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Solid-phase extraction of trace Ni(II) ions on ethylenediamine-silica material synthesized by sol–gel method

Emir Akdemir, Mustafa Imamoglu*

Faculty of Arts and Sciences, Chemistry Department, Sakarya University, 54187 Sakarya, Turkey
Tel. +90 264 295 60 53; Fax: +90 264 295 59 50; email: imamoglu@sakarya.edu.tr

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ABSTRACT

A solid-phase extraction method using ethylenediamine-silica (EDA-SIL) material for the determination of Ni(II) ions at trace level by flame atomic absorption spectrometry (FAAS) was presented in this study. EDA-SIL was synthesized with 3-(2-aminoethylamino) propyltrimethoxysilane (EDA-silane) and tetraethyl orthosilicate by sol–gel technique performing acidic hydrolysis and basic gelation procedure. EDA-SIL was characterized by FT-IR and C, H, and N elemental analysis. Solid-phase extraction of Ni(II) ions was carried out using mini column filled with EDA-SIL. The important variables governing the recovery of Ni(II) including pH, flow rate, eluent type, eluent volume, and matrix ions were studied. At the optimum preconcentration conditions, the recovery of Ni(II) was found to be 100 ± 3% at 95% confidence level. The detection limit of Ni(II) was calculated based on the three times of standard deviation of blanks and found to be $0.32\,\mathrm{ng\,mL^{-1}}$ using a preconcentration factor of 50. The developed method was validated using certified water samples (Ontario Lake water, NWTMDA-54.4) and applied to synthetic sea water samples for the determination of Ni concentration by FAAS.

Keywords: Solid-phase extraction; Chelating resin; Silica gel; Sol–gel; Flame atomic absorption spectrometry

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1. Introduction

Determination of heavy metal ions at trace levels in water, waste water, vegetable, and food samples is very important because of their toxic effect to living organisms [1–3]. Various modern instrumental techniques, such as flame or electrothermal atomic absorption spectrometry (FAAS or ETAAS), inductively coupled plasma optical emission, or mass spectrometry, have been widely used for the determination of metal ions in various samples including water, wastewater, food, biological, agricultural and industrial samples. The main problems encountered in these techniques are low-concentration level of the metal ions and/or matrix effect of the samples, especially in FAAS technique which has been widely used in many laboratories. To cope with these issues, several separation/preconcentration methods, such as solid-phase extraction, liquid–liquid extraction, flotation, ion-exchange, cloud point extraction and coprecipitation have been widely employed [4–9].

Solid-phase extraction technique based on the retention of analyte on solid sorbents is very effective preconcentration method due to its rapidity,

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*Corresponding author.

simplicity, and productiveness a high preconcentration factor [10–12]. In the last decade, various solid sorbents including activated carbon [12,13], porous and/or functional polymers [14,15], and modified silica gels [16–20] and etc. were prepared for preconcentration and/or adsorption of metal ions and/or organics. The desirable properties of the sorbents are ease of regeneration, fast, and quantitative adsorption. Chelating resins are widely preferred to the other sorbents due to their selective adsorption abilities. These resins are prepared by the incorporation of organic functional groups containing donor atoms, such as N, O, S, and P, to solid supports including porous polymer or silica gel [21]. Silica gel is preferred to the polymers due to its extra superiorities including high surface area, good mechanical strength, high thermal stability, and nonswelling in several solvents [22]. Modified silica gels are prepared by three methods including: (1) covalent attachment of functional group onto silica surface, (2) loading of chelating ligands on the silica gel, and (3) sol–gel synthesis.

The sol–gel procedure contains hydrolysis and polycondensation of TEOS and the functional alkoxysilane compounds in water and ethanol mixture in the presence of catalysts such as hydrochloric acid, sodium hydroxide, ammonium fluoride, etc. [23]. Synthesis of modified silicas at ambient temperature and high degree of functionalization are advantages of sol–gel technique over the covalent attachment and loading methods [23–30]. Hydrolysis, cocondensation and gelation of TEOS are carried out in basic or acidic conditions in the synthesis of sol–gel materials. Novel sol–gel synthesis procedure was proposed by Lee et al. including two steps: (1) hydrolysis at acidic solution and (2) gelation in basic medium. Thiol functionalized organoceramic adsorbent having a high adsorption capacity was prepared by this procedure [26].

