Column Solid Phase Extraction of Ni(II) and Cu(II) Using Salicylaldehyde-Modified Polyamine Polyurea Resin for Their Determination by FAAS in Waters

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INTRODUCTION

There is a strong relationship, which may be direct or indirect, between human health and water pollution. People might use contaminated water directly or any nutrient-treated contaminated water indirectly and thus, water purification is a global concern. A significant portion of water pollution is from heavy metals which can enter the water through a variety of ways (1). Heavy metals are toxic at high concentrations and accumulate and are harmful to aquatic species directly and human beings indirectly (2).

Several techniques have been used for the determination of metal levels, such as capillary electrophoresis (CE) (3), electrothermal atomic absorption spectrometry (ETAAS) (4), microwave plasma-atomic emission spectrometry (MP-AES) (5), anodic and cathodic stripping voltammetry (ASV-CSV) (6), inductively coupled plasma mass spectrometry and inductively coupled plasma-optical emission spectroscopy (ICP-MS and ICP-OES) (7, 8), and flame atomic absorption spectrometry (FAAS) (9-11). Each technique has its advantages and disadvantages. For example, ICP-MS, ICP-OES, and ETAAS have higher accuracy but are more expensive compared to the other techniques. Although ETAAS is less expensive than ICP-MS, it is more affected from com-

ABSTRACT

A novel column solid phase extraction-preconcentration procedure was developed by using a salicylaldehyde modified polyamine polyurea resin as solid phase adsorbent for the determination of Ni(II) and Cu(II) ions at trace level in waters by flame atomic absorption spectrometry. The preconcentration process was optimized by investigating various analytical parameters such as pH of the sample solution, eluent flow rate and concentration, volume and flow rate of the sample solution, and matrix ion content of the sample solution. The Ni(II) and Cu(II) ions were quantitatively recovered from the sample solution at pH 8.0 using 5 mL of 1.0 M HNO₃ as an eluent. The limit of detection of Ni and Cu based on three times the standard deviation of the blanks was calculated to be 0.11 and 0.03 µg L⁻¹, respectively, using a preconcentration factor of 100. The accuracy and precision of the method was validated by using a trace element fortified standard reference water sample (TMDA-54.4). The optimized solid phase extraction method was successfully employed for the determination of Ni(II) and Cu(II) in environmental water samples.

plex matrices compared to FAAS (12, 13). FAAS is preferred because of its low cost, ease-of-use, has a wide operating range and speed (14). As with other determination techniques, FAAS also has difficulties measuring low analyte concentrations and causes matrix effects.

To eliminate these difficulties, separation and preconcentration methods, including solvent extraction (ASE) (15), liquid-liquid extraction (LLE) (16), supercritical fluid extraction (SFE) (17), pressurized liquid extraction (PLE) (18), cloud point extraction (CPE) (19), and solid phase extraction (SPE) (20-23) have been widely investigated in recent years (24-26). Among these methods, solid phase extraction (SPE) is commonly performed due to its selective properties such as uncomplicated nature, low cost, high recovery, selectivity, and enrichment factor (3, 27-30). The success of SPE is closely associated with the nature of the solid phase used as the sorbent (31). Activated carbon (32), bio-sorbents (33), modified silica gel (9), nano-structured and magnetic materials (34), molecular recognition sorbents (35), and chelating resins (36,37) have been used as solid phases for the extraction of heavy metals in many studies. Because they have the characteristics of a good sorbent, such as chemical stability, large surface area, and high selectivity and high enrichment factor, chelating resins have been used as solid phases in various SPE processes (38).

In this study, the solid phase extraction of Ni(II) and Cu(II) ions are investigated by using a salicylaldehyde-modified polyamine polyurea resin as sorbent and FAAS as the measurement technique. This paper describes the preparation of the salicylaldehyde-modified polyamine polyurea resin, optimization of the SPE process, accuracy and limit of detection (LOD) data, adsorption capacity of the resin,

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verification of the developed method, and applications to natural water samples.

