

# Chemically-Modified Activated Carbon with L-Arginine for Selective Solid Phase Extraction and Preconcentration of Metal Ions

*Abedi, Fatemeh; Shabani, Rostam\*\**

*Chemistry Department, Firoozabad Branch, Islamic Azad University, Firoozabad, I.R. IRAN*

**ABSTRACT:** *In this study, a new sorbent of chemically-modified activated carbon with L-arginine (AC-Arg) has been produced as solid-phase extraction, to trace Zn(II) and Cd(II) ions in real samples, including soil and water samples, by Flame Atomic Absorption Spectrometry (FAAS). Once the surface coverage value is determined, the surface modification has been investigated and assessed, while having employed both elemental analysis as well as Attenuated Total Reflection InfraRed (ATR-IR) spectroscopy. The separation/preconcentration factors of the analyte, including the effect of pH, shaking time, sample volume, elution condition, and interfering ions have been studied. Following the International Union of Pure and Applied Chemistry (IUPAC) recommendations, the detection limits ( $3\sigma$ ) of these methods are 2.4 and 1.6 ng/mL, using AC-Arg for Zn(II) and Cd(II) respectively. The Relative Standard Deviation (RSD) under optimum conditions is less than 1% ( $n=6$ ).*

**KEYWORDS:** *Chemically-modified activated carbon(AC); L-arginine(Arg); Solid Phase Extraction (SPE); Flame Atomic Absorption Spectrometry (FAAS).*

## INTRODUCTION

Water and soil pollution caused by heavy metals has recently turned out to be one of the main environmental problems [1, 2, 3]. Heavy metal water pollution has resulted in severe ecological problems in many areas around the world. Different techniques such as polarography [4], inductively coupled plasma atomic emission [5], voltammetry [6], and UV-Vis. Spectrometry [7], applied for the determination of heavy metals in aqueous samples. Flame Atomic Absorption Spectrometry (FAAS) is among the most extensively applied methods to determine heavy metals at trace levels, but, the sensitivity and selectivity of FAAS are typically inadequate

to determine heavy metals in trace concentration in complex environmental sample matrices [8-10]. In trace analysis, therefore, preconcentration or separation of trace elements from the matrices is quite essential for the development of their detection and selectivity by FAAS.

Among the preconcentration methods, Solid Phase Extraction (SPE) has been extensively popular for preconcentration of heavy metals, because of some advantages such as high efficiency, easy handling, speed, low consumption of material, especially toxic organic solvents, and the potential combination of a variety of on-line or off-line detection techniques [11-16].

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\* To whom correspondence should be addressed.

+ E-mail: Rostamshabani@yahoo.com

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The selection of suitable adsorbent in SPE procedure is considered an important factor to achieve high recovery and high enrichment factors [17-19].

Many sorbents were used in preconcentration of metal ions, such as Activated Carbon (AC) [20-25], silica gel [26-28], carbon nanotubes [29], resins like Amberlite XAD [30-33], Dowex Optipore V-493 [34], and polymers acrylamino-phosphonic-dithiocarbamate [35]. AC is the most widely used adsorbent in the environmental pollution control due to its large surface area, high adsorption capacity, porous structure, selective adsorption, and high purity standards [36-38].

However, AC can not solely adsorb quantitatively inorganic materials at trace and ultra-trace levels [39]. Therefore, there are different methods of surface treatments such as oxidative and non-oxidative methods which are extensively applied to modify the interfacial region by increasing surface functional groups, and thus, developing its potential low adsorption capacity. Several research groups have so far investigated the non-oxidative surface modification, including immobilization [40-42], loading [43-44], anchoring [45] and grafting [46] of organic molecules, which has recently achieved a substantial consideration.

The chemical structure of L-arginine is shown in Fig. 1. Chemically modified activated carbon with amino acids is expected to be more selective than untreated and oxidized activated carbon for the solid-phase extraction of metal ions. The main reason for using L-arginine as a chemical modifier for AC was that amino acids possess different functional groups including amine and carbonyl with different metal binding capacities.

Therefore, in this investigation, AC was oxidized to nitric acid to achieve carboxylic derivative (AC-COOH), afterward, the AC reacted with ethylenediamine (EDA) through an amide linkage to obtain AC-EDA. Finally, the (AC-EDA) product required a covalent modification of L-Arg, using glutaraldehyde as a covalent cross-linking agent. It is noteworthy that the binding of the (L-arginine) compound on the surface of the AC-COOH was achieved in a three-step reaction and characterized by ATR-IR spectroscopy and elemental analysis. At previously work the modifier adsorbed on the surface of the base adsorbent and washed after elution. In this study, the modifier chemically bonded on the carbon active and therefore don't remove simply

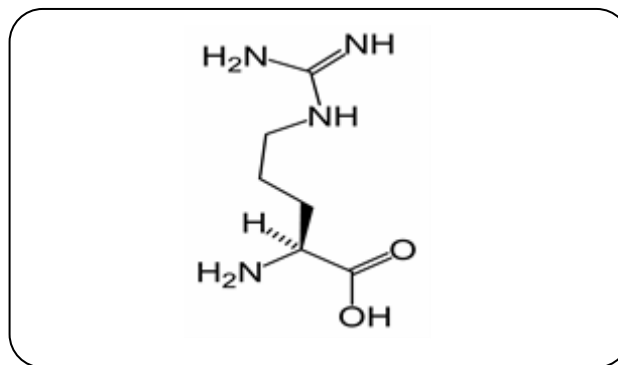


Fig. 1: Chemical structure of L-arginine

from the adsorbent after elution. The new sorbent has been used for the preconcentration and separation of Zn (II) and Cd (II) before their determination by FAAS. Parameters that influence the sorption and elution efficiency of the Zn (II) and Cd (II) were also investigated in the batch mode. Then, a validation standard for this method was analyzed using Certified Reference Materials (CRMs), so that it can be utilized for analyzing water and biological samples.

