

# A modified nanoporous stir bar for simultaneous determination of Cu(II) and Cd(II) ions in natural samples prior to flame atomic absorption spectroscopy

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In this work, the application of stir bar sorptive extraction (SBSE), as a fast and conventional method, has been investigated for the simultaneous preconcentration and determination of trace amounts of Cd(II) and Cu(II) ions in natural samples. For this purpose, the surface of stir bar was functionalized by amine functionalized nanoporous silica and characterized by IR spectroscopy, X-ray powder diffraction (XRD), Atomic force microscopy (AFM) and N<sub>2</sub> adsorption. In this approach, after the preconcentration of Cd(II) and Cu(II) ions and removing the matrix interferences using modified stir bar, the amounts of these ions were determined in eluent by flame atomic absorption spectroscopy (FAAS). Various parameters on adsorption and elution steps including pH of sample, adsorption kinetic, eluent parameters (type, volume and concentration) and elution time, have been optimized in this study. The limits of detection (LOD) were 1.6 and 13.8 ng mL<sup>-1</sup> (recovery of 83.5 and 88.1%) for cadmium and copper ions, respectively. The preconcentration factors were 133 and 137 and the relative standard deviations (RSD) of the method were 5.7 and 4.6% for Cd(II) and Cu(II) ions, respectively. As the key point in this study seems to be stir bar nanoporous structure, the analytical performance of this stir bar was compared to non-porous ones. The accuracy of this novel method has been confirmed using some standard references materials. Finally the potential of this method was investigated by determination of Cd(II) and Cu(II) ions in some real samples with complicated matrixes.

**Keywords:** stir bar sorptive extraction, nanoporous structure, Cd(II) and Cu(II) determination, FAAS.

## INTRODUCTION

Copper is an essential element, found in trace levels, plays an important role in carbohydrate and lipid metabolism as well as the maintenance of heart and blood vessel activity<sup>1</sup>. Conversely, copper can be toxic to humans and animals if they are exposed to it at high concentrations. The most commonly reported adverse health effects of copper are gastrointestinal diseases and liver symptoms<sup>2</sup>.

On the other hand, cadmium is a cumulative nephrotoxicant which can be easily absorbed into the human body from various dietary sources<sup>3</sup>. The World Health Organization (WHO) set the criteria of the allowable concentration of cadmium ions as no higher than 3 µg L<sup>-1</sup> for drinking water quality. However, the presence of cadmium ions in water, air, soil, sediment and food induced a series of environmental problems and exposed human health to potential risks<sup>4</sup>. For these reasons stringent monitoring and identification of cadmium and copper in the natural samples is of great importance.

Copper and cadmium ions have been determined by graphite furnace atomic absorption spectrophotometer (GFAAS)<sup>5</sup>, differential pulse stripping voltammetry (DPSV)<sup>6</sup>, X-ray fluorescence (XRF)<sup>7</sup>, atomic emission spectrometry with inductively coupled plasma excitation (AES-ICP)<sup>8</sup>, FAAS<sup>9</sup>, and fluorescence spectrometry<sup>10</sup>. But in most cases as a result of low concentrations of these analytes in real samples, a preconcentration step is usually necessary. Therefore, different methods such as coprecipitation<sup>11</sup>, cloud point extraction<sup>12</sup>, ion exchange resins<sup>13</sup> and solid phase extraction (SPE)<sup>14, 15</sup> have been introduced.

Stir bar sorptive extraction (SBSE) is a preconcentration method which was introduced in 1999, to overcome some of existing techniques limits, particularly in the recovery of medium to high volatility analytes when

sampled in liquid phase with polydimethylsiloxane-open tubular traps (PDMS-OTT); a further aim was to improve the limited recovery in ultra-trace analysis with solid-phase microextraction (SPME), particularly under undesired phase ratios, when working with small volumes of sorptive materials (in general PDMS) coating the fused-silica fiber<sup>16</sup>.

The main advantages of SBSE are derived from the fact that these techniques are easy to apply and automate, highly flexible (the same SBSE device can be used, not only for sampling in vapor or liquid phases, but also for heterogeneous aqueous samples), robust, repeatable, reproducible and last but not least, can be applied to various samples containing analytes with significantly different chemical structures<sup>17</sup>.