EXPERIMENTAL

Instrumentation and Chemicals

A Shimadzu AA-7000 flame atomic absorption spectrophotometer (Shimadzu Corporation, Kyoto, Japan) was used for the determination of the Ni(II) and Cu(II) ions. The pH values of the solutions were examined with a Schott CG 840 digital pH meter. An Ismatec peristaltic pump (Cole-Parmer GmbH, Wertheim, Germany) was used to regulate the flow of the sample solution and eluent from the column through the separation and enrichment system. The C, H, N elemental analyses of the modified polymer was determined using a Thermo Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

All chemicals used were of analytical reagent grade. Distilled and deionized water (chemical resistivity of 18 M Ω -cm) from a Millipore[®] Milli-Q[™] water system (Millipore Corporation, USA) was used for all experiments. The stock standard solutions of Ni(II) and Cu(II) (1000 mg L⁻¹) were procured from Merck KGaA (Darmstadt, Germany). The metal solutions in different concentrations were prepared daily by serial dilution of the stock solutions.

For synthesis of the polymer resin, salicylaldehyde, toluendiisocyanate (TDI), dimethylformamide (DMF), ethanol, and diethylether were purchased from Merck KGaA (Darmstadt, Germany).

Preparation of Salicylaldehyde-Modified Polyamine Polyurea Resin

The synthesis of polyamine polyurea polymer (PPP) is described in a previous study (39). The following procedure was applied to modify PPP with salicyl-

aldehyde. The salicylaldehyde (10 mmol) and PPP (1 g) were suspended in 30 mL of ethanol and stirred for 4 hours at 50 °C. The obtained product (salicylaldehyde-modified polyamine polyurea resin) (SMPPR) was washed with distilled deionized water to remove the unreacted components, followed by washing with ethanol and ether, respectively, to remove the water. Lastly, the resin was dried at 40 °C for 24 hours and used in these studies.

Column SPE Procedure

A 10 mm x150 mm column having a Teflon[®] stopcock was loaded with 1.0 g of SMPPR. The column was first washed with 1.0 M HNO₃, followed by 100 mL of distilled water and then conditioned with 10 mL of 0.1 M ammonium acetate buffer solution at pH of 8.0 and using a 2-mL min⁻¹ flow rate. Then the sample solution (25 mL) containing the Ni(II) and Cu(II) ions (0.16 mg L⁻¹) was adjusted to pH 8.0 and passed through the column with a peristaltic pump at a flow rate of 1.0 mL min⁻¹. The Ni(II) and Cu(II) ions adsorbed on the column were eluted into a 5-mL volumetric flask with 1.0 M of HNO₃. The metal ion concentration in the eluates was determined by FAAS. The experiments were performed in triplicate, and their averages and standard deviations were summarized. After the experiment, the column was re-used for further experiments. A new column was prepared after it was used 50 times.

The recoveries were calculated using Equation 1:

Eq. 1

$$\text{Recovery, \%} = \frac{C_e}{C_s \times P_f} \times 100$$

where C_s and C_e are the analyte concentration in the sample solutions and eluates, and P_f is the preconcentration factor obtained from the ratio of the sample volume to eluate volume (40).

Sample Preparation

The preconcentration method was used for the determination of the Ni(II) and Cu(II) levels in environmental water samples which includes river, lake, and synthetic seawater. River water was collected from the Sakarya River and lake water was taken from Sapanca Lake, Sakarya, Turkey. The water samples were subjected to pretreatment by acidifying (1% v/v) and filtering (0.45- μ m membrane). For applying the SPE procedure, the pH of the sample (150 mL) was adjusted to 8.0 and then passed through the column under optimum conditions.

Synthetic seawater was prepared to determine the efficacy of the developed SPE procedure for Ni(II) and Cu(II) ions from seawater samples. Twenty-five mL of synthetic seawater was prepared, containing 380 mg L⁻¹ K⁺, 400 mg L⁻¹ Ca²⁺, 1,350 mg L⁻¹ Mg²⁺, 10,500 mg L⁻¹ Na⁺ ions (41), and the pH was adjusted to 8.0. The seawater was passed through the column, and the adsorbed metal ions were eluted in to a 5-mL volumetric flask with 1.0 M of HNO₃ using a sample flow rate of 1.0 mL min⁻¹.

The preconcentration procedure was validated by the analysis of a fortified water certified reference material (Ontario Lake water NWT-MDA-54.4) obtained from LGC, UK. The pH of an aliquot (10 mL) of the certified water sample was adjusted to 8.0 using an ammonia-ammonium acetate buffer solution and the proposed preconcentration procedure was applied for the determination of Ni(II) and Cu(II) levels.

