , Ca^{2+} , Ag^+ , Cl^- , SCN^-	1000
Ba^{2+} , HCO_3^-	600
Mg^{2+} , Fe^{2+} , Ni^{2+} , I^-	400
Fe^{3+} , Zn^{2+}	200
Hg^{2+} , Co^{2+}	100
Cu^{2+}	60

Table 2. Results of Cadmium Measurements in Well Water

No.	Added ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)	Recovery (%)	Calculated t	Content of cadmium in well water ($\mu\text{g l}^{-1}$)
1	-	$3.7(\pm 0.1)^a$	-	-	
2	5.0	$8.6(\pm 0.1)$	98.0	2.0	4.6
3	10.0	$13.4(\pm 0.4)$	97.0	1.5	
4	15.0	$18.5(\pm 0.8)$	98.7	0.5	

^aNumbers in parentheses are standard deviations for four replicate measurements ($t_{\text{critical, df}=3} = 3.18$).

Table 3. Results of Cadmium Measurements in an Agricultural Soil Sample

No.	Added ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)	Recovery (%)	Calculated t	Content of cadmium in gram of agricultural soil ($\mu\text{g g}^{-1}$)
1	-	$13.8(\pm 0.3)^a$	-		
2	5.0	$18.9(\pm 0.6)$	102.0	0.34	0.43
3	10.0	$24.1(\pm 0.7)$	103.0	0.86	
4	15.0	$29.2(\pm 0.4)$	102.7	2.0	

^aNumbers in parentheses are standard deviations for four replicate measurements ($t_{\text{critical, df}=3} = 3.18$).

Table 4. Comparison of Figures of Merit for the Proposed Method and some other Reported Methods

Adsorbent	Ligand	Eluent	Sample volume (ml)	Preconcentration factor	LDR ($\mu\text{g l}^{-1}$)	LOD ($\mu\text{g l}^{-1}$)	Ref.
Chloromethylated polystyrene	N,N-bis(naphthylideneimino) diethylenetriamine	HNO ₃	10	50	1-30	0.25	[19]
Amberlyst	-	HNO ₃	100	20	15-5000	0.23	[37]
polyhydroxybutyrate	Diethyl dithiocarbamate	HCl	600	100	2.1-75	0.42	[38]
Silica gel	2-[N,N'-bis(2,3-dihydroxybenzaldimin)]	HCl	5	12.3	10-200	0.65	[39]
Rice husks	-	HNO ₃	24	72.4	0-200	1.14	[40]
Nano-hybrid material (ZrO ₂ /B ₂ O ₃)	-	HNO ₃	150	15	10.3-3000	3.1	[41]
Manganese oxide-silica	-	HNO ₃	20	39.4	1-50	0.2	[42]
Diaion SP-207	1-Phenyl-1H-tetrazole-5-thiol	HOAC	75	37.5	20-1500	1.2	[43]
Duolite XAD-761	4-(2-Pyridylazo) resorcinol	Ethanol/ HNO ₃	800	160	1.26-22	0.38	[44]
PVC	3-(2'-Thiazolylazo) 2,6-diaminopyridine	HCl	10	52.6	2-40	0.7	This work

the experimental and real values.

Comparison with some other Reported Methods

From the viewpoints of preconcentration factor, linearity, and LOD, a comparison was made between the proposed method and some recently reported methods for the preconcentration and determination of cadmium (Table 4). The detection limit of the proposed method in a preconcentration volume of 10 ml is better than that of the methods reported in references 40, 41 and 43. The linear range of the proposed method is comparable or better than that of the methods reported in references 19, 39 and 44. Also the preconcentration factor for the proposed method is higher than that for the methods reported in references 37,

39 and 41-43. As it can be seen, a number of cited methods have a better LOD and LDR [37,38] but they have consumed a large volume of sample and consequently need a more amount of sample.

CONCLUSIONS

The on-line preconcentration method coupled with FAAS was employed for determination of trace amounts of cadmium in different real samples. This method is based on the solid-phase extraction of cadmium by PVC-TADAP resin. The proposed synthetic resin has special benefits such as infinite lifetime, high chemical stability, and fast kinetic in the adsorption and desorption processes that make it

appropriate for preparation of the column in on-line systems. The designed system is simple, fast, and automated, has a high sensitivity and selectivity for cadmium measurement, and illustrates satisfactory results in the determination of trace levels of cadmium in real samples such as soil and well water. Comparing the figures of merit for the proposed method with some recently published research works show that although a number of cited methods have a better analytical performance, they consume a large volume of sample, and consequently, require a more amount of sample.

ACKNOWLEDGEMENTS

The authors are thankful to the Shahrood University of Technology Research Council for the financial support of this work.

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