To the best of our knowledge there are no reports on synthesis of nanoporous stir bar for extraction and preconcentration of elements in trace levels. In this work for the first time, an amine modified nanoporous stir bar sorptive was developed and used for extraction, preconcentration and determination of copper and cadmium ions. Different parameters affecting adsorption and desorption of copper and cadmium ions on modified SBSE, comprising the effect of solution's pH, desorption time, type, concentration and volume of eluent, were optimized. The method validation was performed by analyzing some standard reference materials. Finally the method was used for the determination of metallic content of some real sample.

## EXPERIMENTAL

### Reagents and materials

All reagents were of analytical grade and used as received. Acids and solvents were purchased from Merck

Company (Darmstadt, Germany). 1000 mg L<sup>-1</sup> standard solutions of cadmium and copper ions were purchased from Aldrich Company (Milwaukee, USA). The working solutions of ions were obtained by diluting appropriate amounts of the stock solutions with buffer solutions. All pH adjustments were performed using buffer solutions. All the required solutions were prepared using deionized water provided from a Milli-Q (Bedford, MA, USA) purification system. Stir bars coated with a 0.5 mm thick PDMS layer (24 mL), were obtained from Gerstel (Mulheim an der Ruhr, Germany). 3-Aminopropyl triethoxysilane, Cetyl trimethyl ammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) were purchased from Merck Company.

### Preparation of amine functionalized nanoporous silica stir bar (NH<sub>2</sub>-NP-SB)

For the preparation of amine functionalized nanoporous silica stir bar (NH<sub>2</sub>-NP-SB), the surface of the stir bar was activated using 20 mL mixture of H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/HCl (5:1:1, V:V) for 5 min<sup>18</sup>. Coating the surface of stir bar with amine functionalized nanoporous silica was performed according to a previous report which was used for silica coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>19</sup>. Briefly, the activated stir bar was placed in a 50 mL solution of distilled water and ethanol (1:1, v:v) containing 2 mL concentrated ammonia (32%) and 0.6 g of CTAB. Afterwards, 6.4 g of TEOS and 1.6 g of 3-Aminopropyl triethoxysilane were added dropwise. After 6 h the stir bar was separated and washed by ethanol and the surfactant was removed by refluxing with Acetone. A schematic diagram for this modification is shown in Figure 1.

### Instrumentation

Determination of Cd(II) and Cu(II) ions concentrations were performed with AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer in an air-acetylene flame. Cadmium and copper hollow cathode lamps were used as the radiation sources with wavelengths of 228.8 and 324.8 nm, respectively. All the analyses were performed under the conditions suggested by the manufacturer. All the pH measurements were carried out at 25 ± 1°C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. The surface analysis was performed on a DME (DS-95-200E) instrument. X-ray diffraction patterns were obtained on a STOE diffractometer with Cu K<sub>α</sub> radiation. The specific surface area was measured by nitrogen adsorption technique using a Micromeritics ASPS 2010 analyzer. IR spectra were recorded on a Bruker IFS-66 FT-IR Spectrophotometer.

### Precondition process

The stir bar was preconditioned by stirring in 5 mL HCl 3 mol L<sup>-1</sup> for 5 min, in 5 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub> for 5 min and in 5 mL Acetone for 5 min. This precondition process was carried out the day before the use of the stir bar.

### Preconcentration procedure

The pH of 25 mL of standard solution containing 100 µg L<sup>-1</sup> cadmium and copper ions was adjusted to the pH of 6.0 manipulating Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffer solution. The solution was placed in 100 mL glass vial containing the modified stir bar. After stirring at 300 rpm for 12 min, the stir bar was removed from the solution sample using a strong magnet, dried with a filter paper and again placed into a small glass tube containing 3 mL of 1 mol L<sup>-1</sup> HClO<sub>4</sub> and stirred at 300 rpm for 5 min. Afterwards, the analytes in the eluent were determined by FAAS.

### Real sample preparation

The water samples were analyzed without any pre-treatment. The solid samples were digested with 6 mL of HCl (37%) and 2 mL of HNO<sub>3</sub> (65%) in a microwave digestion system. Digestions were carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then vented for 8 min. Afterwards, the residues of digestion were diluted with deionized water<sup>20</sup>.

Three certified reference materials comprising SRM 1643e (Trace Elements in Water), SRM 2710 (Montana Soil) and SRM 1573a (Tomato Leaves), were used for method validation, digested in the same way of the above procedure.