## EXPERIMENTAL SECTION

### Chemicals and reagents

Analytical and spectral Reagents of high purity were employed throughout the experiments along with deionized water; hence, no higher purity was required [47]. A standard stock solution containing 1000 µg/mL of zinc and cadmium was prepared by dissolving Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cd (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Merck, Darmstadt, Germany) in deionized water respectively. More dilute solutions were prepared daily out of the standard stock solution. The following buffer solution was used for SPE procedures: CH<sub>3</sub>COOH / CH<sub>3</sub>COONa buffer for pH 4-6; Na<sub>2</sub>HPO<sub>4</sub> / NaH<sub>2</sub>PO<sub>4</sub> buffer for pH 7-8 [48]. The pH was adjusted by adding dilute chloric acid or sodium hydroxide to analytes solution. AC in the average diameter of 40-60 mesh purchased, ethylene diamine (EDA), glutaraldehyde (GA), N,N'-dicyclohexylcarbodiimide (DCC) and L-arginine (Merck) were used in this work.

### Instruments and apparatus

In this research, a Perkin-Elmer FAAS instrument Model Analyst 300, equipped with Zn and Cd hollow cathode lamps, was operated at 10 mA and with

an air-acetylene flame. The wavelength used was 213.9 and 228.8 nm respectively, slit width of 0.7 nm, the fuel of 1.08 L/min, and burner height of 4-12 mm. The pH of each the sample solution was adjusted within the range of 4-8, using a Metrohm model 699 pH/ Ion digital meter equipped with a glass-saturated calomel electrode. It was calibrated with two standard buffer solutions pH 4 and 7, shaken using a mechanical shaker placed into a water bath at  $25 \pm 0.1$  °C. The attenuated total reflection infrared (ATR-IR) spectra of surface-modified of AC were achieved by a (model Tensor 27, Bruker instrument, Karlsruhe, Germany) in the wavenumber range of 600-4000  $\text{cm}^{-1}$ . Samples were run using Costech 4010 elemental analysis to determine CHN and O atoms present.

#### **Pretreatment of real samples**

Analysis of water samples in determining analyte contents was carried out as follows: About 8 mL of concentrated  $\text{HNO}_3$  and 3 mL of  $\text{H}_2\text{O}_2$  of (30%) were added to a beaker containing 250 mL of sample to eliminate and decompose organic matter. The sample was heated to one-fourth volume under stirring in optimum pH, followed by performing the preconcentration procedure presented above [49].

A well-homogenized soil sample of precisely 3.0 g was placed in a 250 mL beaker and digested with an oxidizing agent. Afterward, 14 mL concentrated  $\text{HNO}_3$  and 3 mL of  $\text{HClO}_4$  70% (w/w) were added, and heating is continued for 1 h. The content of the beaker was filtered through Whatman 40 filter paper into a 250 mL calibrated flask and its pH adjustment was made to optimum pH with KOH and acetate buffer and was diluted to mark with de-ionized water [50].

#### **Synthesis**

##### *Synthesis of the carboxylic derivative of activated carbon (AC-COOH)*

Activated carbon was purified using 10% (v/v) hydrochloric acid solution for 24 h to dissolve the metal ions and other impurities in the sorption step. Then, 10 g of purified activated carbon was immersed in 300 mL of 32.5% (v/v), nitric acid solution under stirring and heated for 5 h at 60 °C. The mixture was filtered and washed with deionized water until the pH of washing water became neutral and dried in an oven at 80 °C for 8 h.

The result was carboxylic derivative of activated carbon (AC-COOH).

##### *Synthesis of activated carbon-bound L-arginine (AC-Arg)*

An effective amount of 5.0 g AC-COOH was suspended in 150 mL of ethylenediamine, stirred and heated; then, 5.0 g of N, N'-dicyclohexylcarbodiimide (DCC) was added to the suspension and refluxed at 120 °C for 48 h. The result (AC-EDA) was filtered off, washed with ethanol, and dried at 80 °C for 8 hr. The activated carbon-bound ethylene diamine (AC-EDA) was afterward immersed in a 1% (w/v) glutaraldehyde solution (pH=7) for 40 min at room temperature and stirred and dried in an oven at 80 °C for 8 hr [51,52]. The glutaraldehyde treated activated carbon (AC-GA) were washed with distilled water and incubated in a 2% (w/v) L-arginine solution at pH=7 and stirred at room temperature on L-arginine modified carbon. The three-step synthesis of AC-Arg is illustrated in Scheme 1.

##### *(ATR-IR) Characterization and elemental analysis*

The modified activated carbons were also analyzed by ATR-IR analysis, as illustrated in Fig. 2. In the ATR-IR spectrum of AC-COOH with activated carbon, a new band ( $1720 \text{ cm}^{-1}$ ) appeared in AC-COOH, due to C=O of the carboxylic acid group, revealing that the carboxylic derivative of activated carbon was successfully prepared. Upon modification of AC-COOH by L-Arg, several new bands appeared in the spectrum. Based on the existing literature, the new bands can be assigned as follows: the peak at  $1537 \text{ cm}^{-1}$  was attributed to the asymmetrical vibration of carboxyl anion (-COO<sup>-</sup>), and the band at  $1647 \text{ cm}^{-1}$  was attributed to imine bond (C=N) or the N-H bending vibration. The band at  $3372 \text{ cm}^{-1}$  was assigned because of the N-H stretching vibration [53-54].