Types of chelating ligands immobilized to solid phases are very important for the quantitative uptake of metal ions. Among the metal ions, Ni(II) has fairly hard characteristic. Hence, Ni can form stable complexes with hard bases containing N and/or O heteroatoms. For this reason, ethylenediamine (EDA) was selected as a chelating ligand for covalent attachment to silica. It should also be noted that EDA can form stable five-membered chelate rings with Ni(II) ions.

In this study, synthesis of EDA-SIL material using the sol–gel method based on the hydrolysis at acidic conditions and gelation at basic conditions was attempted. The prepared EDA-SIL was used for the development of an analytical procedure for the determination of Ni(II) at trace level using FAAS. EDA-SIL was characterized by BET surface area measurement, elemental analysis and FT-IR spectroscopic investigation. EDA-SIL was tested for the solid-phase extraction of Ni(II) ions by investigating various effective factors including pH, volume and flow rate of the Ni(II) sample solution, and concentration, volume and kind of eluent solutions. The optimized method was validated by the determination of Ni(II) levels in certified reference water sample (NWTMDA-54.4) and spiked synthetic seawater.

2. Materials and methods

2.1. Instruments and chemicals

FAAS (Shimadzu, AA-6701F) was used for the determination of Ni(II) concentrations and its working conditions were set according to manufacturer's guide book. Elemental analysis of EDA-SIL was carried out by elemental analyzer (Carlo Erba, 1106). Determination of BET surface area of EDA-SIL was performed using Quantachrome Autosorb BET surface analyzer. A peristaltic pump (Cole-Parmer Instrument Co.) was used to control a flow rate of Ni(II) solution. A pH meter (Schott CG 840) was used for pH measurement throughout the study.

All chemicals and reagents used in this study were of analytical reagent grade. Distilled-deionized water was used throughout the study. The working solutions of Ni(II) were prepared daily by the dilution of Ni(II) stock solution at $1,000\,\mathrm{mg\,L^{-1}}$ supplied by Merck KGaA, Darmstadt, Germany. TEOS and EDA-silane were also purchased from Merck and used without any purification.

2.2. Synthesis of EDA-SIL material

Simultaneous hydrolysis of TEOS and EDA-silane was carried out separately by stirring of them with magnetic stirrer at ambient temperature. EDA-silane was hydrolyzed in a mixture of ethanol (1.95 mL) and $6\,\mathrm{mol\,dm^{-3}}$ HCl (1 mL) for a period of 120 min. TEOS was hydrolyzed in a mixture of ethanol (5.2 mL) and 0.083 M HCl (1.6 mL) for a period of 30 min. Then, EDA-silane hydrolysate and triethylenetetramine (2 mL) were added simultaneously on the TEOS hydrolysate. After about 10 min, a solid material was formed, and then, it was aged for one day at ambient temperature and for one day at 80°C. Finally, the material was washed with toluene, ethanol, and diethyl ether and dried at 60°C for one day [25–30]. The obtained EDA-SIL material was ground and sieved. The particle sizes less than 200 μm were used in the study. The proposed structure of the modified silica was given in Fig. 1. Also blank silica material

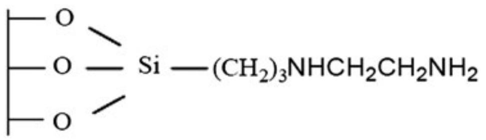

Fig. 1. Proposed structure of EDA-SIL sorbent.

was prepared at the same conditions without addition of EDA-silane.

