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A novel thiocarbohydrazide derivative for preconcentration of copper(II), nickel(II), lead(II), and cadmium(II) in water samples for flame atomic absorption spectrophotometry (FAAS)

Ebru Çetinkaya[a,*], Adnan Aydın[b]

[a]*Mir Unique Solutions, Materials & Chemical Research Department, Esenler, İstanbul 34220, Turkey, email: ebrucetinkaya@mirarge.com*
[b]*İstanbul Bilim University, School of Health, Esentepe, Şişli, İstanbul 34394, Turkey, email: adnanaydin.aa@gmail.com*

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ABSTRACT

A preconcentration procedure has been developed by using a thiocarbohydrazide derivative (1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide) as a novel sorbent. The ligand was synthesized and used for preconcentration of Cu(II), Ni(II), Pb(II), and Cd(II) ions from water samples by batch and column procedures to enrich metal concentrations appropriate for flame atomic absorption spectrophotometry (FAAS). The optimum pHs for effective solid-phase extractions were 5 and 7 for Cu(II), and Ni(II), Pb(II) and Cd(II) adsorptions, respectively. The method detection limits 0.73, 0.05, 1.14 and 0.04 ng mL^{-1}; the method determination limits 2.4, 0.15, 3.76 and 0.13 ng mL^{-1} and the enrichment factors 30, 65, 26 and 50 were found for Cu(II), Ni(II), Pb(II) and Cd(II), respectively. The sorption and desorption yields and overall recoveries of metals were almost quantitative except Pb(II) of which sorption yield was around 72% with relative standard deviation value around 1.8%. Langmuir, Freundlich and Temkin models were examined for the metal adsorptions. The Langmuir isotherm model provided a better fit with high correlation coefficients. Regarding the Langmuir parameters, the maximal adsorption capacities on 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide were 18.25, 7.99, 13.26 and 12.96 mg g^{-1} for Cu(II), Ni(II), Pb(II) and Cd(II), respectively. The adsorption kinetics for the adsorptions of metals were studied by using linear forms of pseudo-first-order and pseudo-second-order kinetic models. Pseudo-second-order kinetic model fitted very well. The developed method has been successfully applied to the preconcentration of Cu(II), Ni(II), Pb(II) and Cd(II) in water samples (tap water, seawater and mineral water samples), and satisfactory and reproducible results were obtained in FAAS analysis.

Keywords: Preconcentration; Cu(II), Ni(II), Pb(II) and Cd(II) adsorptions; FAAS; Solid-phase extraction; Thiocarbohydrazide derivative; Water analysis

1. Introduction

Pollution with heavy metals is one of the major problems in the management of environmental protection. Insufficiently controlled growth of industrialization along with unplanned urbanization threatens the human health and the ecosystem.

The heavy metals emitted into the atmosphere are mostly in their forms of oxides, sulfides, silicates and aluminates, which are located in particulate materials with various matrices. Heavy metals play important roles in atmospheric reactions. Transportation of metals from the atmosphere into the aquatic environment occurs via precipitations and through the mixing of gaseous and liquid phases above the water surfaces.

Industrial wastewater discharges are the most frequently encountered sources for heavy metal pollution in the water and soil environment. The solubilities of metallic compounds in water are controlled by chemical behaviors of metals and vastness of the water body. Practically insoluble compounds can also be an effective and continuous polluting source to

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* Corresponding author.

cause pollutant concentrations at trace levels. Trace heavy metal concentrations in water or in food may be hazardous for the living species; in order to keep them under control, it is important to analyze them rapidly by use of reliable methods. The atomic absorption spectrophotometry is a low-cost tool for such an analysis provided that abundance of metals in water should not be below the determination limits. Analytical problems arisen from the matrix effects are also to be overcome. Thus, reduction of matrix interferences and preconcentration of elements should be achieved simultaneously by use of selected procedures, which involve several reagents specific for certain metals.

A number of preconcentration and cleanup procedures for trace metal ions are given in the literature, such as co-precipitation, liquid–liquid extraction, ion exchange, separations with membranes, electro-deposition, cloud-point extraction and solid-phase extraction (SPE) [1–8].

Of the preconcentration techniques, SPE method depends primarily on the adsorption processes, which work by the principles of physical, chemical or ionic interactions between the ions and the solid material. SPE offers several advantages over other procedures by its high enrichment factor, low cost, decreased operating time, ease of automation and ability to be applied in a continuous flow system [1,9–12].

Many substances such as bentonites [13], zeolites [14,15], clinoptilotites [16], clays [17], fly ashes [18], activated carbons [19], metal oxides and hydrous oxides [5,20,21] are used as sorbents for SPE of elements in trace concentrations. Metal chelating properties of a sorbent facilitate the adsorption process and can have advantages of high chemical stability. High surface areas are preferred for an effective interaction between metal ions and sorbents [22]. The chelating agents can be used without any support or can be loaded on an inert or ion exchangeable supporting material. Some examples for especially Cu(II), Cd(II), Ni(II) and Pb(II) enrichment from water samples before atomic absorption spectrophotometry are 1-(2-pyridylazo)-2-naphthol (PAN) [23], dithiooxamide [24], dithiocarbamates [25], xylenol orange [26] and methylthymol blue [27] on activated carbon; iminodithiocarbamates [28], 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide [29], zirconium(IV)phosphate [30] on silica gel; PAN [31], nitroso-R salt [32] and calmagite [33] on Amberlite XAD-2; PAN [4] on Chromosorb-106; and 4-aminoantipyrine [34] on bentonite.

Modified polyamine-polyurea resins [35]; functionalized or unfunctionalized ion exchangers such as Amberlite XAD-1180 [36] or Amberlite XAD-4 [37,38]; functionalized polymers and co-polymers such as poly(methacrylate) [39] or polystyrene/divinylbenzene [10,40]; modified celluloses with ester, ethyleneimine, polyethyleneimine, 2-aminoethyl, 2-diethylaminoethyl, *p*-aminobenzoic, imidazole substituents [41–45]; modified silica gels [46–49]; chitosan-containing composites [50–52]; and modified metal oxides[53] can act as sorbents for heavy metals.

Heavy metal ion adsorptions of thiourea-containing sorbents are dependent on the abundance of the effective complexation sites in the molecules, which bear electron-donating atoms such as nitrogen and sulfur. The resins, oligomers or simple ligands containing thiourea or isothiourea moieties have been found to give complexes and to adsorb heavy metal ions including some precious metal ions such as Ag(I), Au(I), Au(III), Pd(II) and Pt(II) [54–62].

Thiocarbohydrazide and thiosemicarbazide as well as their derivatives become the subject of a number of research works because of their electron donating atoms, which coordinate transition metals. Of the derivatives, the Schiff bases have an important share in works concerned with their metal chelating properties [63–69].

In the presented work, 1,5-bis(phenylthiocarbamoyl) thiocarbohydrazide was used as a new solid-phase sorbent for preconcentration and separation of Cu(II), Ni(II), Pb(II) and Cd(II) ions from aqueous solutions. Extraction conditions were optimized for both batch and column procedures. The parameters such as pH, contact time, amount of the adsorbent and type of the eluent solution were investigated.

2. Experimental

2.1. Instruments

A ZEEnit flame atomic absorption spectrometer, Model 700, equipped with hollow cathode lamps and with air–acetylene flame was used for the determination of metal concentrations. Of the operating parameters, the wavelengths used were 324.8, 232.0, 283.3 and 228.8 nm with the lamp currents 30, 30, 15 and 20 mA, and the slit widths 0.7, 0.2, 0.7 and 0.2 nm to ensure the detection limits (LOD) of 0.002, 0.008, 0.015 and 0.0007 ppm for Cu, Ni, Pb, and Cd, respectively.