## RESULTS AND DISCUSSION

### Characterization of surface modified stir bar

The grafting of amine functionalized nanoporous silica on the surface of stir bar was performed in the same way as it was previously reported for Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>18</sup>. In this report, the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticle was coated by silica containing activated silanol group (Si-OH), then the mesoporous silica was grafted on it. By activating the surface of the stir bar, the silanol groups were formed on the surface, and then according to the reported procedure, the nanoporous silica was grafted. The formation of the modified stir bar was assessed by IR spectroscopy, XRD, AFM and N<sub>2</sub> adsorption. The IR spectra of the smashed stir bar before and after the

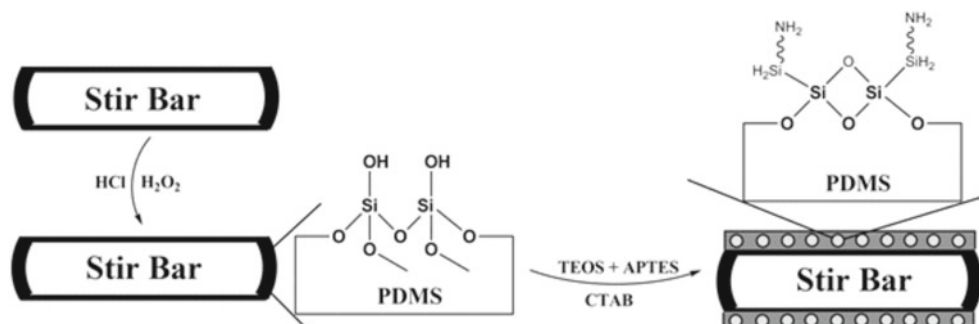
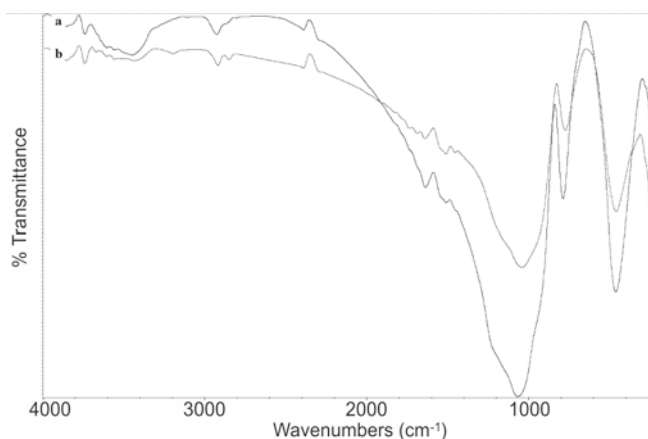
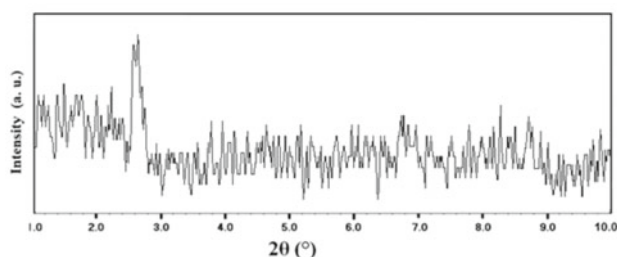


Figure 1. A schematic model for modification of nanoporous silica stir bar



**Figure 2.** The IR spectra of the smashed stir bar a) before, b) after modification

modification are shown in Figure 2. As it can be seen in this figure, the differences between these spectra in 1600–1800  $\text{cm}^{-1}$  could be attributed to the formation of nanoporous silica and its amine groups. Also a broad peak at 3200  $\text{cm}^{-1}$  which is presented only in the modified SBSE, is corresponded to amine group. For further investigations, the stir bar was smashed and its XRD pattern was recorded. As it can be seen in Figure 3, the presence of a peak at  $2\theta = 2.5$  is a good evidence for the formation of nanoporous silica on the surface of this stir bar. Also comparing the  $\text{N}_2$  adsorption results for smashed stir bar, (8 and 53  $\text{m}^2 \text{g}^{-1}$  for before and after modification) is another evidence for the formation of nanoporous silica on the surface of this stir bar. By formation of the nanoporous silica on the surface of stir bar, the active sites will be increased (according to  $\text{N}_2$  adsorption analysis). Also the surface of the stir bar has been investigated by AFM micrograph. As it can be seen in Figure 4 the smooth surface of stir bar has been coated by a porous material. Finally, the amount of amine group on the surface of SBSE was calculated using elemental analysis. According to this analysis, approximately 0.31 mmol amine group is grafted on the surface of SBSE.