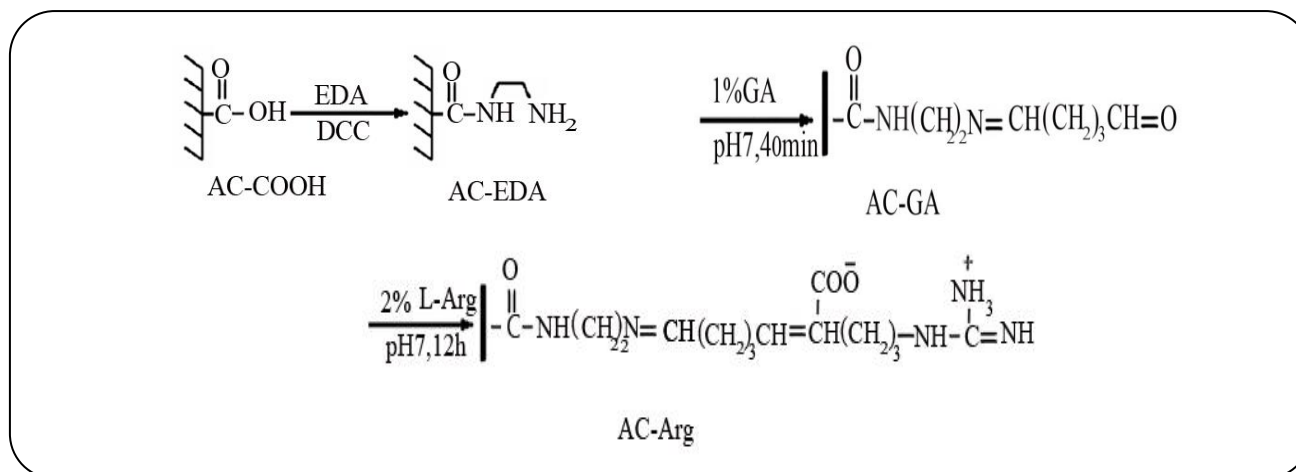
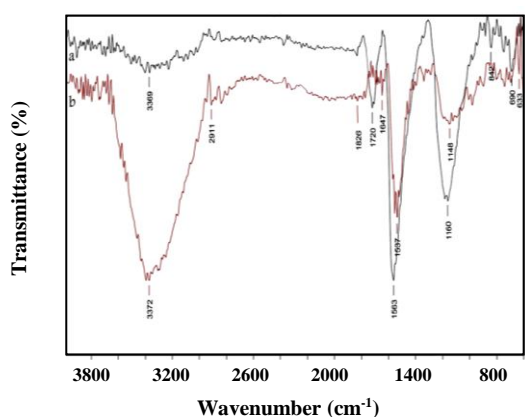
To ratify the attachment of L-Arg to activated carbon, elemental analysis was carried out. The results of the elemental analysis, before and after modification, are listed in Table 1. Accordingly, elemental analysis results show that the activated carbon is successfully modified by Arg.

##### **Preconcentration procedure**

Two sample solutions, including 0.2  $\mu\text{g/mL}$  of Zn(II) and Cd(II) ions in 250 mL, were taken, and by using different acetate buffers, it was adjusted to pH 5 for AC-Arg.

**Table 1: Elemental analysis results for activated carbon and activated carbon modified by L-arginine.**

Elemental atomic contents				
Element	%C	%H	%N	%O
AC	68.95	2.21	0	28.84
AC-Arg	77.36	2.13	11.60	8.91

**Scheme 1: Three-step synthesis of activated carbon with L-arginine****Fig. 2: ATR-IR spectra of AC(a) and AC-Arg (b).**

This batch procedure was carried out while 0.6 g of AC-Arg was added to the above solutions and stirred at room temperature for 30 min, so as to assist the adsorption of the zinc and cadmium ions onto the sorbents. The concentrations of the zinc and cadmium ions in the solutions were directly determined by FAAS. The sorbent was then eluted with 5 mL of 1 M  $\text{HNO}_3$  solution of optimal concentrations and the desorbed zinc and cadmium ions were measured by FAAS.

## RESULTS AND DISCUSSION

### Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects recovery. Therefore, the effect of the mass of sorbent on quantitative retention Cd(II) and Zn(II), different amounts of AC-Arg (range 0.2-1 g) were added into the solution following the experimental method. The results showed in Fig. 3. So to achieve higher recovery, subsequent extraction experiments were carried out using 0.6 g of the sorbent.

### Influence of pH of sample solution

The effect of pH of sample solution on the preconcentration step of Zn(II) and Cd(II) onto AC-Arg was studied over the range of 4–8 keeping other parameters constant. To achieve these purposes, 250 mL of 0.2  $\mu\text{g/mL}$  Zn(II) and Cd(II) at various pH values (4-8) were treated with the AC-Arg. Afterward, these were stirred at optimum stirring times. The eluent solution was checked for Zn(II) and Cd(II) concentration, using FAAS. Fig. 4 shows that the effective adsorptions of these ions take place at pH of 5.0. The pH during the

preconcentration procedure was controlled at 5.0 by addition of buffer solution with pH 5.0, the metal ions recoveries were increased from pH 4.0–5.0 and a decreased in the pH range 6.0–8.0. In acidic medium, these metal ions were seen in free cation, and then carboxylate and amine functional groups of adsorbent can be adsorbed the metal ions. With an increase of  $H^+$  concentration, dissociation of the acidic functional group of the adsorbent was suppressed and amine groups of adsorbent protonated and decreasing in sorption took place. With the increase of pH value causes facilitated dissociation of the acidic functional group of the L-arginine and thus more sorption of metal cations increased.

The decrease in absorption at  $pH > 5$  is probably due to the precipitation of metal ions as insoluble  $M(OH)_2$  or  $M(OH)^+$  in the reaction medium.

#### Effect of stirring time on the sample solution

The stirring time is a critical factor in determining the likelihood of using AC-Arg for the selective extraction of metal ions. In this study, the stirring time varied between 10–90 min while preconcentration of 250 mL of 0.2  $\mu\text{g/mL}$  zinc and cadmium solution was underway. The eluent solution for Zn(II) and Cd(II) concentration as well as the adsorption of the solution were checked and measured by FAAS. The results achieved revealed that 30 min of stirring was enough for the quantitative enrichment of Zn(II) and Cd(II) on AC-Arg Fig. 5. Hence, these times were adopted all through the subsequent studies.

#### Influence of sample volume

To achieve trustworthy and reproducible analytical results and a high concentration factor, it is very critical to obtain acceptable recoveries for all the compounds investigated in as large a volume of sample solution as possible. Therefore, it is essential to achieve the maximum volume in the SPE. To establish the maximum volume, various volumes of buffer solution at pH 5 for AC-Arg were spiked by maintaining Zn(II) and Cd(II) at 0.2  $\mu\text{g/mL}$  concentration levels. The influence of the sample volume on the recovery of analyte is illustrated in Fig. 6. The results revealed that the maximum sample volume could be up to 1000 mL for AC-Arg recovered to  $>95.5\%$ . At higher volumes, the percentage of recovery declined.