The structural characterizations of the adsorbent were made using PerkinElmer Spectrum 100 Fourier transform infrared spectrophotometer, CHNS elemental analysis (Thermo Finnigan Flash EA 1112) and Varian Unity Inova 500 MHz 1H nuclear magnetic resonance spectrometer (NMR). Scanning electron microscope (SEM) images were acquired using Phenom Pro Tabletop scanning electron microscope (Netherlands) operating at 10 kV. Samples were deposited onto a double-sided carbon tape fixed to a brass sample holder and gold film coated for 18 s at 10 mV. pH measurements were done by a WTW Instrument, Model pH-7310, equipped with a glass electrode. A peristaltic pump Welco (WP 1000) was used to control the flow rate of the solution in the column works.

2.2. Chemicals

All reagents and solvents were of analytical reagent grade. Ultrapure water with a maximum resistivity of 18.2 MΩ.cm (25°C) was obtained from a Millipore (USA) Direct-Q3. Standard solutions were prepared from CertiPUR copper, nickel, lead and cadmium standard solutions (Merck (Germany), 1,000 mg L^{-1}), and appropriate dilutions were made by using these solutions, wherever necessary. Standard solutions (Merck, 1,000 mg L^{-1}) of potassium, sodium, acetate, phosphate, cobalt, iron, aluminum, manganese and zinc were used in the works to understand the effects of foreign ions on the preconcentration steps. Silica gel 70–230 mesh and 60 Å high purity grade (Sigma) was used in the preparation of the column material.

Thiocarbohydrazide (98%, Aldrich, USA), phenyl isothiocyanate (≥98%, Aldrich), ethanol (≥99.8%, Fluka, Switzerland) and hydrochloric acid (37%, Merck) were used in the preparation of the adsorbent.

Buffer solutions were prepared by using appropriate mixtures of KCl + HCl for pH 2–3; CH_3COONa + CH_3COOH

for pH 4–6, NaH_2PO_4 + Na_2HPO_4 for pH 7 and NH_4Cl + NH_4OH for pH 8.

2.2.1. Synthesis of the adsorbent [1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide] [70]

To the solution of thiocarbohydrazide (3.0 g) in 1 M HCl (30 mL) in a double-necked flask under reflux condenser was added dropwise a solution of phenyl isothiocyanate (6.7 mL) in ethanol (50 mL) in 5 min during stirring. The mixture was heated with stirring at 70°C for 2 h. After cooling to room temperature, the white precipitate was filtered, washed with ethanol and dried at 80°C–100°C. The product was refluxed in ethanol (50 mL) for 30 min to remove the impurities and dried, to give 9.38 g adsorbent with melting point (m.p.): 196.4°C–197.6°C (dec) (yield: 88%). The adsorbent can be purified by precipitation from alkaline solution with dilute hydrochloric acid (m.p.: 198°C–199°C (dec)). The synthesis of 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide is given in Fig. 1.

CHNS analysis of the product washed by boiling ethanol is as follows:

Calculated for $C_{15}H_{16}N_6S_3$: C, 47.84%; H, 4.28%; N, 22.32%; S, 25.55%

Found: C, 45.84%; H, 4.42%; N, 21.48%; S, 24.70%

The adsorbent is soluble in dimethylsulfoxide and alkaline solutions (e.g., 1 M NaOH), and insoluble in water, ethanol, acetone, acetonitrile, toluene, chloroform, methylene chloride and 1,4-dioxane.

The infrared (IR) spectrum of the sorbent is given in Fig. 2(b). The characteristic bands for the important vibrations are N–H bands at 3,248 (m), 3,212 (w) and 3,131 (w) cm^{-1}; aromatic C–H bands at 3,062 (m), 3,017 (m) and 737 (s) cm^{-1}; aromatic C=C bands at 1,601 (m), 1,499 (m) and 1,445 (m) cm^{-1}; N–C–N and C=S bands at 1,547 (m), 1,163 (m), 1,199 (w), 1,102 (m), 1,076 (w), 1,034 (m) and 751 (m) cm^{-1}; C–N bands at 1,478 (m), 1,376 (m) and 1,229 (m) cm^{-1}. The characteristic bands of the starting compound thiocarbohydrazide (Fig. 2(a)) are primary amine NH_2 bands at 3,305 (m), 3,270 (m), 1,638 (s) and 1,619 (s) cm^{-1}; N–H bands 2,960–3,200 (m) cm^{-1}; N–C–N and C=S bands at 1,528 (s), 1,139 (s), 1,079 (m), 1,006 (s) and 751 (s) cm^{-1}; and C–N bands at 1,487 (s) and 1,284 (m) cm^{-1}. Some of the bands belonging to the vibrations in the thiocarbohydrazide are not found in the spectrum of the ligand, such as 3,270 and 3,305 cm^{-1} bands of NH_2 stretching as well as the bands of NH deformations of primary amines at 1,638 and 1,619 cm^{-1}. Instead, in the spectrum of the ligand, 3,062 and 3,017 bands of aromatic C–H stretching and 1,601, 1,499 and 1,445 cm^{-1} bands of C=C stretching of the aromatic ring as well as the band of monosubstituted aromatic C–H out-of-plane vibration at 737 and 686 cm^{-1} are observed.

1H-NMR spectrum of the adsorbent in DMF has shown the existence of aromatic protons that appear at 7.32 (aromatic CH, 1H, t), 7.52 (aromatic CH, 2H, t), 7.85 (aromatic CH, 2H, d) ppm, and N–H protons appear between 3.70 and 4.40 ppm as a broad band.

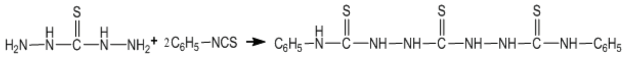
The microstructure and surface morphology of the uncrushed sorbent were identified by scanning electron microscope images, which are given in Fig. 3. SEM images showed 20–100 μm sized bulky aggregates with tunnelling structure constructed with narrow leaflets, by which the contact of the sorbent with aqueous samples may be improved without clogging.

2.3. Preconcentration procedures

Adsorption properties of the ligand 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide were studied by using both batch and column procedures.

2.3.1. Batch procedure

The effects of pH, contact time, amount of the ligand on the metal adsorption process and the effects of the volume and type of the eluent solution on the desorption process were investigated by the batch procedure. In a general procedure, an appropriate buffer solution for pHs between 2.0 and 8.0 was added to calculated volume of copper, nickel,



$$H_2N{-}\overset{H}{N}{-}\overset{S}{\overset{\|}{C}}{-}\overset{H}{N}{-}NH_2 + 2C_6H_5{-}NCS \rightarrow C_6H_5{-}\overset{H}{N}{-}\overset{S}{\overset{\|}{C}}{-}NH{-}NH{-}\overset{S}{\overset{\|}{C}}{-}NH{-}NH{-}\overset{S}{\overset{\|}{C}}{-}NH{-}C_6H_5$$

Fig. 1. Synthesis of 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide.