**Figure 3.** XRD pattern of nanoporous silica stir bar

### Optimization experiments

The presented method is divided into two steps of extraction and desorption, which have lots of parameters to be optimized before applying the method for determination of cadmium and copper ions.

#### The pH effect

Since pH is one of the most critical parameters for adsorption of ions on the functionalized stir bar, the pH value was selected as the first parameter for optimization. For this reason, the pH of 50 mL standard sample solution containing 100  $\mu\text{g L}^{-1}$  of Cd(II) and Cu(II) ions, was adjusted in the range of 1–8 using

NaOH and HCl solutions. After stirring at 300 rpm for 12 min, the stir bar was removed from the solution sample by a strong magnet, dried with a filter paper and again placed in a small glass tube containing 3 mL of 1 mol  $\text{L}^{-1}$   $\text{HClO}_4$  and stirred at 300 rpm for 5 min. Afterwards, the analytes in the eluent were determined by FAAS. The results show that quantitative recovery for extraction Cd(II) and Cu(II) ions by this modified stir bar was obtained in the pH of 6.0 for both Cd(II) and Cu(II) ions (Fig. 5). At the acidic pHs the recovery was decreased as the amine group is protonated and could not coordinate to the metal ions. Decreasing at alkaline pHs could be attributed to the formation of  $\text{Cd}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$ . So in all further experiments, the pH of the samples was adjusted to pH = 6.0 using  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer solution.

#### Investigation of adsorption kinetic

The pH of 25 mL of the standard solution containing 100  $\mu\text{g L}^{-1}$  cadmium and copper ions was adjusted to the pH of 6.0 by  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer solution. The solution was placed in a 100 mL glass vial containing modified stir bar. After stirring at 300 rpm for the desired time, the stir bar was removed from the solution sample, dried with a filter paper and again placed in a small glass tube containing 3 mL of 1 mol  $\text{L}^{-1}$   $\text{HClO}_4$  and stirred at 300 rpm for 5 min. Afterwards, the analyte in the eluent were determined by FAAS. The results show that the minimum time required for quantitative adsorption is 12 min (Fig. 6).

#### Optimization of the eluent parameters

In order to desorb Cd(II) and Cu(II) ions from the modified stir bar, a series of selected eluent solutions such as HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$  at different concentrations were used. It was found that 1 mol  $\text{L}^{-1}$   $\text{HClO}_4$  solution was the best eluent for desorption of cadmium and copper ions from the stir bar (Table 1). The effect of eluent volume on the recovery of these ions was also studied. As it can be seen in Table 1, the quantitative recovery can be obtained with 3 mL of 1 mol  $\text{L}^{-1}$   $\text{HClO}_4$  solution.

#### Optimization of desorption time

The pH of 25 mL of the standard solution containing 100  $\mu\text{g L}^{-1}$  cadmium and copper ions was adjusted to the pH of 6.0 by  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer solution.

**Table 1.** Effect of eluent type and concentration in recovery of Cu(II) and Cd(II) from modified nanoporous stir bar sorptive

Eluent type [mol $\text{L}^{-1}$ ]	Recovery [%]	
	Cd(II)	Cu(II)
HCl (0.1)	65.3	62.3
HCl (0.5)	71.2	70.3
HCl (1)	79.6	77.5
$\text{HNO}_3$ (0.1)	64.3	59.9
$\text{HNO}_3$ (0.5)	70.6	70.6
$\text{HNO}_3$ (1)	78.5	77.5
$\text{H}_2\text{SO}_4$ (0.1)	49.5	50.3
$\text{H}_2\text{SO}_4$ (0.5)	58.6	54.6
$\text{H}_2\text{SO}_4$ (1)	65.4	63.5
$\text{HClO}_4$ (0.1)	65.6	67.5
$\text{HClO}_4$ (0.5)	79.5	78.1
$\text{HClO}_4$ (1)	84.8	85.3