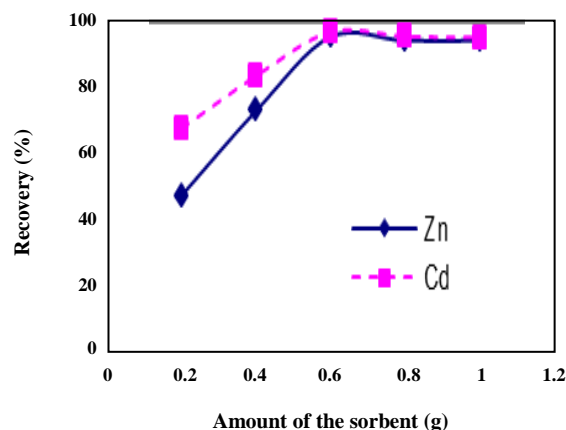


Fig. 3: Effect of amount of the sorbent .

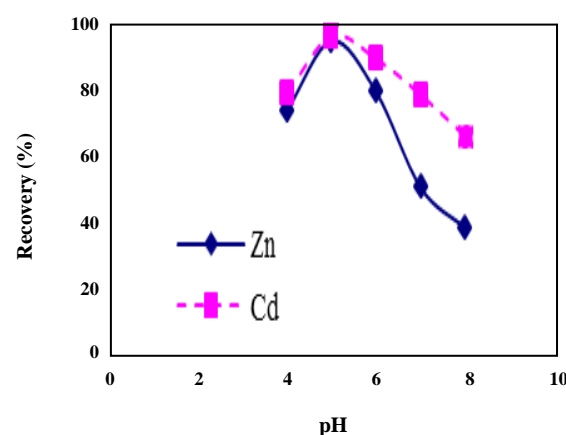


Fig. 4: Effect of pH on adsorption of Zn (II) and Cd (II) on the modified activated carbon.

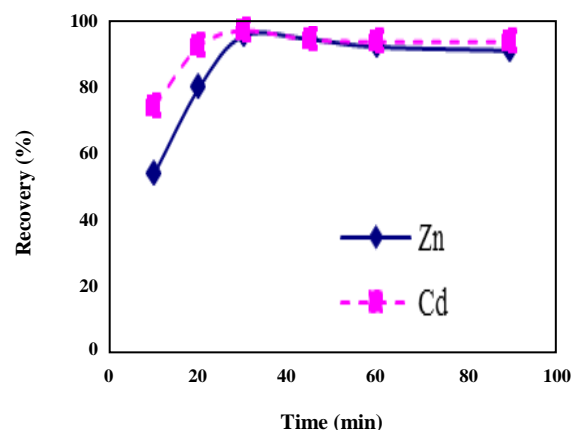


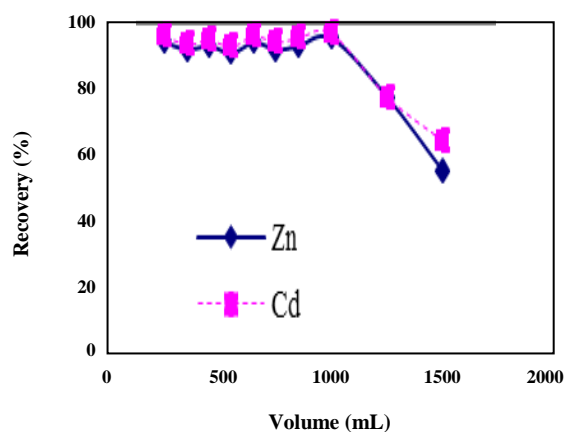
Fig. 5: Effect of stirring time in sample solution.

**Table 2: Effect of coexisting ions recovery percentage of 0.2  $\mu\text{g mL}^{-1}$  Zn (II) and Cd (II) adsorbed in AC-Arg.**

Interference ions	Tolerance limits (mg/L)
$\text{K}^+$ , $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	1000
$\text{NO}_3^-$ , $\text{SO}_4^{2-}$	750
$\text{Al}^{3+}$ , $\text{F}^-$ , $\text{CH}_3\text{COO}^-$	500
$\text{Fe}^{3+}$ , $\text{Co}^{2+}$ , $\text{Cu}^{2+}$	250

**Table 3: Specification of the presented method at optimum conditions for Zn (II) and Cd (II).**

Parameters	Zn/AC-Arg	Cd/AC-Arg
Linear range ( $\mu\text{g mL}^{-1}$ )	0.01-0.8	0.009-0.4
Regression equation	$Y=0.4508X+0.2309$	$Y=0.753X+0.999$
$R^2$	0.9989	0.999
Limits of detection( $\text{ng mL}^{-1}$ )	2.4	1.6
Preconcentration factor	200	200
RSD	0.86	0.70
Recovery(%)	95.6	96.72

**Fig. 6: Effect of the sample volume on adsorption 0.2  $\mu\text{g/mL}$  Zn (II) and Cd (II) on AC-Arg.**

#### The influence of coexisting ions

Levels of diversions is a critical problem in the atomic absorption spectrometry determination of heavy metal ions. In these tests, solutions of 0.2  $\mu\text{g/mL}$  of Zn(II) and Cd(II) maintaining the added interfering ions were treated as the above procedure suggests. The results are illustrated in Table 2. The highest level of foreign ions with the relative error of less than 5% while combining both SPE and atomic absorption spectrometry determination methods, was defined as a tolerable limit.

Apparently, the existence of the main cations has no outward effects on the determination of Zn(II) and Cd(II) at controlled conditions.

#### Analytical features

The calibration curve was achieved using a 250 mL solution at pH 5 AC-Arg at optimal condition. The results are illustrated in Table 3, where adsorption ability is an important factor, because it determines the amount of sorbent required to quantitatively concentrate the analytes from a specific solution. To determine the adsorption capacity, 0.6 g of adsorbent were treated with 0.2  $\mu\text{g/mL}$  of different volumes (250-1500 mL) of Zn(II) and Cd(II) solutions for AC-Arg. The primary volume of Zn(II) and Cd(II) was increased till the plateau volumes (adsorption capacity volumes) were achieved. A high preconcentration factor, as the ratio of the highest volume of initial solutions (1000 mL) to the volume of eluting solution (5 mL) for zinc and cadmium, was 200 for AC-Arg.