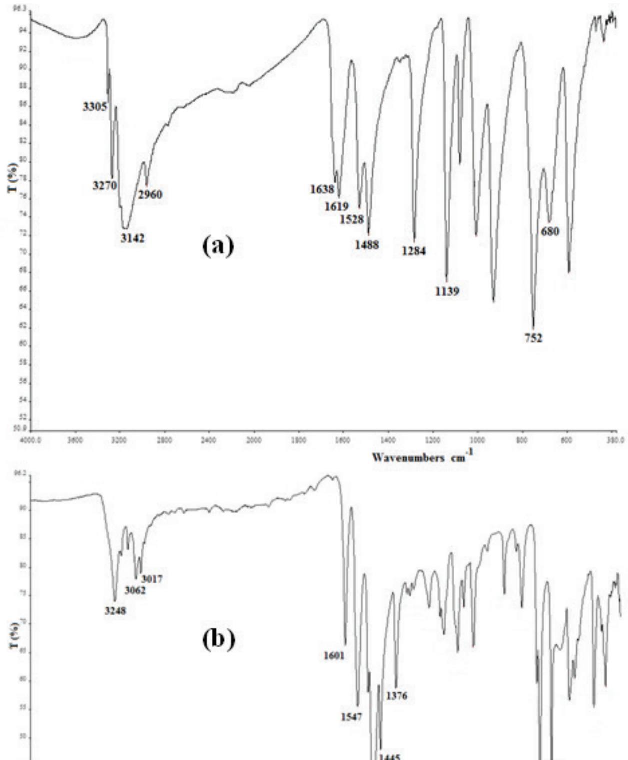


Fig. 2. IR spectra of (a) thiocarbohydrazide and (b) the ligand 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide.

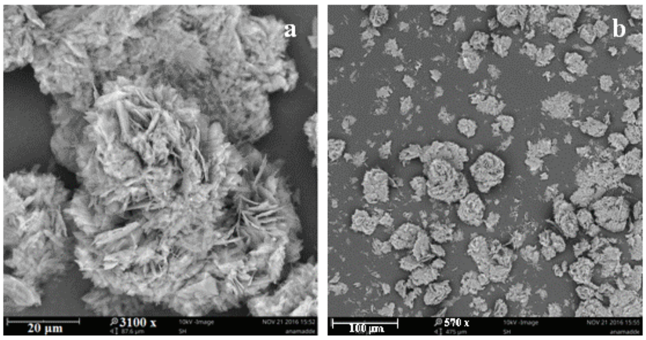


Fig. 3. SEM images of the ligand with different magnifications: (a) 3,100× with 20 μm legend, (b) 570× with 100 μm legend.

lead or cadmium solution to get 4 mg L^{-1} metal ion concentration in totally 25 mL of mixture. Following the addition of 0.05–0.50 g of adsorbent, the mixture was stirred for a selected time.

The metal adsorbed solid phase was separated from the solution by filtration. The metal concentrations in the starting solutions and in the filtrates were determined, and the adsorbed metal amounts per gram of the adsorbent were calculated. Additionally, metals adsorbed by the solid phase were eluted with different eluents in different concentrations (5–20 mL of 2–5 M HCl, 2–5 M HNO_3 or 0.05 M ethylenediaminetetraacetic acid [EDTA]). The eluates containing HNO_3 were evaporated on a steam bath to get a dampy residue. Following the dilution of the eluates or residues to an appropriate volume with 1 N HCl, metals were analyzed by flame atomic absorption spectrophotometry (FAAS) and evaluated using calibration curves, which were plotted using absorption data of standard metal solutions prepared in 1 N HCl. All samples and blanks were prepared in triplicate.

The Langmuir adsorption isotherms of the metals were examined at 25°C ± 1°C, and the maximum adsorption capacities of the solid phase were calculated for each metal.

2.3.2. Column procedure

0.10 g adsorbent was mixed well with 0.40 g of unactivated silica gel and was filled into a glass mini-column with 1 cm inner diameter and 1.0 cm adsorption bed length, which was plugged with small portions of glass wool at both ends. The column was conditioned with appropriate buffer solution before the flowing of metal solutions.

The column procedure was tested with a 100-mL metal solution in 1 mg L^{-1} concentration, which was adjusted to working pH. Metal solutions were passed through the column by means of a peristaltic pump under working conditions of 1.0–7.5 mL min^{-1} flow rate at 25.0°C ± 1.0°C. The metal ions trapped by the adsorbent were eluted with appropriate eluents, such as 2–5 M HCl for Ni(II), Pb(II) and Cd(II) and 5 M HNO_3 for Cu(II) or 5 M HNO_3 for all of the concerned metals, diluted with 1 M HCl to a known volume and were analyzed by FAAS using calibration curves prepared with standard metal solutions in 1 N HCl.

2.4. Method validation

The validity of the proposed adsorption method for Cu(II), Ni(II), Pb(II) and Cd(II) were tested for the recovery (%), limit of detection (LOD), limit of quantification (LOQ), precision, and accuracy. The method LOD was found according to its common definition given as an analyte concentration giving a signal equivalent to mean blank signals plus three times the standard deviation of blank signals divided by the preconcentration factor. The method LOQs were calculated by blank signals plus ten times the standard deviation of the blank signals divided by the preconcentration factor. The precisions of the proposed method for metals were expressed as RSD for the repeated independent determinations applied to metal solutions in the same concentration. The accuracy of the method was evaluated by measuring the recoveries of Cu(II), Ni(II), Pb(II) and Cd(II) in spiked real samples. Method precisions were determined for different metal concentrations by repeated experiments in the same day and in the consecutive days.

Preconcentration factors were taken as the ratio of highest sample volume in which maximum recoveries were obtained to the volume of eluate.

2.5. Analysis of real samples

The proposed method was applied to Cu(II), Ni(II), Pb(II) and Cd(II) ions in different water samples. Water samples such as tap water (from Esenyurt district of İstanbul), mineral water (commercial mineral water) and seawater (from the Gemlik Bay of Sea of Marmara, surface water from 50 cm depth, with salinity of 21‰) were collected to apply the developed preconcentration procedure. The samples were filtered through Millipore cellulose membrane. The samples were acidified to 1% with nitric acid and stored in polyethylene bottles. Aliquots (60 mL) of tap water, mineral water or seawater samples (60 mL) were analyzed after dilution to 100 mL with buffer solutions by using the proposed preconcentration method. The adsorbed metals were eluted with appropriate eluents such as 2 M HCl, 3 M HCl or 5 M HNO_3, and metal concentrations were determined by FAAS.

The accuracy of the method was examined by adding known amounts of metal ions into tap water, seawater and mineral water samples. The samples spiked with 200 and 400 μL aliquots taken from 0.1 M metal solutions were analyzed following the preconcentration method.

2.6. Determination of adsorption capacities

The maximum adsorption capacities of 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide for Cu(II), Ni(II), Pb(II) and Cd(II) ions have been obtained according to Langmuir approach [71]. Freundlich approach could not be used since linear relationships have not been observed [72]. Metal solutions of 25 mL in increasing concentrations (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300 and 350 mg L^{-1}) were prepared in appropriate pH buffers. Following the addition of 0.1 g of sorbent to metal solutions, the mixtures were stirred at room temperature (25.0°C ± 1.0°C) for appropriate periods to get equilibrium state, which were determined in preliminary experiments. The metal contents were analyzed both in the liquid and solid phases.

The adsorption capacity (q_e, mg g^{-1}) and adsorption efficiency (A, %) were calculated according to the following equations, where m is the adsorbent amount (g); V is the volume of solution (L); C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) of metal ions, respectively.

$$q_e\ (\text{mg g}^{-1}) = V\,(C_0 - C_e)/m \text{ and } A\ (\%) = (C_0 - C_e) \times 100/C_0 \qquad (1)$$

3. Results and discussion

3.1. Extraction with batch procedure

The investigations to understand the conditions of adsorption and desorption processes of Cu(II), Ni(II), Pb(II) and Cd(II) ions on the ligand were performed using the batch technique at 25°C ± 1°C and in the pH range 2–10. The optimum adsorption and desorption conditions for each metal were determined. The optimized conditions were applied in the column procedure to preconcentrate the metals in water samples for atomic absorption spectrophotometry analysis.