RESULTS AND DISCUSSION

Characterization of Salicylaldehyde-Modified Polyamine Polyurea Resin

Modification of the polyamine polymer with salicylaldehyde can

be visually recognized by the appearance of a yellowish color formed by a Schiff base. In this study, white color of the PPP was converted to an egg yolk color by modification.

According to elemental analysis results, the C, H, and N content of polyamine polymer given in a previous study was 53.25, 7.58, and 21.10%, respectively (39). In this study, it was determined that salicylaldehyde-modified polyamine polyurea resin has C: 53.63%, H: 6.06%, and N:16.42% using Thermo Flash 2000 Elemental Analyzer. The percent decrease of nitrogen of the modified polyamine polymer shows that the modification was done successfully because salicylaldehyde does not contain N atoms.

The FTIR spectrum of the polyamine polymer was given in our previous study (39). The FTIR spectrum of salicylaldehyde-modified polyamine polymer showed an OH stretching at 3371 cm^{-1} , NH stretching of the secondary amine groups at 3273 cm^{-1} , aliphatic C-H stretching at 2930-2848 cm^{-1} , stretching of the C=O functional groups at 1645

cm^{-1} , stretching vibrations belong to the Schiff bases at 1612 cm^{-1} , aromatic C=C stretching at 1539 cm^{-1} , and C-C stretching of aliphatic chains at 1497-1414 cm^{-1} .

Effect of pH

The pH of the solution is the main factor for the interaction between the active sites of the resin and the metal ions (18, 42). Therefore, the dependence of the recoveries of Ni(II) and Cu(II) ions on the solution pH was studied. For this purpose, sample solutions in the pH range of 2-9 were passed through the column at a flow rate of 1.0 mL min^{-1} and then eluted with 1.0 M HNO_3 at the same flow rate. As can be seen from Figure 1, the recovery percentage of both metal ions increased rapidly up to pH 6.0. Quantitative recoveries were obtained from the pH of 6.0 to 9.0. In all subsequent experiments, the pH value of 8.0 was used as the optimal value.

Effect of Eluent

The elution of the Ni(II) and Cu(II) ions from the column filled with SMPPR as a solid phase was

investigated by examining different concentrations (0.1, 0.5, 1.0 M) and flow rates (1.0, 2.5, 5.0 mL/min) of the nitric acid solution; the obtained results are listed in Table I. The Ni(II) and Cu(II) ions were quantitatively eluted with 1.0 M of HNO_3 solution at a flow rate of 1.0 mL min^{-1} . For subsequent studies, nitric acid concentration and flow rate were used as 1.0 M and 1.0 mL min^{-1} , respectively.

Effect of Sample Flow Rate

Determination of the proper sample flow rate is an important factor for the effective recovery of heavy metal ions in solid phase extraction procedures (33, 43). For the purpose of defining the required contact time for quantitative recovery of the Ni(II) and Cu(II) ions with the SMPPR, sample solutions were passed through the column at three different flow rates (1.0, 2.5, and 5.0 mL/min), while other factors were held constant (pH: 8.0, eluent flow rate: 1.0 mL min^{-1} , HNO_3 concentration: 1.0 M, sample volume: 25 mL, eluent volume: 5 mL). The results are shown in Figure 2. Quantitative recoveries were obtained at the sample flow rate of 1.0 mL min^{-1} . When the sample flow rate was increased from 2.5 to 5.0 mL min^{-1} , a significant reduction in the recovery of both metal ions was observed. Hence, the optimal sample flow rate was selected as 1.0 mL min^{-1} .

Fig. 1. Effect of pH on the recoveries of Ni(II) and Cu(II) ions on SMPPR loaded column.