Following the general procedure described in this experiment, eight portions of standard solutions were simultaneously enriched and analyzed under control conditions. The limits of detection ( $3\sigma$ ) of the method defined by IUPAC were understood to be 2.4 and 1.6  $\text{ng/mL}$ , using chemically modified active carbon with L- arginine for Zn(II) and Cd(II) respectively.

**Table 4: Analytical results for the determination Zn (II) and Cd (II) in water samples for AC-Arg. (N=3).**

Ion	Added ( $\mu\text{g/mL}$ )	Found ( $\mu\text{g/mL}$ )	Recovery (%)	R.S.D (%)
Zn <sup>a</sup>	0	0.010	-	1.4
	0.3	0.297	99.0	1.0
	0.6	0.601	100.2	0.9
Cd <sup>a</sup>	0.0	0.009	-	1.2
	0.3	0.300	100.0	1.1
	0.6	0.602	100.3	1.1
Zn <sup>b</sup>	0	ND	-	-
	0.3	0.302	100.6	1.9
	0.6	0.611	101.8	1.6
Cd <sup>b</sup>	0	ND	-	-
	0.3	0.303	101.0	1.1
	0.6	0.605	100.8	1.0
Zn <sup>c</sup>	0	0.019	-	1.2
	0.3	0.298	96.3	0.9
	0.6	0.6	100.0	1.8
Cd <sup>c</sup>	0	0.012	-	1.1
	0.3	0.304	101.3	1.1
	0.6	0.613	102.2	0.9
Zn <sup>d</sup>	0	0.127	-	0.9
	0.3	0.302	100.6	1.2
	0.6	0.608	101.3	1.3
Cd <sup>d</sup>	0	0.021	-	1.6
	0.3	0.299	99.7	1.2
	0.6	0.6	100	1.0

a) Underground water; b) Tap water; c) Sea water; d) Effluent combined cycle power plant of Kazeroon; ND: not detected

The Relative Standard Deviation (RSD) for the six replicate determinations of lower 1% revealed that the method is accurate enough for the analysis of trace of Zn(II) and Cd(II) in solution samples. The results reveal the capability of the solid phase to recover the high amount of Zinc and Cadmium (Table 3).

#### Accuracy and application

To ascertain the accuracy of the suggested procedure, the method was successfully applied to determine trace of Zn(II) and Cd(II) in various samples, including soil and natural water samples. We used the standard addition

method while spiking experiments to check reliabilities. The percent recoveries and relative standard deviation for Zn(II) and Cd(II) in spiked water samples and soil are presented in Tables 4 and 5 respectively. These results reveal that AC-Arg can be considered an appropriate method for selective SPE and determination of trace of Zn(II) and Cd(II) in an environmental sample.

#### Comparison with other methods

Comparative information from some studies for the preconcentration procedures of Cd(II) and Zn(II) using

**Table 5: Analytical results for the determination Zn (II) and Cd (II) in soil for AC-Arg. (N=3).**

Ion	Added ( $\mu\text{g/mL}$ )	Found ( $\mu\text{g/ml}$ )	Recovery (%)	R.S.D (%)
Zn <sup>a</sup>	0	0.077	---	1.9
	0.3	0.295	98.3	0.9
	0.6	0.614	102.3	1.3
Cd <sup>a</sup>	0	0.034	---	1.7
	0.3	0.339	101.7	1.9
	0.6	0.613	102.2	1.3

a: Soil sample was collected from agricultural soil of firoozabad university, Iran.

**Table 6: Comparison with the other preconcentration procedures of Zn (II) and Cd (II) using various modified adsorbents.**

Method	Metals	P.F.	D.L.	L.R.	Method and apparatus	Reference
SDS-coated alumina – DPTQO	Cd(II)	N. R.	1.4	0.02 -0.85	SPE/FAAS	[55]
	Zn(II)	N. R.	1.3	0.01-0.9		
(IPBATP-Ag-NP-AC	Cd(II)	100	1.4	0.01-0.34	SPE/FAAS	[56]
	Zn(II)	100	1.3	0.01-0.32		
IPBATP-AC)	Cd(II)	50	1.6	0.01-0.3	SPE/FAAS	[57]
	Zn(II)	50	1.6	0.01-0.35		
(PNP-SBNPK 21	Cd(II)	80	2.1	0.2-0.7	SPE/FAAS	[58]
	Zn(II)	80	2.2	0.1-0.7		
PNP-SBNPK 22)	Cd(II)	80	2.6	0.4-0.7	SPE/FAAS	[58]
	Zn(II)	80	1.4	0.1-0.7		
MWCNT-MPSTO	Cd(II)	91	2.0	0.02–0.01	SPE/FAAS	[58]
	Zn(II)	91	1.4	0.02–0.12		
AC-Arg	Cd(II)	200	1.6	0.009-0.4	SPE/FAAS	Present work
	Zn(II)	200	2.4	0.01-0.8		

N. R. : Not Reported; P. F. : Preconcentration factor; D.L. : Detection Limit (ng/mL); L.R. : Linear range ( $\mu\text{g/mL}$ );

SDS-coated alumina – DPTQO: sodium dodecyl sulfate (SDS)-coated alumina as their 2,3 Di Hydro 2,3 para tolyl Qinzoline (1 H)- 4 one (DPTQO)

(IPBATP-Ag-NP-AC) and (IPBATP-AC): Silver nanoparticle loaded on activated carbon and activated carbon modified with 2-(4- isopropyl benzylideneamino) thiophenol (IPBATP)

(PNP-SBNPK 21 and PNP-SBNPK 22): Silica chemically bonded N-propyl kriptofix 21 and 22 with immobilized palladium nanoparticles

MWCNT-MPSTO: MultiWalled Carbon Nanotube (MWCNT)chemically modified with(3 mercaptoprop yl) silanetriolate

AC-Arg : Activated carbon chemically modified with L-arginine

various modified adsorbents are given in Table 6. As seem from data, Chemically-modified activated carbon with L-arginine (AC-Arg) show the detection limits of the measurement were remarkably better and a wider linear range, obtaining high preconcentration factor as well as being a convenient, safe, sensitive, simple, rapid, and inexpensive method as compared with other methods reported solid-phase extraction in Table 6.