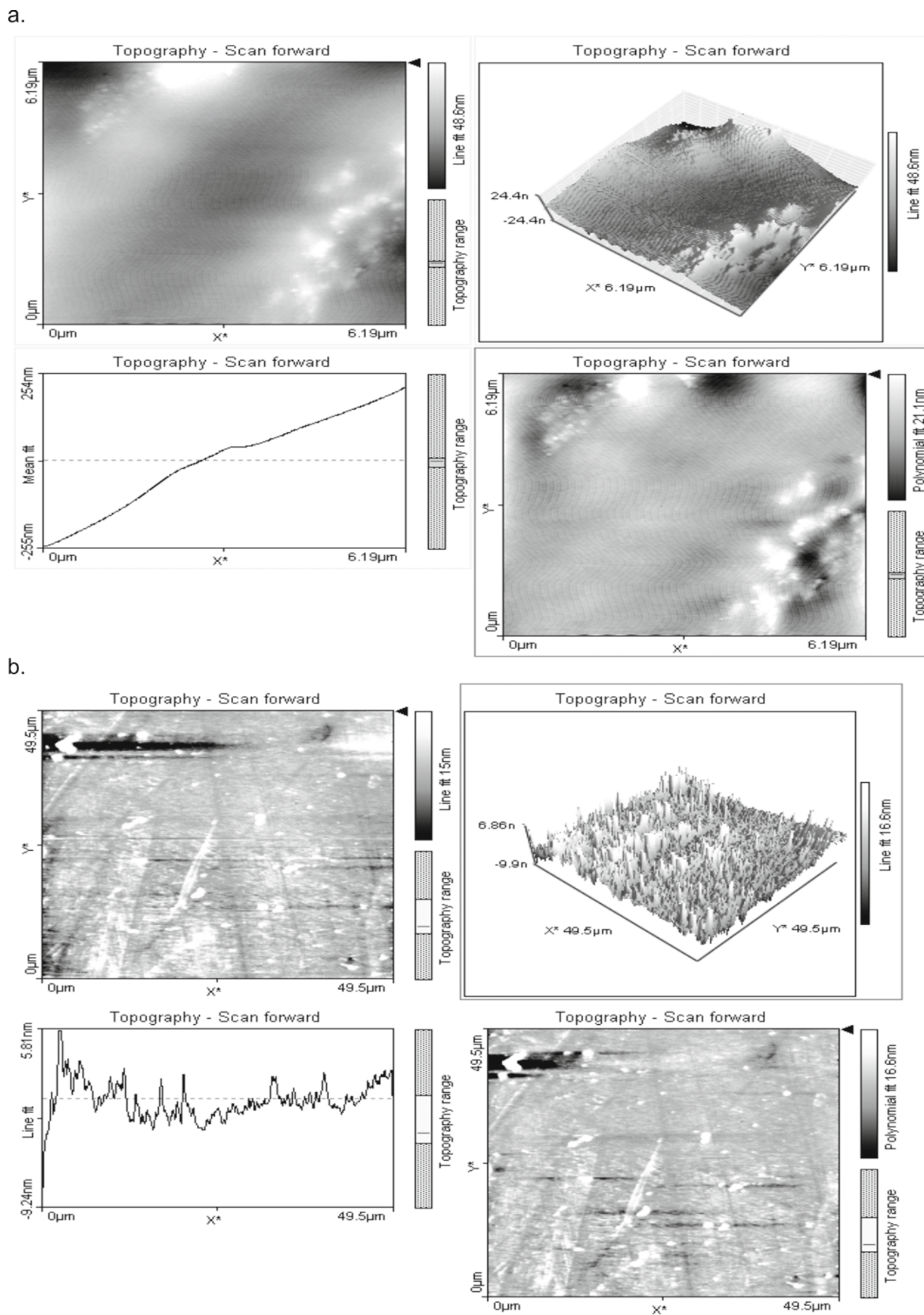
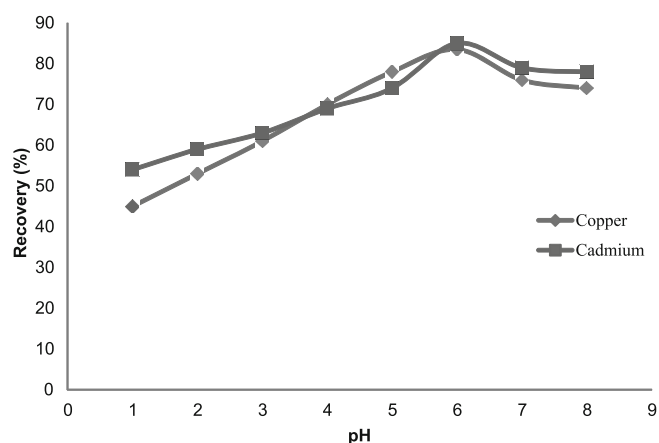
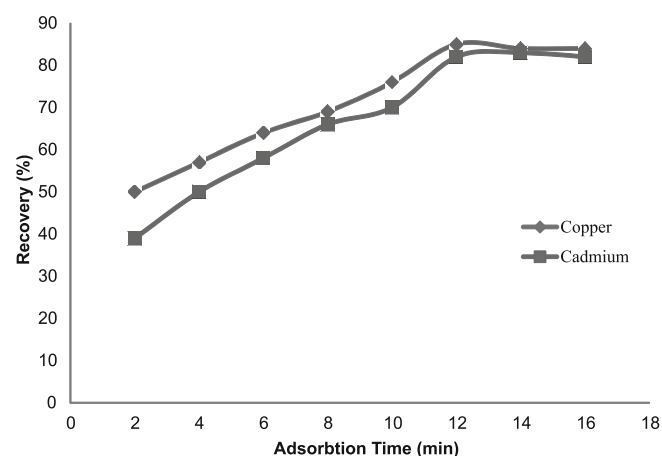