3.1.1. Effect of initial pH

Complexation process is one of the major adsorption processes in which the metal ions Cu(II), Ni(II), Pb(II) and Cd(II) are coordinated by the sorbent acting as ligand, and the pHs of aqueous metal solutions are crucial to ensure quantitative adsorption. The presence of three adjacent thioamide moieties in the adsorbent 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide causes thione–thiol tautomerization in the molecule to give iminothiol groups (N=C–SH), which can deprotonate depending on the pH of the medium. All of the three iminothiol groups could be methylated with methyl iodide in alcoholic KOH to give trimethylthio derivative [73]. In aqueous solutions of our work, strong alkaline conditions were not present. However, thiol and thione groups along with the nitrogen can contribute to intermolecular and intramolecular hydrogen bonding as well as to the formation of metal complexes.

The drawings showing the pH dependences of metal adsorptions are given in Fig. 4. The experiments were run in triplicate with 25 mL of final solution, which contains 4 mg L^{-1} metal in the buffer and by 1 h mixing after addition of 0.1 g adsorbent. For all metals, adsorption efficiencies were low at acidic pHs below 5 (Fig. 4).

High adsorption efficiencies were met in pH ranges of 5–6, 6–8 and 7–8 for Cu(II), Ni(II) and Cd(II), respectively. Maximum Pb(II) adsorption around 75% was obtained in pH range of 7–8, which was lower than adsorptions of other metals. In case of Cu(II) and Pb(II), higher pHs above the mentioned pH ranges caused formations of metal hydroxides to lessen the sorption by the ligand.

From Fig. 2, pH 5 was selected for Cu(II) adsorption, and pH 7 was selected for Ni(II), Pb(II) and Cd(II) adsorptions. pH 8 or higher pHs were not selected to avoid metal precipitation.

3.1.2. Effect of contact time on the metal adsorptions

The metal-adsorbent equilibration rate is important in the standardization of the enrichment procedure. Thus, metal adsorption efficiencies were determined following the establishment of metal adsorption–desorption equilibria. The model solutions prepared at optimized pHs for each metal were stirred in a temperature-controlled water bath (25°C ± 1°C) for a time period selected between 1 and 105 min. Metal adsorptions by the ligand were studied with different contact times, and metal adsorptions vs. contact times are illustrated in Fig. 5. The contact times were selected as 30 min for Cu(II) and Ni(II) adsorptions and 45 min for Pb(II) and Cd(II) adsorptions to apply in the further adsorption experiments.

The adsorption kinetics for the adsorptions of metals were studied by using linear forms of pseudo-first-order and pseudo-second-order kinetic models, where q_e (mg g^{-1}) is the adsorption capacity at the equilibrium state; q_t (mg g^{-1}) is the amount of the adsorbed metal at time t; k_1 (min^{-1}) is the pseudo-first-order rate constant; and k_2 (g mg^{-1} min^{-1}) is the rate constant for the pseudo-second-order approach [51,74–78].

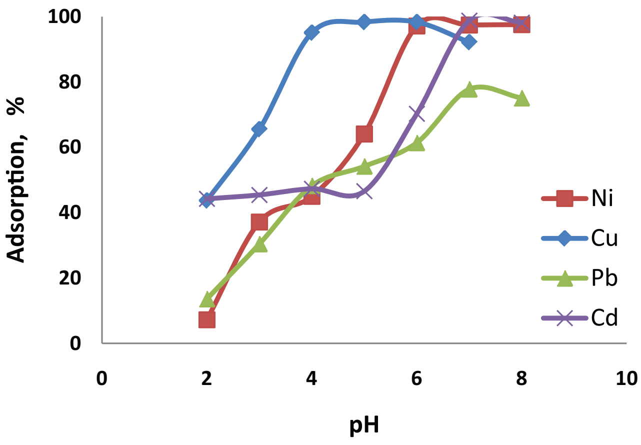


Fig. 4. Effect of pH on the adsorptions of Cu(II), Ni(II), Pb(II) and Cd(II) by the adsorbent: metal concentration – 4 mg L^{-1} in 25 mL final solution; adsorbent – 0.1 g and contact time – 60 min (n = 3).

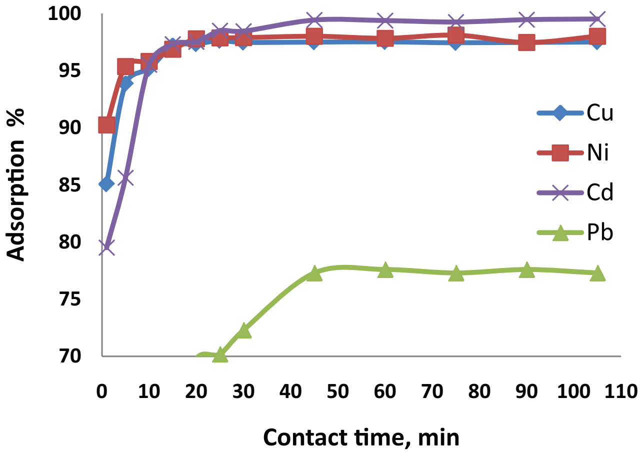


Fig. 5. Effect of contact time on the metal adsorption efficiencies by adsorbent: metal concentration – 4 mg L^{-1} in 25 mL final solution; adsorbent – 0.1 g; Ph – 5.0 for Cu(II) and pH – 7.0 for Ni(II), Pb(II) and Cd(II) (n = 3).

Pseudo-first-order kinetic model: $\ln(q_e - q_t) = \ln q_e - k_1 t$ (2)

Pseudo-second-order kinetic model: $t/q_t = (1/k_2 q_e^2) + t/q_e$ (3)

$\mathrm{Ln}(q_e - q_t)$ vs. t plotting to examine the pseudo-first-order kinetics gave R^2 values lower than 0.96 even in the early stages of adsorption (for the first 20–30 min), but t/q_t vs. t plotting (Fig. 6) gave high R^2 values. Of the models, pseudo-second-order kinetic model fits very well ($R^2 = 0.9992$ for Pb(II) and $R^2 = 1$ for Cu(II), Ni(II) and Cd(II) adsorptions), and Fig. 6 shows the fitting results of pseudo-second-order kinetic model with k_2 constants of 8.76, 15.83, 0.3725 and 2.21 g mg^{-1} min^{-1} for Cu(II), Ni(II), Pb(II) and Cd(II), respectively. The pseudo-second-order model indicates the dependence of the sorbed metal concentrations on the sorption processes, which also included chemisorption as well as complexation.

In order to understand the effective mechanisms in adsorption processes square root analysis of contact time were applied according to the equation $q_t = k_{id} t^{1/2} + c$, where k_{id} is the diffusion coefficient (mg g^{-1} min$^{-1/2}$), and c is the intercept. The plotting between q_t vs. $t^{1/2}$ have given curves from which linear lines had been plotted with R^2 values between 0.5 and 0.7 without passing through the origin to indicate several rate-determining factors (intraparticle diffusion, surface adsorption, film diffusion, etc.), which could be co-effective and competitive in the adsorptions.

3.1.3. Effect of the adsorbent/metal (L/Me) mole ratio

In order to determine the lowest amount of adsorbent for complete removal of certain amount of metals from the solution, the curves were plotted between the adsorption efficiencies and adsorbent/metal mole ratios (Fig. 7) using 0.050–0.500 g sorbent amounts. Ligand/metal mol ratios were found as 1 L:10 Cu; 1 L:3 Ni; 1 L:3 Cd and 1 L:2 Pb. The ratios helped to calculate the lowest ligand amounts for the estimated metal amounts in solutions. Since metal trapping simultaneously occurred via physical and chemisorption processes, the ratios do not reflect the exact metal complex compositions.