2.3. Preconcentration procedure

A glass column with PTFE stopcock (inner diameter: 5 mm) was used for the SPE studies of Ni(II). 300 mg of EDA-SIL was loaded to the column, and a peristaltic pump was connected to the end of the column for passing of the Ni(II) solution at appropriate flow rate. The proposed preconcentration method was optimized using a model sample solution (100 mL) containing Ni(II) at $0.2\,\mathrm{mg\,L^{-1}}$. The model solution was passed through the column at the various flow rate, and then, the retained Ni(II) ions on the column was eluted using 10 mL of 2.0 M HCl. Ni(II) concentration in the eluates was determined by FAAS, and the recoveries were calculated.

The developed preconcentration technique was applied for the determination of Ni(II) in spiked synthetic sea water and certified reference water sample (Ontario Lake water, NWTMDA-54.4) obtained from LGC Standards GmbH (Wessel, Germany). Synthetic sea water containing $10{,}500\,\mathrm{mg\ L^{-1}}$ of Na^+, $1{,}350\,\mathrm{mg\,L^{-1}}$ of Mg^{2+}, $400\,\mathrm{mg\,L^{-1}}$ of Ca^{2+} and $380\,\mathrm{mg\,L^{-1}}$ of K^+ was prepared from their chloride salts according to the literature [31].

3. Results and discussion

3.1. Characterization of the sorbent

Elemental analysis (C, H, and N) and FT-IR spectroscopic investigation are widely used for the characterization of sorbents. C, H, and N content (%) of the EDA-SIL were found to be 8.51, 2.73, and 4.05, respectively. Amount of EDA per gram of the EDA-SIL was calculated based on the N content and found to be $1.45\,\mathrm{mmol\,g^{-1}}$, which was higher than those of covalently functionalized silica gels with EDA [16]. Covalent attachment of EDA group was performed in anhydrous conditions and firstly, 3-chloropropyl bonded silica gel was prepared, and then, it was reacted with EDA in the presence of triethylamine under N_2 atmosphere. Modification of the product was reported $0.98\,\mathrm{mmol\,g^{-1}}$ based on the N content [16]. The high EDA content of EDA-SIL material is advantage of the presented method. Also, BET surface area of EDA-SIL was found to be $96.1\,\mathrm{m^2\,g^{-1}}$. p-Anisidine/silica material was prepared using sol–gel method and BET surface area of the sorbent was found between 83 and $375\,\mathrm{m^2\,g^{-1}}$, and it was concluded that BET surface area decreased by increasing of the quantity of the attached organic groups [24]. BET surface area of aniline [25] and thiol [26] functionalized silica material were reported to be 80 and $340.3–639.9\,\mathrm{m^2\,g^{-1}}$, respectively. FT-IR spectrum of EDA-SIL was compared with the spectrum of blank silica, and spectrum of EDA-SIL showed N–H conformation peaks at $1{,}466\,\mathrm{cm^{-1}}$ and C–H peaks at 2,884 and $2{,}951\,\mathrm{cm^{-1}}$ over the spectra of blank silica.

3.2. Optimization of Ni(II) preconcentration

The pH of the aqueous sample solution is the most critical parameters of the adsorption and/or preconcentration for metal ions [19,32]. Effect of pH on the recovery of Ni(II) ions was studied using model solutions (100 mL) containing Ni(II) ions at $0.2\,\mathrm{mg\,L^{-1}}$. According to the results depicted in Fig. 2, the recovery (%) of Ni(II) ions was fairly dependent on the pH of the model solution. At pH values lower than 4.0, the recovery is nearly zero. This situation is due to protonation amine group of EDA-SIL. By increasing of pH from 4.0 to 7.0, the recoveries were increased and reached quantitative levels ($\geqslant$95) at pH values of 7.0 and 8.0. At these neutral and slightly basic conditions, level of H_3O^+ was decreased, and N atoms have free unpaired electrons which can form complexes with Ni (II) ions. The subsequent experiments were performed at pH 8.0.