Figure 4. AFM micrograph of a) non-porous, b) nanoporous silica stir bar



**Figure 5.** Effect of pH on recovery of Cu(II) and Cd(II) ions on modified nanoporous silica stir bar



**Figure 6.** Investigation of adsorption kinetic of Cu(II) and Cd(II) ions on modified nanoporous silica stir bar

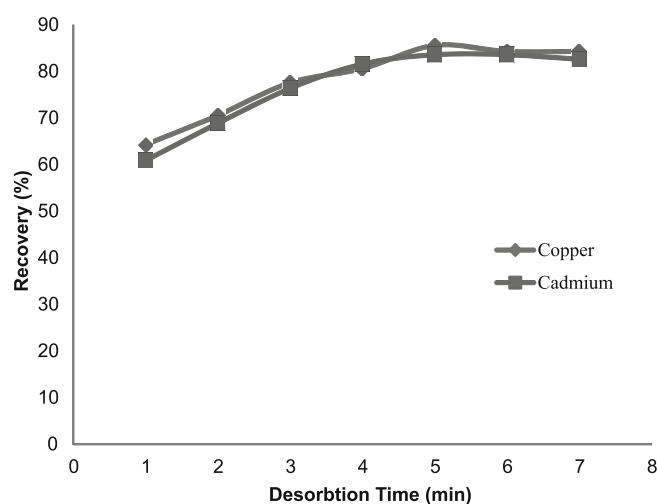
The solution was placed in 100 mL glass vial containing modified stir bar. After stirring at 300 rpm for 12 min, the stir bar was removed from the solution sample by a strong magnet, dried with a filter paper and again placed into a small glass tube containing 3 mL of 1 mol L<sup>-1</sup> HClO<sub>4</sub> and stirred at 300 rpm for various intervals of time. After collecting the results by FAAS, it was found out that the minimum time required for quantitative desorption was 5 min (Fig. 7).

#### Influence of interference ions

In order to investigate the effect of various cations found in natural samples, elements representing alkaline, alkaline earth, and transition metals such as Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> were added to 100 mL of solution containing 10 μg L<sup>-1</sup> cadmium and copper ions in pH = 6.0. The results show that most of the cations at pH of 6.0, do not interfere in Cd(II) and Cu(II) ions determination and the method is selective toward these ions determination (Table 2).