## CONCLUSIONS

This selective method was successfully applied for the analysis of trace Zn(II) and Cd(II) in soil and water samples with satisfactory results. The benefits of the newly synthesized chemically-modified activated carbon with (AC-Arg), as the data obtained in this investigation suggests, can be summarized as follows. The synthesis of AC-Arg is comparatively straightforward and can be used



several times without a marked loss in sorption capacity, demonstrating the stability of the covalent bond between the AC-COOH with L-Arg.

The results are given in Table 6. The new sorbent has outstanding selectivity, short contact time, easy elution, stable structure after 6 elution, and good preconcentration factor for determination cadmium and zinc ions.

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## REFERENCES

- [1] Sabermahani F., Madadi Mahani N., [Extraction and Preconcentration of Pb\(II\) from Water and Soil Samples Using Modified Activated Carbon](#), *Iran. Chem. Commun.*, **3**: 48-56 (2015).
- [2] Sanchooli Moghaddam M., Rahdar S., Taghavi M., [Cadmium Removal from Aqueous Solutions Using Saxaul Tree Ash](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(3): 45-52 (2016).
- [3] Mohammad Beigi S., Babapoor A., Maghsoodi V., Mousavi S. M., Rajabi N., [Batch Equilibrium and Kinetics Studies of Cd \(II\) Ion Removal from Aqueous Solution Using Porous Chitosan Hydrogel Beads](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **28**(3): 81-89 (2009).
- [4] Copeland L.C., Griffith F.S., [Manual Polarograph for Rapid Determinations of Lead and Cadmium in Zinc](#), *Anal. Chem.*, **22**(10): 1269-1271 (1950).
- [5] Carroll S. A., O'Day P., Piechowski M., [Rock-Water Interactions Controlling Zinc, Cadmium, and Lead Concentrations in Surface Waters and Sediments, U.S. Tri-State Mining District. 2. Geochemical Interpretation](#), *Environ. Sci. Technol.*, **32**(7): 956-965 (1998).
- [6] Pei J., Tercier-Waeber M. L., Buffle J., [Simultaneous Determination and Speciation of Zinc, Cadmium, Lead, and Copper in Natural Water with Minimum Handling and Artifacts, by Voltammetry on a Gel-Integrated Microelectrode Array](#), *Anal. Chem.*, **72**(1): 161-71 (2000).
- [7] Rouhollahi A., Tavakoli H., Nayebi S., Ghasemi J., Noroozi M., Hashemi M., [Simultaneous Spectrophotometric Determination of Heavy Metal Ions Using Several Chemometrics Methods: Effect of Different Parameters of Savitzky-Golay and Direct Orthogonal Signal Correction Filters](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **26**(2): 41-51 (2007).
- [8] Burham N., Azeem S. A., El-Shahat M. F., [Solid Phase Selective Separation and Green Preconcentration of Cu, Zn, Pb and Cd in Drinking Water by Using Novel Functionalized Resin](#), *Cent. Eur. J. Chem.*, **7**: 945-954 (2009).
- [9] Ensafi Ali A., Ghaderi A. R., [On-Line Solid Phase Selective Separation and Preconcentration of Cd\(II\) by Solid-Phase Extraction Using Carbon Active Modified with Methyl Thymol Blue](#), *J. Hazard. Mater.*, **148**: 319-325(2007).
- [10] Narin, I., Surme, Y., Brcin, E., Soylak, M., [SP70- \$\alpha\$ -Benzoin Oxime Chelating Resin for Preconcentration-Separation of Pb\(II\), Cd\(II\), Co\(II\) and Cr\(III\) in Environmental Samples](#), *J. Hazard. Mater.*, **145**: 113-119 (2007).
- [11] Angelova M., Schentov B., Nedkova V., Nikoloff G., Alexiev A., Petrova Ch., Petrova Ch., [Serum Zinc in Children with Enterocolitis, Chronic Diarrhoea with Malabsorption Syndrome and Type 1 Diabetes](#), *Trakia. J. Sci.*, **4**: 11-17(2006).
- [12] Dogan Y., Durkan N., Baslar S., [Trace Element Pollution Biomonitoring Using the Bark of Pinus Brutia \(Turkish red Pine\) in the Western Anatolian Part of Turkey](#), *Trace Elements. Electol.*, **24**: 146-150 ( 2007).
- [13] Abbaspour A., Lzadyar A., [Carbon Nanotube Composite Coated Platinum Electrode for Detection of Cr\(III\) in Real Samples](#), *Talanta.*, **71**: 887-892 (2007).
- [14] Alvarez A. M., Alvarez J. R. E., Alvarez R. P., [Heavy Metal Analysis of Rainwaters: A Comparison of TXRF and ASV Analytical Capabilities](#), *J. Radioanal Nucl. Chem.*, **273**: 427-433 (2007).
- [15] Ghaedi M., Asadpour E., Vafaie A., [Simultaneous Preconcentration and Determination of Copper, Nickel, Cobalt, Lead and Iron Content Using a Surfactant Coated Alumina](#), *Bull. Chem. Soc. Jpn.*, **79**: 432-436 ( 2006).
- [16] Gopi Krishna P., Gladis J. M., Rao K. S., Prasada Rao T., Naidu G. R. K., [Synthesis of Xanthate Functionalized Silica Gel And its Application for the Preconcentrative Separation of Uranium \(VI\) from Other Inorganics and Geological Samples](#), *J. Radioanal. Nucl. Chem.*, **266**: 251-257 (2005).