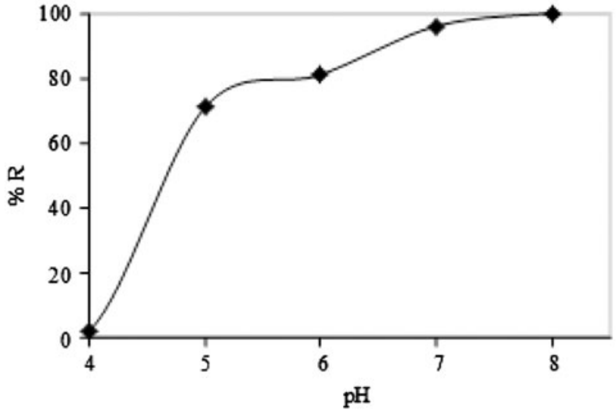

Fig. 2. Effect of solution pH on the recoveries of Ni(II) ions ($n = 3$).

Ten milliliters of nitric and hydrochloric acid solutions at the concentrations between 0.5 and 2.0 M were tested for the elution of Ni(II) ions retained on the column. Nitric acid solutions (0.5–2.0 M) could not quantitatively elute Ni(II) ions from the column. Also, 0.5 and 1.0 M of HCl solutions did not provide a complete desorption of Ni(II) ions. Quantitative recovery of Ni(II) ions was only achieved using 2.0 M HCl solution. Hence, 10 mL of 2.0 M HCl solution was chosen to be optimum eluent.

The effect of flow rate of the model solution on the recovery of Ni(II) was studied at various flow rates ranged from 1 to 20 mL min^{-1}. The recovery was slightly decreased by increasing the flow rate of the model solution; even so, quantitative recoveries for Ni(II) ions were obtained in all studied flow rates.

The effect of the model solution volume was investigated at various volumes (between 100 and 1,000 mL) containing same amount of Ni (0.020 mg). According to the results illustrated in Fig. 3, quantitative recoveries were obtained up to volumes of 500 mL, and then, the recoveries were decreased to 67%. Hence, maximum applicable sample volume of the developed method is 500 mL. Eventually, the preconcentration factor was obtained to be 50 by dividing the sample solution volume of 500 mL by the eluent volume of 10 mL. Maximum applicable sample volume using multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo) resorcinol was reported as 75 mL [33]. Maximum volume was found to be 200 mL for the determination of copper(II), cobalt(II), lead(II), and iron(III) as violuric acid chelates on multiwalled carbon nanotubes [34].

The effect of matrix ions, such as alkaline and alkaline earth metal ions and some anions, was studied. The model solution (100 mL) containing Ni(II) at the concentration of 0.2 mg L^{-1} was spiked with matrix ions and then, passed through the column. The matrix ions were selected from the common cations and anions widely exist in water and/or wastewater samples. The calculated recoveries were given in Table 1, and it was found that the recovery of Ni(II) was not significantly affected from the investigated matrix ions except phosphate anion. The negative effect of phosphate may be due to precipitation losses of nickel [35,36].

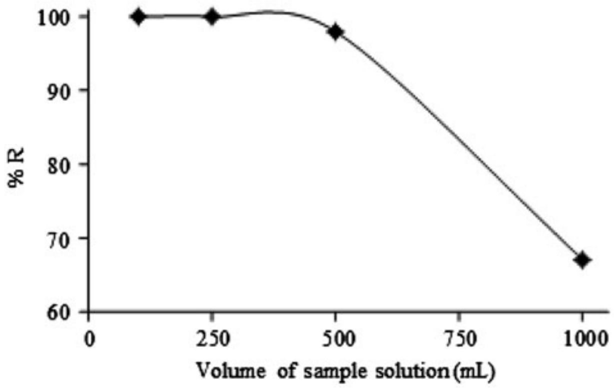

Fig. 3. Effect of sample solution volume on the recoveries of Ni(II) ions ($n = 3$).

In order to determine precision of the proposed method, Ni(II) model solution (100 mL) was preconcentrated at the optimum conditions (see Table 2) and the recovery of Ni(II) and standard deviation was found to be 100 and 3 at 95% confidence level, respectively. The instrumental detection limit of Ni based on three times the standard deviation of the blank ($n = 10$) was 16 ng mL^{-1}. The analytical detection limits were calculated to be 0.32 ng mL^{-1} by dividing the instrumental detection limits by the preconcentration factor of 50. The effect of repetitive usage of the column was also investigated and its performance was not changed up to using of 30 times.