**Table 3.** A comparison between this work and similar works

Sorbent	Method	Cu-LOD [ng mL <sup>-1</sup> ]	Cd-LOD [ng mL <sup>-1</sup> ]	Ref.
Ammonium pyrrolidine dithiocarbamate-MWCNT	SPE	0.30	0.45	22
Cresolphthalein-MWCNT	SPE	1.64	–	23
Pseudomonas aeruginosa-MWCNT	SPE	–	0.24	24
1 nitroso-2-naphthol-Diaion resin	SPE	0.29	0.18	25
–	Membrane filtration	0.40	0.32	26
This work	SBSE	13.8	1.6	–



**Figure 7.** Effect of desorption time on recovery of Cu(II) and Cd(II) ions on modified nanoporous silica stir bar

**Table 2.** The tolerance limit of diverse ions in the determination of Cu(II) and Cd(II)

Interfering ions	Tolerable Concentration Ratio X/Cd and Cu	Recovery % For Cd(II)	Recovery % For Cu(II)
Na <sup>+</sup>	2000	84.6	85.1
K <sup>+</sup>	2000	84.3	84.6
Cs <sup>+</sup>	2000	82.1	83.6
Ca <sup>2+</sup>	2000	80.1	82.8
Mg <sup>2+</sup>	1500	82.4	83.4
Zn <sup>2+</sup>	500	79.5	80.5
Hg <sup>2+</sup>	250	73.4	76.4
Fe <sup>2+</sup>	250	79.9	81.9
Mn <sup>2+</sup>	250	80.7	82.7

#### Analytical features

In order to determine the limit of detection (LOD) of this method, the modified stir bar was placed in a 500 mL blank solution (n = 10) under optimal experimental conditions. The values of LOD for Cd(II) and Cu(II) ions are 1.6 and 13.8 μg L<sup>-1</sup>, respectively. The results were obtained from the relationship expressing  $C_{LOD} = K_b S_b / m$  where  $k_b = 3^{20}$ . The LOD values of this method were compared with other methods (Table 3). Although the LODs do not show a high improvement, this method is faster and more conventional.

The precision of the method under the optimal conditions was determined by performing ten replicates of preconcentration of 100 mL solution of Cd(II) and Cu(II) ions with the concentration of 100 μg L<sup>-1</sup>. The Cd(II) and Cu(II) ions recoveries were found to be 83.5% ± 5.7 and 88.1% ± 4.6, respectively.

In order to investigate the enrichment factor, different volumes of solutions all containing 1 μg L<sup>-1</sup> cadmium and copper ions in pH = 6.0 were placed in 1000 mL glass vial containing modified stir bar. After stirring at 300 rpm for 12 min, the ions were eluted with 3 mL of 1 mol L<sup>-1</sup> HClO<sub>4</sub> and the amounts of Cd(II) and Cu(II) ions in eluent were determined by FAAS. As these ions

could be recovered from 500 mL solution with 80.3 and 82.4% efficiency, the enrichment factors are 133 and 137 for Cd(II) and Cu(II) ions, respectively.<sup>21</sup>

### Sorbent Reuse

The long-term stability of the modified stir bar sorbent was investigated by successive sorption and elution cycles of 25 mL of standard solution containing 100  $\mu\text{g L}^{-1}$  cadmium and copper ions. By monitoring the change in the recoveries of the extraction, the stability of the sorbent was estimated. The results show that after seven adsorption-desorption cycles the recovery decreases.

### Effects of nanoporous structure of stir bar on its analytical efficiency

In order to investigate the effects of the nanoporous structure of the stir bar on its analytical efficiency, the non-porous stir bar was also synthesized according to the previous report<sup>18</sup>. The figures of merit of these two stir bars such as recovery, enrichment factor and detection limit, were obtained and compared. As the results in Table 4 show, by coating the nanoporous silica on the surface of stir bar, its efficiency increased and the key point in this method is the stir bar nanopore structure.

### Validation of the method

The accuracy of the presented method was investigated by determining the Cd(II) and Cu(II) ions content of certified reference materials. The samples were prepa-

red by the mentioned procedure and after applying the presented method. The certified values and the analytical results are shown in Table 5. As can be observed in this table, there is a good agreement between the certified amounts and obtained ones, which shows that the interfering ions had no effect on the recovery of Cd(II) and Cu(II) ions by this method.

### Analysis of real samples

The mentioned method was applied to determine cadmium and copper ions amounts in water, soil and rice samples of different places in the North of Iran (Mazandaran and Guilan). The samples were digested and the amounts of copper and cadmium ions were determined using the presented method. The results of this study are presented in Tables 6 and 7.