- [17] Poole C. F., *New Trends in Solid-Phase Extraction, Trac, Trends Anal. Chem.*, **22**: 362-373 (2003).
- [18] Dean J. R., "Extraction Methods for Environmental Analysis", John Wiley & Sons, Inc. New York. (1998).
- [19] Zang Z., Hu Z., Li, Z., He Q., Chang X., *Synthesis, Characterization and Application of Ethylenediamine-Modified Multiwalled Carbon Nanotubes for Selective Solid-Phase Extraction and Preconcentration of Metal Ions, J. Hazard. Mater.*, **172**: 958-963 (2009).
- [20] Tavallali H., Daneshyar A., *Chemically Modified Activated Carbon with Ethylenedimine for Selective Solid-Phase Extraction of Cr(III) and Fe (III), Int. Chem. Tech. Res.*, **4**: 1163-1169 (2012).
- [21] Ghaedi M., Ahmadi F., Baezat M. R., Safari J., *Preconcentration and Extraction of Copper(II) on Activated Carbon Using Ethyl-2-quinolyl- $\beta$ (p-carboxyphenyl hydrazone)dioxo Propionate, Bull. Chem. Soc. Ethiop.*, **22**: 331-338 (2008).
- [22] Mikula B., Puzio B., *Determination of Trace Metals by ICP-OES in Plant Materials after Preconcentration of 1,10-phenanthroline Complexes on Activated Carbon, Talanta.*, **71**: 136-140 (2007).
- [23] Ghaedi M., Ahmadi F., Soylak M., *Preconcentration and Separation of Nickel, Copper and Cobalt Using Solid Phase Extraction and Their Determination in Some Real Samples, J. Hazard. Mater.*, **147**: 226-231 (2007).
- [24] Cerutti S., Silva M. F., Gasquez J. A., Olsina R. A., Martinez L. D., *On-Line Preconcentration/Determination of Cadmium in Drinking Water on Activated Carbon Using 8-hydroxyquinoline in a Flow Injection System Coupled to an Inductively Coupled Plasma Optical Emission Spectrometer, Spectrochim. Acta B.*, **58**: 43-50 (2003).
- [25] Ensafi Ali A., Zendegi Shiraz A., *On-line Separation and Preconcentration of Lead(II) by Solid-Phase Extraction Using Activated Carbon Loaded with Xylenol Orange and Its Determination by Flame Atomic Absorption Spectrometry, J. Hazard. Mater.*, **150**: 554-559 (2008).
- [26] Kocjan R., *Retention of Some Metal Ions and Their Separation on Silica Gel Modified with Acid Red 88, Microchim. Acta.*, **131**: 153-158 (1999).
- [27] Padilha P. D. M., Gomes L. A. D. M., Padilha C. C. F., Moreira J. C., Filho N. L. D., *Determination of Metal Ions in Natural Waters by Flame-AAS after Preconcentration on a 5-Amino-1,3,4-Thiadiazole-2-Thiol Modified Silica Gel, Anal. Lett.*, **32**: 1807-1820 (1999).
- [28] Akl M. A. A., Kenawy I. M. M., Lasheen R. R., *Organically Modified Silica Gel and Flame Atomic Absorption Spectrometry: Employment for Separation and Preconcentration of Nine Trace Heavy Metals for Their Determination in Natural Aqueous Systems, Microchem. J.*, **78**: 143-156 (2004).
- [29] Stafiej A., Pyrzynska K., *Solid Phase Extraction of Metal Ions Using Carbon Nanotubes, Microchem. J.*, **89**: 29-33 (2008).
- [30] Kumar M., Rathore D. P. S., *Amberlite XAD-2 Functionalized with O-aminophenol: Synthesis and Applications as Extractant for Copper(II), Cobalt(II), Cadmium(II), Nickel(II), Zinc(II) and Lead(II), Talanta.*, **51**: 1187-1196 (2000).
- [31] Saxena R., Singh A. K., *Pyrocatechol Violet immobilized Amberlite XAD-2: Synthesis and Metal-Ion Uptake Properties Suitable for Analytical Applications, Anal. Chim. Acta.*, **340**: 285-290 (1997).
- [32] Grag B. S., Sharma R. K., Bhojak N., Mittal S., *Chelating Resins and Their Applications in the Analysis of Trace Metal Ions, Microchem. J.*, **61**: 94-114 (1999).
- [33] Bilba D., Bejan D., Tofan L., *Chelating Sorbents in Inorganic Chemical Analysis, Croat. Chem. Acta.*, **71**: 155-178 (1998).
- [34] Melek E., Tuzen M., Soylak M., *Flame Atomic Absorption Spectrometric Determination of Cadmium(II) and Lead(II) after Their Solid Phase Extraction as Dibenzylthiocarbamate Chelates on Dowex Optipore V-493, Anal. Chim. Acta.*, **578**: 213-219 (2006).
- [35] Wen B., Shan X. Q., Liu R. X., Tang H. X., *Preconcentration of Trace Elements in Sea Water with Poly (Acrylamino-phosphonic - Dithiocarbamate) Chelating Fiber for Their Determination by Inductively Coupled Plasma Mass spectrometry, Fresen. J. Anal. Chem.*, **363**: 251-255 (1999).