TABLE I
Effect of Eluent Concentration and Flow Rate
(n=3, $\pm$ standard deviation)

Eluent Conc. (M)	Eluent Flow Rate (mL min^{-1})	Recovery (%)	
		Ni(II)	Cu(II)
0.1 M	1.0	75 $\pm$ 1	81 $\pm$ 5
0.5 M	1.0	100 $\pm$ 1	90 $\pm$ 1
1.0 M	1.0	101 $\pm$ 4	100 $\pm$ 3
1.0 M	2.5	98 $\pm$ 1	93 $\pm$ 1
1.0 M	5.0	98 $\pm$ 1	95 $\pm$ 5

Effect of Solution Volume

The sample volume is an important parameter for the SPE process because the enrichment factor and the maximum applicable volume for real samples are determined based on this parameter. Therefore, samples of varying volumes that ranged from 25 to 500 mL were passed through the column under optimal conditions, and the results clearly indicate that the percent recoveries decreased slightly with increasing sample volumes (Figure 3). Nevertheless, the recovery of the Ni(II) and Cu(II) ions was quantitative for samples at at 500-mL volume. So, the maximum pre-concentration factor (PF) could be

obtained as 100 by using 500 mL of sample volume and 5 mL of the eluent volume. In the application of the developed SPE method to real environmental water samples, the PF of 100 may not be achieved when a 0.5 L sample is not available.

Effects of Matrix Ions

The effect of the concentrations of some possible matrix ions in environmental samples on the recovery of the Ni(II) and Cu(II) ions was investigated by spiking sample solutions with Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- ions at various concentrations. The results listed in Table II show that there are no substantial effects of matrix ions at the

concentrations tested. The recoveries with SMPPR and the determination with FAAS on Ni(II) and Cu(II) ions were unaffected. Hence, the proposed SPE method can be used reliably for enrichment of the Ni(II) and Cu(II) ions in highly saline water samples.

Analytical Figures of Merit

The optimum conditions for the suggested solid phase extraction method are listed in Table III. To test the precision of the suggested method, the solution containing $20 \mu\text{g L}^{-1}$ of Ni(II) and $20 \mu\text{g L}^{-1}$ of Cu(II) ions was prepared in deionized water and then was passed through the column under

TABLE II
Effect of Matrix Ions on the Recovery of Ni(II) and Cu(II) Ions ($n=3$, $\pm$ standard deviation)

Matrix Ion	Added as	Conc (mg L ⁻¹)	Recovery (%)	
			Ni(II)	Cu(II)
Na^+	NaCl	1,000	101 $\pm$ 2	103 $\pm$ 3
K^+	KNO_3	1,000	100 $\pm$ 1	104 $\pm$ 2
Ca^{2+}	CaCl_2	1,000	100 $\pm$ 1	101 $\pm$ 1
Mg^{2+}	MgCl_2	1,000	103 $\pm$ 3	101 $\pm$ 1
Cl^-	NaCl	20,000	100 $\pm$ 3	102 $\pm$ 3

TABLE III
Optimum SPE Conditions of Cu(II) and Ni(II)

Parameters	Optimum Conditions
pH of sample solution	8.0
Flow rate of sample solutions	1 mL min ⁻¹
Eluent	1.0 M HNO_3
Flow rate of eluent solutions	1 mL min ⁻¹
Volume of eluent	5 mL
Maximum practicable volume of sample solution	500 mL

Fig. 2. Effect of sample flow rate on the recoveries of Ni(II) and Cu(II) ions on SMPPR loaded column.

Fig. 3. Effect of sample solution volume on the recoveries of Ni(II) and Cu(II) ions.

the optimum conditions. The recovery values ($n=3$) were $103\% \pm 2$ and $98\% \pm 2$ for the Ni(II) and Cu(II) ions, respectively.

The repeated measurements ($n=10$) of the blank solutions were performed in order to calculate the limit of detection (LOD) of FAAS for Ni and Cu using $3 \times \text{SD}/\text{slope}$ of the calibration equation. The LOD of Ni and Cu was found to be 11 and $3 \mu\text{g L}^{-1}$, respectively. The LOD of the proposed SPE method for Ni and Cu was calculated to be 0.11 and $0.03 \mu\text{g L}^{-1}$, respectively, using the preconcentration factor of 100. The DLs of Cu(II) and Ni(II) with different preconcentration factors depending on the sample volume are listed in Table IV.

Adsorption Capacity of SMPPR for Ni(II) and Cu(II) Ions

Batch experiments were used to determine the adsorption capacity

of SMPPR for the Ni(II) and Cu(II) ions. A 50-mg quantity of SMPPR resin was added to 50 mL of sample solution containing Ni(II) and Cu(II) ions at 300 mg L^{-1} , and then the suspension was stirred for six hours at ambient temperature. After filtration of the suspension, the equilibrium concentration of the Ni(II) and Cu(II) ions remaining in the solutions was measured by FAAS. The adsorption capacities of SMPPR for Ni(II) and Cu(II) ions were calculated as 39.5 mg g^{-1} and 61.4 mg g^{-1} , respectively.