3.1.4. Desorption of metals from the sorbent

Desorption conditions of trapped metals from the sorbent with different eluents were studied. 5–20 mL aliquots of HCl (2–5 mol L^{-1}), HNO_3 (2–5 mol L^{-1}) and EDTA disodium salt (0.05 mol L^{-1}) were examined with 45 min contact time at room temperature. The extractant volumes <10 mL yielded insufficient elutions of Cu(II) and Ni(II) for 0.1 g sorbent amount. The triplicate experiments gave mean leaching yields for Cu(II), Ni(II), Pb(II) and Cd(II) ions from the sorbent with 10–20 mL aliquots of the eluents were ~98.5% with 5 mol L^{-1} HNO_3 for Cu(II); 97.0% with 2 M HCl for Ni(II); 93.5% with 3–5 M HCl or 92.9% with 3–5 M HNO_3 for Pb(II) and 98.0% with 2–5 M HCl or 97.6% with 2–5 M HNO_3 for Cd(II). EDTA solution (0.05 M) provided poor recoveries (around 40%–45%) for all metals trapped by the sorbent. Thus, desorption at the room temperature can be performed from 0.1 g sorbent by 10 mL of acidic solutions such as 2 M HCl for Ni(II); 2–5 M HCl for Cd(II); 3–5 M HCl or 3–5 M HNO_3 for Pb(II) and 5 M HNO_3 for Cu(II) and Cd(II) (Table 1). For quantitative leaching from the mixed metal adsorbed samples, the best desorption can be done by use of 5 M HNO_3 or mixed acid solutions such as aqua regia (10 mL) and by heating gently to destroy organic matrix. The evaluations were done using calibration curves that have been plotted with the data obtained from the standard metal solutions prepared with acidic solutions in relevant concentrations.

The recoveries from the column procedure can be done effectively by use of 5 M HNO_3 for all of the concerned metals with flow rate of 2.5 mL min^{-1} (see section 3.2.1).

3.1.5. Adsorption capacities for metals

Adsorption capacity of any material is an indicator to help in the selection of an adsorbent, which will be used for the preconcentration of ions or molecules. Adsorption is a multistep process that consists of monolayer coating followed by film diffusion, intraparticle diffusion and sorption in interior sites. Several isotherm models are available. Of which, Langmuir and Freundlich adsorption isotherms

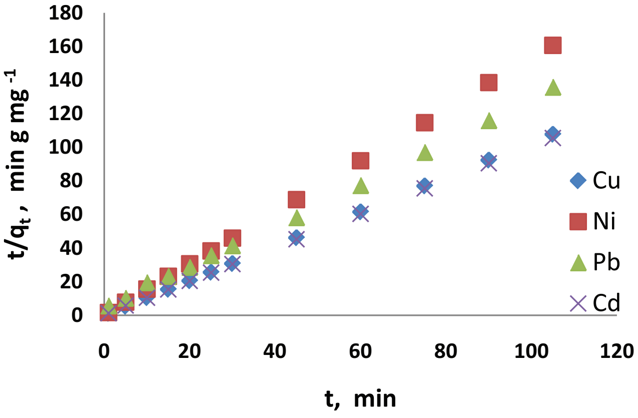


Fig. 6. Pseudo-second-order kinetic model for adsorption of metal ions: metal concentration – 4 mg L^{-1} in 25 mL final solution; adsorbent – 0.1 g; pH – 5.0 for Cu(II) and pH – 7.0 for Ni(II), Pb(II) and Cd(II).

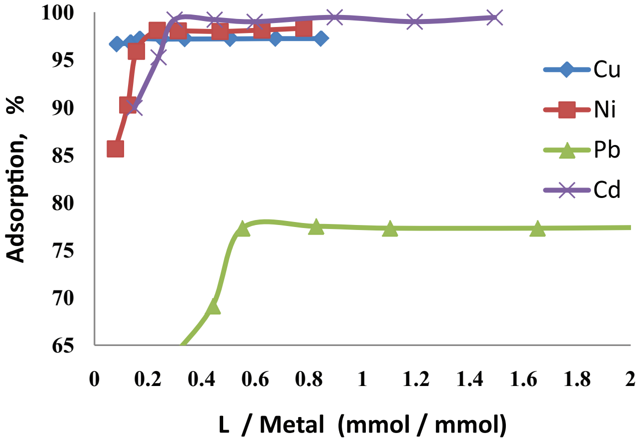


Fig. 7. Effect of ligand/metal mol ratios on the adsorption of metal ions: pH – 5.0 for Cu(II) and pH – 7.0 for Ni(II), Pb(II), and Cd(II) with contact time of 30 min for Cu(II) and Ni(II) and 45 min contact time for Pb(II) and Cd(II) ($n = 3$).

Table 1
Leaching yields of Cu(II), Ni(II), Pb(II) and Cd(II) from the sorbent using different solutions[a,b]

Leaching solution	Volume (mL)	Leaching yield, %			
		Cu(II)	Ni(II)	Pb(II)	Cd(II)
2 M HCl	20	18.32	96.98	88.08	97.98
	15	–	97.01	–	98.01
	10	–	96.78	–	97.89
	5	–	85.87	–	97.15
3 M HCl	20	43.15	94.23	93.45	96.89
	15	–	–	93.88	–
	10	–	–	93.42	–
	5	–	–	93.77	–
4 M HCl	20	50.75	93.75	93.43	97.45
5 M HCl	20	70.23	93.29	93.13	96.45
2 M HNO_3	20	25.67	89.01	89.60	97.86
3 M HNO_3	20	28.76	90.87	92.64	96.49
4 M HNO_3	20	70.87	88.32	92.91	97.65
5 M HNO_3	20	98.48	87.32	91.68	98.45
	15	97.89	–	–	–
	10	98.54	–	–	–
	5	85.16	–	–	–
0.05 M EDTA	20	45.13	43.24	54.55	43.15

[a] Experiments with 0.1 g sorbent and for contact time 45 min.
[b] $n = 3$.

are extensively used [71,72]. While the Freundlich model assumes adsorptions on heterogeneous surfaces with several kinds of binding sites, the Langmuir model assumes equivalent adsorption sites and monolayer adsorptions. The correlations between the experimental data and the models help to deduce the character of the adsorptions. The regression coefficients of isotherm models can be compared along with adsorption capacities.

In order to characterize the interactions between the adsorbent and the metal sorbate, at the equilibrium state of interactions, the metal ion concentrations in the solution and the amount of the adsorbed metal on a definite amount of adsorbent were determined, and the adsorption isotherms were established (Fig. 8).

The linearized Langmuir isotherm allows to calculate adsorption capacities. Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right)C_e \qquad (4)$$

where C_e (mg L^{-1}) is the equilibrium concentration of metal ion in solution; q_e (mg g^{-1}) is the amount of metal adsorbed at equilibrium; K_L (L g^{-1}) and a_L (L mg^{-1}) are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. Maximum monolayer adsorption capacity (mg g^{-1}) is K_L/a_L. From the plotting between (C_e/q_e) and C_e, the slopes (a_L/K_L) and the intercepts $(1/K_L)$ were revealed for each metal (Fig. 9). The Langmuir parameters are given in Table 2.