### CONCLUSIONS

In this study, a novel modified stir bar was synthesized by coating a nanoporous amine functionalized silica. This stir bar was characterized by IR spectroscopy, X-ray powder diffraction, AFM and  $\text{N}_2$  adsorption. The application of this stir bar was investigated for determination of trace amounts of Cd(II) and Cu(II) ions in aqueous samples. The selectivity of this stir bar toward Cd(II) and Cu(II) ions allows the method to determine Cd(II) and Cu(II) ions in different matrixes including various interfering ions. Also the comparison between the results

**Table 4.** The effect of nanoporous structure on the performance of modified Stir bar sorptive

Stri Bar	Analyte type	Recovery [%]	enrichment factor	detection limit [ $\mu\text{g L}^{-1}$ ]
nanoporous structure	Cu (II)	88.1	137	13.8
	Cd (II)	83.5	133	1.6
non-porous structure	Cu (II)	82.8	38	69.9
	Cd (II)	80.3	33	29.2

**Table 5.** Results for the determination of Cu(II) and Cd(II) in certified reference materials

Sample	Unit	Analyte	Concentration		Recovery [%]	RSD [%]
			Certified	Found (n = 5)		
SRM 1643e (Trace Elements in Water)	$\mu\text{g kg}^{-1}$	Cu(II)	22.20 $\pm$ 0.31	18.7	84.2	4.9
	$\mu\text{g kg}^{-1}$	Cd(II)	6.408 $\pm$ 0.071	5.2	81.1	5.6
SRM 2710 (Montana Soil)	$\text{mg kg}^{-1}$	Cu(II)	2950 $\pm$ 130	2401.3	81.4	5.1
	$\text{mg kg}^{-1}$	Cd(II)	21.8 $\pm$ 0.2	18.5	84.9	5.5
SRM 1573a (Tomato Leaves)	$\text{mg kg}^{-1}$	Cu(II)	4.70	3.9	82.3	4.6
	$\text{mg kg}^{-1}$	Cd(II)	1.52	1.2	85.5	5.3

**Table 6.** Data recoveries for determination of copper in real sample by modified nanoporous stir bar sorptive

Location	Sample	$C_{\text{added}}$ [ $\mu\text{g kg}^{-1}$ ]	$C_{\text{found}}$ Mean ( $\bar{X}$ ) [ $\mu\text{g kg}^{-1}$ , n = 5]	Recovery [%]	RSD [%] [n=5]
Mazandaran	water	0.0	0.1	–	8.5
		5.0	4.4	86.2	7.4
		10.0	9.2	91.0	6.9
	soil	0.0	47.4	–	5.4
		10.0	56.3	89.0	4.6
		20.0	64.9	87.5	4.4
	rice	0.0	3.7	–	5.5
		5.0	8.3	91.9	5.1
		10.0	12.3	86.1	4.3
Guilan	water	0.0	0.4	–	7.4
		5.0	4.8	88.0	6.6
		10.0	9.5	91.1	5.9
	soil	0.0	69.4	–	4.3
		10.0	77.9	84.9	3.4
		20.0	87.0	88.1	3.7
	rice	0.0	7.9	–	5.4
		5.0	12.2	86.0	4.8
		10.0	16.8	89.0	4.4



**Table 7.** Data recoveries for determination of Cadmium in real sample by modified nanoporous stir bar sorptive

Location	Sample	C <sub>added</sub> [ $\mu\text{g kg}^{-1}$ ]	C <sub>found</sub> Mean ( $\bar{X}$ ) [ $\mu\text{g kg}^{-1}$ , n = 5]	Recovery [%]	RSD [%] [n=5]
Mazandaran	water	0.0	ND	–	8.3
		5.0	4.4	88.0	7.7
		10.0	8.9	89.0	6.3
	soil	0.0	0.9	–	7.4
		10.0	9.3	83.9	6.9
		20.0	18.4	87.5	6.3
	rice	0.0	0.2	–	7.1
		5.0	4.3	82.1	6.6
		10.0	8.6	84.0	6.3
Guilan	water	0.0	ND	–	7.2
		5.0	4.3	86.0	6.6
		10.0	8.4	84.0	6.2
	soil	0.0	1.4	–	6.9
		10.0	9.8	84.1	6.4
		20.0	19.5	90.5	6.2
	rice	0.0	0.4	–	7.0
		5.0	4.8	88.0	6.3
		10.0	9.3	88.9	6.1

of this stir bar and non-porous ones shows that the nanoporous structure increases its analytical efficiency. The results also demonstrate that this method is an accurate, selective and reliable for simultaneous determination of Cd(II) and Cu(II) ions in various samples.

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