Ni(II) and Cu(II) adsorption of SMPPR vs. time is illustrated in Figure 4 in order to show the adsorption ability of the polymer for short time contact with the samples.

Validation of Developed Method

A fortified water certified reference material (CRM) (Ontario Lake water NWTMDA-54.4) was used to

validate the suggested SPE procedure using SMPPR. The proposed method was applied to this sample at optimal conditions, and the obtained results listed in Table V show that quantitative recoveries were achieved. Hence, the method can be reliably used for the determination of Ni(II) and Cu(II) in waters.

Determination of Ni(II) and Cu(II) Levels in Waters

The applicability of the proposed method was evaluated by using natural water samples from the Sakarya River and Sapanca Lake and a synthetic seawater. After spiking $5 \mu\text{g L}^{-1}$ of Ni(II) and Cu(II) ions, the overall SPE method was practiced to 150 mL of each water sample. The results given in Table VI demonstrate that the proposed method can be successfully used for the determination of Ni(II) and Cu(II) levels in lake, river, and seawater samples.

CONCLUSION

In the present study, a novel solid phase extraction and preconcentration method using a SMPPR-loaded column was successfully

TABLE IV
DLs of Cu(II) and Ni(II)
With Different Preconcentration Factors

Sample Volume (mL)	Eluent Volume (mL)	Preconcentration Factor	DLs of Ni(II) ($\mu\text{g L}^{-1}$)	DLs of Cu(II) ($\mu\text{g L}^{-1}$)
50	5	10	1.10	0.30
100	5	20	0.55	0.15
150	5	30	0.37	0.10
200	5	40	0.28	0.08
250	5	50	0.22	0.06
300	5	60	0.18	0.05
350	5	70	0.16	0.04
400	5	80	0.14	0.04
450	5	90	0.12	0.03
500	5	100	0.11	0.03

TABLE V
Validation of the Suggested SPE Procedure
Using SMPPR ($n=3$, $\pm$ standard deviation)

Element	Certified Value (mg L^{-1})	Found Value (mg L^{-1})	Recovery (%)
Ni	0.337 ± 0.031	0.331 ± 0.012	98 ± 4
Cu	0.443 ± 0.037	0.439 ± 0.013	99 ± 3

Fig. 4. Adsorption of Ni(II) and Cu(II) vs. time using SMPPR.

Table VI
Determination of Ni(II), Cu(II) Ions in Various Water Samples
(n=3, $\pm$ standard deviation)

Sample	Added ($\mu\text{g L}^{-1}$)	Found Value ($\mu\text{g L}^{-1}$)		Recovery (%)		RSD (%)	
		Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)
Sakarya River	0.0	4.18 $\pm$ 0.15	5.50 $\pm$ 0.17	-	-	3.59	3.09
	5.0	9.00 $\pm$ 0.33	10.35 $\pm$ 0.35	98 $\pm$ 2	99 $\pm$ 2	3.67	3.38
Sapanca Lake	0.0	1.03 $\pm$ 0.03	1.40 $\pm$ 0.07	-	-	2.91	5.00
	5.0	6.07 $\pm$ 0.07	6.28 $\pm$ 0.05	101 $\pm$ 1	98 $\pm$ 1	1.15	0.80
Synthetic Seawater	0.0	< LOD	< LOD	-	-	-	-
	5.0	4.95 $\pm$ 0.21	5.05 $\pm$ 0.30	99 $\pm$ 1	101 $\pm$ 1	4.24	5.94

LOD: Limit of Detection.

developed for the trace level determination of Ni(II) and Cu(II) ions by FAAS. The SPE procedure was able to recover the Ni(II) and Cu(II) ions quantitatively. The flow rate of the sample and eluent solutions was optimized to 1.0 mL min⁻¹. Although the flow rate was not high, the Ni(II) and Cu(II) ions were successfully enriched from 500 mL of sample volume with a high enrichment factor (100).

Ease of elution of the metal ions from the column, usability for highly saline samples, and providing a high preconcentration factor are the advantages of the proposed method.

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