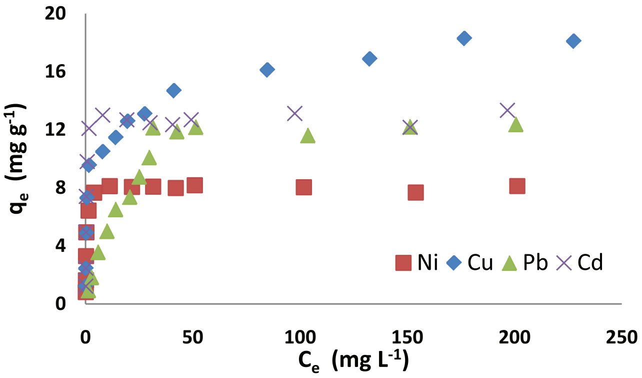


Fig. 8. Adsorption isotherms of Cu(II), Ni(II), Pb(II) and Cd(II).

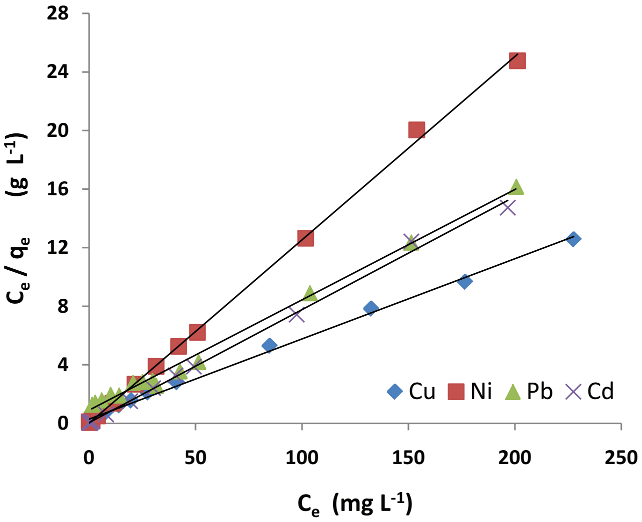


Fig. 9. Langmuir plots for Cu(II), Ni(II), Pb(II) and Cd(II) adsorptions on 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide.

The Freundlich model is represented by its linearized form:

$$\log q_e = \log K_F + (1/n)\log C_e \qquad (5)$$

where q_e (mg g^{-1}) is the amount of the adsorbed metal ion per gram of adsorbent; C_e (mg L^{-1}) is the equilibrium concentration of the metal in the solution. K_F (L g^{-1}) and n are Freundlich constants related to the adsorption capacity and adsorption energy, respectively. From the plots of $\log q_e$ vs. $\log C_e$ values, the slope $(1/n)$ and the intercept $(\log K_F)$ were calculated. Freundlich parameters are given in Table 2.

According to the data of Langmuir and Freundlich isotherm models given in Table 2, Langmuir isotherm model provided a better fit with higher correlation coefficients $R^2 = 0.9963$, 0.999, 0.9938 and 0.9975 for Cu(II), Ni(II), Pb(II) and Cd(II), respectively.

Regarding the Langmuir parameters, the maximal adsorption capacities on 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide were as follows: 18.25 mg g^{-1} for Cu(II), 7.99 mg g^{-1} for Ni(II), 13.26 mg g^{-1} for Pb(II) and 12.96 mg g^{-1}

Table 2
Parameters of Langmuir and Freundlich isotherms for adsorptions of Cu(II), Ni(II), Pb(II) and Cd(II) on 1,5-bis(phenylthiocarbamoyl) thiocarbohydrazide (25°C ± 1°C)

Langmuir isotherm data					
Metal	Equation	R^2	K_L (L g^{-1})	a_L (L mg^{-1})	Capacity K_L/a_L (Q_{max}, mg g^{-1})
Cu	$y = 0.0548X + 0.2933$	0.9963	3.409	0.1868	18.25
Ni	$y = 0.1252X + 0.0226$	0.9989	44.247	5.5398	7.99
Pb	$y = 0.0754X + 0.9062$	0.9938	1.103	0.0832	13.26
Cd	$y = 0.0772X + 0.0520$	0.9975	19.230	1.4840	12.96
Freundlich isotherm data					
Metal	Equation	R^2	K_F (L g^{-1})	n	
Cu	$y = 0.2817X + 0.6969$	0.8610	4.976	3.55	
Ni	$y = 0.2136X + 0.5576$	0.6550	3.610	4.68	
Pb	$y = 0.5051X + 0.1474$	0.8569	1.404	1.98	
Cd	$y = 0.2097X + 0.7703$	0.6365	5.892	4.77	

for Cd(II). The adsorption capacities of metals were at acceptable levels to be used in the preconcentration processes for atomic absorption spectrophotometric analysis [24,26,27,31,79]. Figs. 8 and 9 show the typical adsorption isotherm and Langmuir plot of metals.

The adsorption data obtained for all the interested cations were not fitted well to the Freundlich isotherm model with K_F values between 1.4 and 5.9 L g^{-1} and n values between 1.98 and 4.77 (Table 2). However, the Freundlich parameters indicate normal and favorable adsorptions of cations by the heterogeneous adsorbent (heterogeneity parameter $1/n < 1$). The Temkin model was also examined to understand the uniformity level in distribution of binding energies and found not suitable to use for cations except Cu(II) ($y = 2.0974X + 6.7282$; $R^2 = 0.9837$).

3.1.6. Interference studies

The effects of different ions on metal adsorptions on the adsorbent were studied using the batch procedure. Various nitrate salts of metals were added individually into appropriately buffered solutions containing 4 mg L^{-1} of Cu(II), Ni(II), Pb(II) and Cd(II) ions in 25 mL final solution, and the experiments were performed under the optimum adsorption conditions. The tolerance limit was defined as the ion concentration causing a relative error of ±5% in the adsorption efficiency. The tolerable levels of abundant ions in natural waters (Na^+, Ca^{2+} and Mg^{2+}) were found high. Tolerance level around 1,000 mg L^{-1} for Na^+, K^+, Ca^{2+} and Mg^{2+} were observed for the adsorption of 100 μg metal on 0.1 g of the sorbent for Cu(II), Cd(II) and Pb(II) and on 0.15 g sorbent for Ni(II).

The presence of competing heavy metals significantly reduces the adsorption efficiencies of other metals; in such a case, excess of the adsorbent should be necessary for effective co-adsorption. The experiments were performed to establish the competing adsorptive behaviors of some heavy metals in 10 mg L^{-1} concentration against 0.1 mg of Cu(II), Ni(II), Pb(II) and Cd(II) ions in final solutions of 25 mL. Cu(II) adsorption was affected by the presence of other metals strongly in the order of Cd(II) > Fe(III) > Ni(II) > Pb(II) > Zn(II) > Co(II). The interfering orders of other metals were: Co(II) > Fe(III) > Cd(II) > Zn(II) > Pb(II) > Cu(II); Ni(II) ≥ Fe(III) > Zn(II) > Cd(II) ≥ Co(II) > Cu(II); and Co(II) > Fe(III) > Zn(II) > Ni(II) > Pb(II) ≥ Cu(II) for Ni(II), Pb(II) and Cd(II) adsorptions, respectively, from which metal coordinating tendencies of the ligand can be deducted. In the presence of various metal ions, the ligand should give polynuclear complexes in different compositions.

3.2. Column procedure

Use of columns in preconcentration process has the advantage of the continuous working with high volumes of samples as well as working in the flow injection analysis.

The analytical operation can be planned properly by the establishment of several operational parameters such as sorbent amount, sorbent volume and length in the column, sample and eluent volumes, sample and eluate flow rates, number of the percolation cycles, etc. In the application of column work, the experimental data from the batch method are used.