3.3. Adsorption capacity

Ni(II) adsorption capacity of EDA-SIL was studied batchwise. Fifty milligram of EDA-SIL was added to 50 mL of Ni(II) solution containing 2.5 mg Ni. Initial pH of the solution was adjusted to pH = 8.0 by dilute

Table 1
Effect of matrix ions on the recovery of Ni(II) ($n = 3$)

Matrix Ion	Prepared from	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaCl	10,000	101 ± 1
K^+	KCl	2,000	97 ± 1
Ca^{2+}	$Ca(NO_3)_2$	1,000	101 ± 1
Mg^{2+}	$MgSO_4$	1,000	100 ± 2
Cl^-	NaCl	10,000	101 ± 1
NO_3^-	$Ca(NO_3)_2$	1,000	101 ± 1
SO_4^{2-}	$MgSO_4$	1,000	101 ± 3
PO_4^{3-}	K_2HPO_4	1,000	88 ± 2

Table 2
Optimum preconcentration condition of Ni(II)

Parameters	Optimum value
Sample solution's pH	8.0
Sample solution flow rate	10 mL min^{-1}
Type of eluent	2 M HCl
Eluent volume	10 mL
Maximum applicable volume	500 mL

Table 3
Determination of nickel in synthetic sea water ($n = 3$, s.d.: standard deviation)

Sample	Added (μg)	Found (μg) ± s.d.	Relative Error, %
Synthetic seawater	10	9.9 ± 0.1	−1.0
	20	19.0 ± 0.2	−5.0
	30	28.1 ± 1.1	−6.3

NaOH or HCl solution, and pH values of the solutions at the equilibrium condition were measured to be 5.5. After agitation for 2 h on the orbital shaker, the mixture was filtered and the concentration of Ni (II) retained in the solution was determined by FAAS ($n = 3$). The capacity of EDA-SIL sorbent for Ni(II) was found to be $38 \pm 4\,\mathrm{mg\,g^{-1}}$ ($0.65 \pm 0.07\,\mathrm{mmol\,g^{-1}}$). When the EDA content and the adsorption capacity of the EDA-SIL were compared, it could be concluded that the complex was formed between EDA-SIL and Ni(II) ions at ratio of 2:1. The lower capacity of EDA-SIL than the expected value may be due to inaccessible of some EDA molecules on the structure of EDA-SIL sorbent.

3.4. Application

The proposed method for the determination of Ni at trace level using FAAS was validated by determining Ni concentration in certified reference material (spiked Ontario Lake water). Given value, found value, and relative error are $337 \pm 31\,\mathrm{mg\,L^{-1}}$, $324 \pm 14\,\mathrm{mg\,L^{-1}}$, and −3.9%, respectively.

The proposed method was also tested for the determination Ni(II) concentrations in spiked synthetic seawater samples. According to the results given in Table 3, the developed method could be successfully used for the determination of Ni(II) concentration in highly saline samples.

4. Conclusion

In this study, sol–gel synthesis of EDA-SIL material was prepared by acidic hydrolysis and basic gelation procedure. A higher degree of functionalization than the covalent attachment and loading methods was achieved by this method. EDA-SIL was showed good solid-phase extractive properties towards to Ni (II) ions. The modified silica can collect trace level of Ni(II) ions from large volume sample solution (500 mL) at pH 8.0. The retained Ni(II) ions on the column could be easily eluted using 10 mL of 2.0 M HCl solutions. The proposed solid-phase extraction method of Ni(II) was not affected from matrix ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. The preconcentration method could be applied to highly saline samples for the determination of Ni(II) concentration at trace level. The proposed method provides a simple, accurate and efficient preconcentration technique for the determination of trace Ni(II) levels by FAAS.

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