- [36] Seco A., Marzal P., Gabaidon C., Ferrer J., Adsorption of Heavy Metals from Aqueous Solutions onto Activated Carbon in Single Cu and Ni system and in binary Cu–Ni, Cu–Cd and Cu–Zn System, *J. Chem. Technol. Biotechnol.*, **68**: 23-30 (1997).
- [37] Sanchez-Polo M., Rivera-Utrilla J., Adsorbent-Adsorbate Interactions in the Adsorption of Cd(II) and Hg(II) on Ozonized Activated Carbons, *Environ. Sci. Technol.*, **36**: 3850-3854 (2002).
- [38] Qadeer R., Hanif J., Saleem M., Afzal M., Adsorption of Samarium on Activated Charcoal from Aqueous Solution, *J. Chem. Soc. Pak.*, **14**: 91-96 (1992).
- [39] Ucer A., Uyanik A., Aygun S. F., Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) Ions by Tannic Acid Immobilised Activated Carbon, *Sep. Purif. Technol.*, **47**: 113-118 (2006).
- [40] Monser L., Adhoum N., Modified Activated Carbon for The Removal of Copper, Zinc, Chromium and Cyanide from Wastewater, *Sep. Purif. Technol.*, **26**: 137-146 (2000).
- [41] Monser L., Adhoum N., Tartrazine Modified Activated Carbon for the Removal of Pb(II), Cd(II) and Cr(III), *J. Hazard. Mater.*, **161**: 263-269 (2009).
- [42] Ucer A., Uyanik A., Cay S., Immobilisation of Tannic Acid onto Activated Carbon to Improve Fe(III) Adsorption, *Sep. Purif. Technol.*, **44**: 11-17 (2005).
- [43] Ghaedi M., Shokrollahi A., Kianfar A. H., Mirsadeghi A. S., Pourfarokhi A., Soylak M., The Determination of Some Heavy Metals in Food Samples by Flame Atomic Absorption Spectrometry After Their Separation-Preconcentration on Bis Salicyl Aldehyde, 1,3 Propan Diimine (BSPDI) Loaded on Activated Carbon, *J. Hazard. Mater.*, **154**: 128-134 (2008).
- [44] Starvin A. M., Prasada Rao T., Removal and Recovery of Mercury(II) from Hazardous Wastes Using 1-(2-thiazolylazo)-2-naphthol Functionalized Activated Carbon as Solid Phase Extractant, *J. Hazard. Mater.*, **113**: 75-79 (2004).
- [45] Alves J.A.C., Freire C., Castro B de., Figueiredo J.L., Anchoring of Organic Molecules Onto Activated Carbon, *Colloids Surf A.*, **189**: 75-84 (2001).
- [46] Toumi N., Bonnamour I., Joly J. P., Fingueneisel G., Retailliau L., Khalfat R., Lamartine R., Grafting of Calix[4]arene Derivative on Activated Carbon Surface, *Mater. Sci. Eng. C*, **26**: 490-494 (2006).
- [47] Zang Z., Li Z., Zhang L., Li R., Hu Z., Chang X., Cui Y., Chemically Modified Attapulgite with Asparagine for Selective Solid-Phase Extraction and Preconcentration of Fe(III) from Environmental Samples, *Anal. Chim. Acta.*, **663**: 213-217 (2010).
- [48] Lurie Ju., "Handbook of Analytical Chemistry", Bobrov N., Trans., Russian, MIR Publishers Moscow, Chap. 2. (1975).
- [49] Shokrollahi A., Ghaedi M., Shabani R., Montazerzohori M., Chehreh F., Soylak M., Alipour S., A Preconcentration Procedure for Copper, Nickel and Chromium Ions in Some Food and Environmental Samples on Modified Diaion SP-850, *Food. Chem. Toxicol.*, **48**: 482-489 (2010).
- [50] Ghaedi M., Shabani R., Shokrollahi A., Montazerzohori M., Sahraian A., Soylak M., Preconcentration and Separation of Trace Amount of Copper (II) on N<sub>1</sub>, N<sub>2</sub>-bis(4-fluorobenzylidene) ethane-1,2-diamine Loaded on Sepabeads SP70, *J. Hazard. Mater.*, **170**: 169-174 (2009).
- [51] Ghaedi M., Shabani R., Montazerzohori M., Shokrollahi A., Sahraian A., Hossainian H., Soylak M., SDS-Coated Sepabeads SP70-modified by 4-[(E)-3-phenylallylidene) Amino] Benzenethiol as New Efficient Solid Phase for Enrichment and Determination of Copper, Nickel, Chromium, and Zinc Ions in Soil, Plants, and Mint Water Samples, *Environ. Monit. Assess.*, **174**: 171-186 (2011).
- [52] Li Z., Chang X., Zou X., Zhu X., Nie R., Hu Z., Li R., Chemically-Modified Activated Carbon with Ethylenediamine for Selective Solid-Phase Extraction and Preconcentration of Metal Ions, *Anal Chim Acta.*, **632**: 272-277 (2009).
- [53] Liu Y., Yang Y., Wu F., Effects of L-arginine Immobilization on The Anticoagulant Activity and Hemolytic Property of Polyethylene Terephthalate Films, *Appl. Surf. Sci.*, **25**: 3977-3981 (2010).

- [54] Nakamoto K., "Infrared Spectra of Inorganic and Coordination Compound (in Chinese)", Huang, D., Wang R., Trans., 4th Chemical Industry Press: Beijing, 237-251(1991).
- [55] Raoufi F., Bagheri S., Niknam E., Niknam Kh., Farmani H. R., Flame Atomic Absorption Spectrometric Determination of Cd(II), Zn(II) and Ag(I) in Different Matrixes After Solid Phase Extraction on Sodium Dodecyl Sulfate(SDS)-coated Alumina as Their 2,3-dihydro-2,3 paratolylqinazoline(1H)-4-one(DPTQO), *Der Pharma Chemica.*, **7**: 173-182 (2015).
- [56] Ghaedi M., Tashkhourian, J., Montazerzohori M., Soylak M., Silver Nanoparticle Loaded on Activated Carbon and Activated Carbon Modified with 2-(4-Isopropylbenzylidene amino) Thiophenol (IPBTP) as New Sorbents for Trace Metal Ions Enrichment, *Intern. J. Environ. Anal. Chem.*, **93**: 386-400 (2013).
- [57] Ghaedi M., Niknam K., Zamani S., Abasi Larki H., Roosta M., Soylak M., Silica Chemically Bonded N-Propyl KriptoFix 21 and 22 with Immobilized Palladium Nanoparticles for Solid Phase Extraction and Preconcentration of Some Metal Ions, *Mater. Sci. Eng: C*, **33**: 3180-3189 (2013).
- [58] Ghaedi M., Montazerzohori M., Nazari E., Nejabat R., Functionalization of Multiwalled Carbon Nanotubes for The Solid-Phase Extraction of Silver, Cadmium, Palladium, Zinc, Manganese and Copper by Flame Atomic Absorption Spectrometry, *Hum Exp Toxicol.*, **32**: 687-697 (2013).