3.2.1. Effect of sample and eluent flow rates

The effect of flow rate on the adsorption of Cu(II), Ni(II), Pb(II) and Cd(II) on 1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide column was investigated with the flow rates in the range of 1.0–7.5 mL min^{-1} at 25.0°C ± 1.0°C. The metal solutions (1 mg L^{-1} or less) were adjusted to optimum adsorption pH of the metal, and 100 mL of the solution was passed through the column by using a peristaltic pump. The adsorption efficiencies achieved at different flow rates are illustrated in Fig. 10(a). Contrary to other metals did, Pb(II) was adsorbed with poor yields of around 72%–75%. Increase in the flow rate caused decreasing on the Cu(II), Ni(II), Pb(II) and Cd(II) adsorptions. The optimal flow rate for Cu(II), Ni(II), Pb(II) and Cd(II) adsorptions was determined as 2.5 mL min^{-1}.

Following the adsorption step, metal ions trapped by the sorbent were eluted with appropriate volumes of eluents, and the eluates were diluted with 1 N HCl to be analyzed by FAAS using multipoint calibration curves, which were plotted with the absorptions of standard metal solutions prepared in 1 N HCl. 2–5 M HCl was used for effective desorption of Ni(II), Pb(II) and Cd(II). 5 M HNO_3 was used in the leaching of all the concerned metals from the column.

Eluents containing nitric acid (5 M HNO_3) were evaporated to get a dampy residue. The residues were dissolved and diluted with 1 N HCl to a known volume.

Maximum metal desorption from the sorbent were studied with the flow rates between 1.0 and 7.5 mL min^{-1}. Fig. 10(b) illustrates dependences of overall metal recoveries on the flow rates of the eluents. The optimal flow rates of stripping eluents for all the interested metals were found as 2.5 mL min^{-1} (Fig. 10(b)). The results of the examples given in Fig.10(b) indicated that compared with the batch process in which same volumes of the eluents were used, the column process yielded better overall recoveries with improvements around 0.25% for Pb, 2.9% for Cd, 15.2% for Cu and 4.1% for Ni.

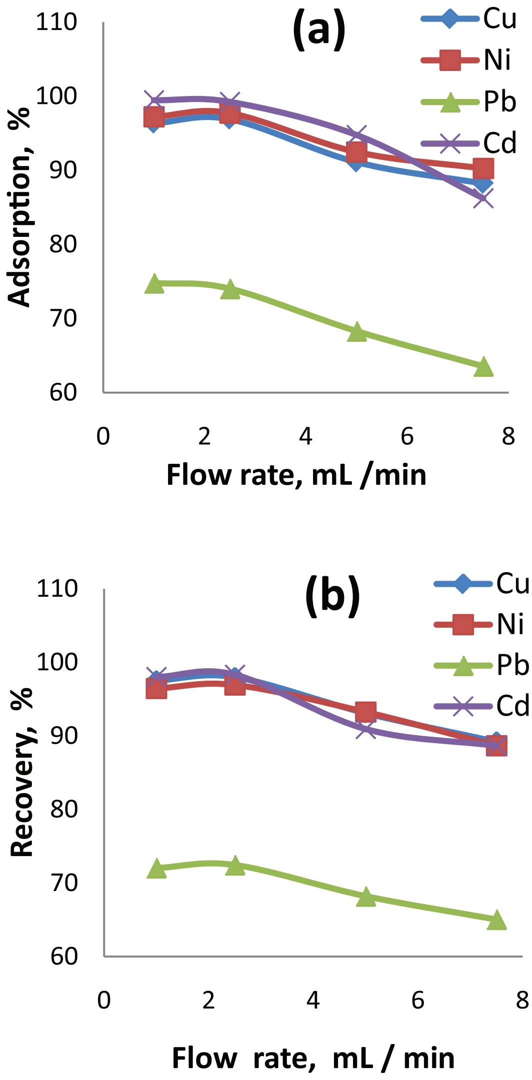


Fig. 10. Effect of flow rate on metal adsorption (a) and overall metal recoveries with appropriate eluents (b): metal concentration – 1 mg L^{-1}; volume of solution – 100 mL; amount of solid phase – 0.10 g adsorbent + 0.40 g silica gel ($n = 3$); eluents (5 mL) – 5 M HNO_3, 2 M HCl (10 mL), and 3 M HCl and 3 M HCl for Cu(II), Ni(II), Pb(II), and Cd(II) desorption, respectively ($n = 3$).

3.3. Enrichment factors

The effect of sample volumes on the adsorption of metal ions was investigated by passing 100–1,000 mL of buffered solutions through the column with 2.5 mL min^{-1} flow rate. The adsorbed Cu(II) was eluted with 10 mL of 5 M HNO_3. Ni(II), Pb(II) and Cd(II) ions were eluted by 10 mL of 2 M HCl, 5 mL of 3 M HCl and 5 mL of 3 M HCl, respectively. The maximum analyte volumes corresponding to the overall adsorption efficiencies were found from the curves given in Fig. 11. Regarding the eluent volumes for each metal, the enrichment factors of Cu(II), Ni(II), Pb(II) and Cd(II) ions on 1,5-bis(phenylthiocarbamoyl) thiocarbohydrazide were found to be as 30, 65, 26 and 50, respectively.

3.4. The detection and determination limits and analytical precision of the method

The proposed enrichment method including the FAAS step was applied to find the detection and determination limits of the procedure. The detection and determination limits were

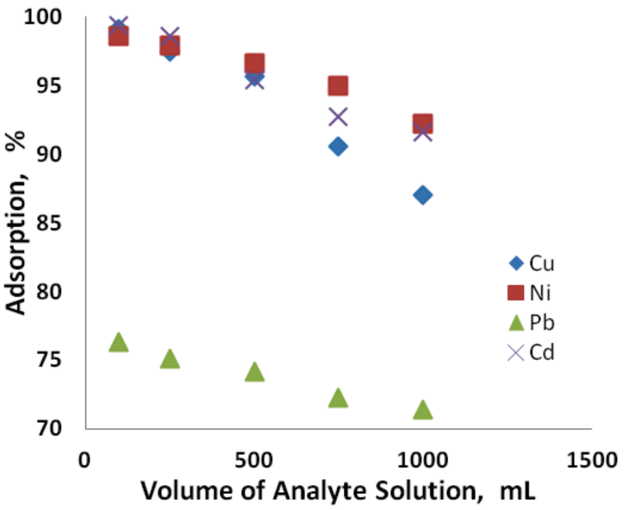


Fig. 11. Effect of sample volumes on the adsorptions of Cu(II) (1.5 mg), Ni(II) (0.8 mg), Pb(II) (1.3 mg) and Cd(II) (1.0 mg) on the column material prepared from 0.10 g ligand and 0.40 g silica gel ($n = 3$).

Table 3
Overall reproducibilities in metal recovery ($n = 10$)[a]

	Metal	Mean ± $t.\sigma/N^{1/2}$	SD	RSD %
Intraday	Cu(II)	97.03 ± 0.59	0.82	0.84
	Ni(II)	95.14 ± 0.62	0.87	0.91
	Pb(II)	71.86 ± 0.92	1.28	1.78
	Cd(II)	98.06 ± 0.44	0.61	0.62
Interday	Cu(II)	96.53 ± 0.92	1.29	1.33
	Ni(II)	97.63 ± 0.88	1.24	1.27
	Pb(II)	74.48 ± 0.92	1.29	1.73
	Cd(II)	98.70 ± 1.01	1.42	1.43

[a] With 95% confidence.

calculated by using the equations $X = 3$ SD/slope and $X = 10$ SD/slope and the enrichment factor, where SD is standard deviation of the blank values. The LOD were found to be 0.73, 0.05, 0.17 and 0.04 ng mL^{-1}, and the determination limits (LOQ) were found to be 2.4, 0.15, 0.56 and 0.13 ng mL^{-1} for Cu(II), Ni(II), Pb(II) and Cd(II), respectively. Analytical precisions were determined for different concentrations of metals by repeated experiments in the same day and in the consecutive days. The RSD were lower than 2.0%, which indicated that the method presented good precisions for the analyses of interested metals (Table 3). Since recoveries for Pb were around 72%–75% with enrichment factors below 20, regarding the high precision in Pb analysis (RSD around 1.8%), one can analyze Pb with confidence by using a correction factor corresponded to maximum recovery, which should be determined separately.

Table 4
The overall recoveries (%) obtained from the real samples with 95% confidence level ($n = 5$).

Metal	Tap water	Mineral water[a]	Seawater[b]
Cu	97.3 ± 0.3	96.2 ± 0.6	97.3 ± 0.5
Ni	96.5 ± 0.7	96.4 ± 0.6	95.8 ± 0.4
Pb	72.0 ± 0.5	72.2 ± 0.6	69.8 ± 0.4
Cd	98.8 ± 0.9	98.4 ± 0.2	96.5 ± 0.5

[a] Na: 189 mg L^{-1}; K: 29 mg L^{-1}; Ca: 223.6 mg L^{-1}; Mg: 81.4 mg L^{-1}; HCO_3^-: 1,493 mg L^{-1}; Cl$^-$: 95 mg L^{-1}; F:1.3 mg L^{-1}; SO_4^{2-}: 27 mg L^{-1}.
[b] Surface water: 0.5 m depth; salinity ‰: 21.5; pH: 7.85.

3.5. Application of the method with real samples

The proposed method has been applied to determine trace amounts of Cu(II), Ni(II), Pb(II) and Cd(II) in water

Table 5
Comparative data for some recent studies for preconcentration of Cu(II), Ni(II), Pb(II) and Cd(II)

	Adsorbent	pH	Adsorption capacity, mg g^{-1}	EF[a]	LOD, ng mL^{-1}	RSD %	Eluent	Ref
Cu(II)	2-Aminothiophenol + XAD-2	6	292	14	0.54	6.1	0.5 M HCl	[80]
	XAD-2010/DDTC	6	6.3	100	0.12	2.1	1 M HNO_3/ acetone	[81]
	Silica gel-2-aminothiazole modified	5	100.4	–	0.28	4.0	2 M HCl	[47]
	Dithizone-modified chitosan		210		0.18	–	–	[82]
	Di-2-pyridylketone thiosemicarbazone / XAD-4	6	–	200	30	–	1 M HNO_3/ acetone	[83]
	Silica gel-aminothioamido-anthraquinone modified	3.5	19		1.0	<5	–	[84]
	The proposed sorbent	5	18.25	30	0.73	0.8	5 M HNO_3	This work
Ni(II)	Silica gel 2-amino thiazole modified	5	67.5	–	0.53	4.0	2 M HCl	[47]
	Silica gel-aminothioamido-anthraquinone modified	4.5	9		2.9	<5		[84]
	Di-2-pyridylketone thiosemicarbazone/XAD-4	6	–	200	30	–	1 M HNO_3/ acetone	[83]
	XAD-2010/DDTC	6	6.1	100	0.15	2.8	1 M HNO_3/ acetone	[81]
	The proposed sorbent	7	8.0	65	0.05	0.9	2 M HCl	This work
Pb(II)	XAD-2010/DDTC	6	5.7	100	0.26	5.1	1 M HNO_3/ acetone	[81]
	Silica gel-aminothioamido-anthraquinone modified	3.5	116		22.5	<5		[84]
	The proposed sorbent	7	13.3	–	1.14	1.8	3 M HCl	This work
Cd(II)	2-Aminothiophenol + XAD-2	8	416	28	0.14	5.8	0.5 M HCl	[80]
	XAD-2010/DDTC	6.	6.0	100	0.08	1.9	1 M HNO_3/ acetone	[81]
	Silica gel-2-aminothiazole modified	5	123.6		0.27	4.0	2 M HCl	[47]
	Silica gel-aminothioamido-anthraquinone modified	3.5	7.9		1.1	<5	HNO_3 1%	[84]
	The proposed sorbent	7	13.0	50	0.04	0.6	2 M HCl	This work

[a] Enrichment factor.

samples. To find the accuracy of the method, the metal ions in the spiked and unspiked samples (60 mL) of tap water, mineral water and seawater were concentrated by the proposed batch method after dilution to 100 mL with appropriate buffer solution, desorbed from the sorbent and analyzed by FAAS. The spiked samples were prepared by the addition of 200 and 400 μL of 10 mg L^{-1} metal solutions to obtain 20 and 40 μg L^{-1} metal solutions. The adsorbed metals were desorbed with appropriate leaching solutions such as 2 M HCl for Ni(II) and Cd(II), 3 M HCl for Pb(II) and Cd(II) or 5 M HNO_3 for Cu(II).

Of the metals, only Cu(II) was naturally found in the tap water and seawater samples in 1.8 and 2.7 μg L^{-1} concentrations, respectively. The overall recoveries of the method were in the range of 96%–99% for Cu(II), Ni(II) and Cd(II) (Table 4). The seawater with salinity around 21‰ slightly affected Pb(II) and Cd(II) determinations by reducing the recoveries by around 2.0% and 1.5%, respectively. Matrix components in mineral water affected only Cu(II) adsorption. Tap water has not significantly affected the adsorptions of interested metals. The results showed that the adsorbent could be used satisfactorily in quantitative determinations of trace Cu(II), Ni(II) and Cd(II) ions in water samples, and the proposed method was reliable for the preconcentration of these metal ions. Although the overall Pb recoveries were around 72%, the RSD values were below 2%, and one could analyze Pb with confidence by using a correction factor calculated from the recovery determined for a definite chemical environment. Similar Pb recoveries in drinking water have been reported in the literature [84].

3.6. Comparison with other sorbents

The effectiveness of the proposed sorbent for Cu(II), Ni(II), Pb(II) and Cd(II) preconcentrations were compared with some of the other sorbents, which bear electron-donating N and S atoms (Table 5). Although low LOD values obtained with the proposed sorbent are comparable with other sorbents, the adsorption capacities maintain the preconcentrations of metals at moderate levels and help to analyze metals with high precision.

4. Conclusions

1,5-bis(phenylthiocarbamoyl)thiocarbohydrazide has been found as a good sorbent for Cu(II), Ni(II), Pb(II) and Cd(II) enrichments for the determinations on an atomic adsorption spectrophotometer. Pb(II) recovery is low (72%), but reliable with RSD of 1.8%. The metal adsorption on the proposed ligand has not been affected significantly by the matrix ions of the environment. The sorbent exhibited good adsorption/elution characteristics. The Langmuir, Freundlich and Temkin isotherm models were examined for metal adsorptions. The Langmuir isotherm model provided a better fit with high correlation coefficients. Although the metal adsorptions were not fitted well to the Freundlich and Temkin models, the Freundlich parameters indicated normal and favorable adsorptions of cations by the heterogeneous sorbent (heterogeneity parameter $1/n < 1$). The adsorption kinetics for the adsorptions of metals were studied by using linear forms of pseudo-first-order and pseudo-second-order kinetic models. Pseudo-second-order kinetic model fitted very well to the experimental data of adsorptions. The proposed sorbent was easy to prepare, and its use was successful in the effective trapping of metal ions from large volumes of samples. The procedure is a promising method for enrichment of studied metal ions in environmental aqueous samples including natural waters. The column process was found superior to the batch process regarding its short analysis time and effectiveness in the adsorption and desorption procedures.

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