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Determination of trace metal ions in water and plant samples using polyurethane foam modified with 2-aminothiazole

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ABSTRACT

2-Aminothiazole (AT) was covalently bonded to polyurethane foam (PUF) via –N=N–NH– group and used for preconcentration/separation of Ni(II), Zn(II), and Cd(II) from water, black tea, and plant leaves prior to flame atomic absorption spectrometry determination. The resulting AT–PUF sorbent was characterized by density measurement, elemental analysis, UV–vis, and IR spectroscopy. The optimum sorption of these elements was achieved at sample pH 5–6. The sorption capacity was found to be 461 ± 1.4, 341 ± 1.3, and 435 ± 2.4 μg g^{-1} and limit of detection (3σ) was 2.0, 3.0, and 3.0 μg L^{-1} for Ni(II), Zn(II), and Cd(II), respectively. The preconcentration factor was 100 for all elements. The developed method was successfully applied for determination of these elements in tap and lake water, spinach and parsley leaves, and black tea samples and the corresponding relative standard deviation values were less than 10%.

Keywords: 2-Aminothiazole; Polyurethane foam; Preconcentration; Metal ions; Water and plant analysis

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1. Introduction

Heavy metals pollution has received tremendous attention because of their ecological risk to aquatic organisms. Toxic heavy metals could also gradually accumulate in human body through food chain and cause damage to human health [1]. They are supposed to be carcinogenic [2], and can damage liver, nerves, and bones as well as interfere with the normal functioning of various metalloenzymes [3]. Heavy metals discharging from a number of industries into wastewaters would create problems [4].

Various techniques have been applied for the determination of trace heavy elements in environmental samples. Among those are the flame atomic absorption spectrometry (FAAS) [5,6], graphite furnace atomic absorption spectrometry [7], inductively coupled plasma optical emission spectrometry [8], and inductively coupled plasma mass spectrometry [9].

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However, the direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. Therefore, a preconcentration and/or separation of trace elements from the matrix are frequently necessary to improve the detection limit and selectivity of determination [10]. Several preconcentration techniques have been extensively developed; however, the solid phase extraction (SPE) technique has been increasingly utilized for preconcentration and separation of trace and ultra-trace amounts of metal ions from various matrices [11].

Polyurethane foam (PUF) is a good sorbent for SPE since it has several advantages over other solid sorbents. It is commercially available, easy to prepare, high surface area, cellular structure, and extremely low cost. Chemical modification of PUF is necessary to increase its selectivity and capacity. Therefore, several reagents have been grafted to PUF such as Nile blue A [12], methylene blue, rhodamine B, and brilliant green [13]. Methylene blue grafted PUF was successfully utilized for online preconcentration of some penicillins [14]. Moreover, the residual primary aromatic NH_2 groups in toluidine moieties were diazotized [15] and azo coupled to several reagents such as 2-aminophenol and subsequently to ß-Naphthol, acetylacetone, and pyrazolone [16]. Also, phenylhydrazone ligand was chemically attached to PUF [17]. Furthermore, azo–hydrazo linkage (–N=N–NH–) was utilized to anchor 2-aminoacetylthiophenol ligand [18]. Quantitative and/or semiquantitative determination of submicrogram amounts of nitrite could be obtained by the treatment of diazotized PUF with α-naphthylamine, α-naphthol, β-naphthol, 8-hydroxyquinoline, resorcinol, or catechol to give azo dye [12]. Furthermore, many organic reagents were physically immobilized onto PUF such as TAC (2-(2-thiazolylazo)-p-cresol) for the determination of cobalt [19], and 2-(2-benzothiazolylazo)-2-p-cresol (BTAC) for the determination of lead [20].

The present study describes the synthesis of the novel sorbent 2-aminothiazole bonded polyurethane foam (AT–PUF) by simple and one-step coupling reaction between the diazotized PUF and $-NH_2$ groups in AT. Parameters that can influence the sorption and elution efficiency of the studied metal ions were investigated in batch and column modes. Finally, the new methodology was applied for the determination trace of Ni, Zn, and Cd in tap and lake water, black tea, and plant leaves.

2. Methodology

2.1. Apparatus

Flame atomic absorption spectrometer model AAS5 FL instrument manufactured by Carl-Zeiss (Darmstadt, Germany), working with air–acetylene flame, was used for the determination of Ni(II), Zn(II), and Cd(II). The optimum operational conditions are depicted in Table 1. The pH measurements were carried out on a WTW 720 pH meter with a combined glass electrode (Dover Kent, UK). Wrist action mechanical shaker model E175 purchased from Burrel (PA, USA) was used for shaking the samples. Vario ELIII Elemental analyzer (Hanau, Germany) was used for CHN analysis. Thermo Scientific Nicolet FT-IR model 6700 (Illinois, USA) was used to record the infrared spectra in the range 400–4,000 cm^{-1} via KBr technique.

2.2. Chemicals and reagents

The reagents used in this work were of analytical-reagent grade. Doubly distilled water (DDW) was used to prepare all solutions. AT with MW 100.14 g mol^{-1} was obtained from Merck (Darmstadt, Germany). Stock solutions (1,000 μg mL^{-1}) of nickel, zinc, and cadmium were prepared by dissolving appropriate amounts from $NiSO_4.6H_2O$ (Fluka, Switzerland), $ZnSO_4.7H_2O$ (Merck, Germany), or $Cd(NO_3)_2.4H_2O$ (Panreac, Barcelona, Spain), respectively, in DDW. A 2.0 mL from concentrated H_2SO_4 or HNO_3 (Adwic, El-Nasr, Egypt) was added; then the solution was diluted to one liter with DDW. Working solution

Table 1
Operational conditions for measurement of Ni(II), Zn(II), and Cd(II) ions by FAAS

	Metal ions		
Parameters	Ni(II)	Zn(II)	Cd(II)
HC lamp current (mA)	6.0	4.0	2.0
Slit width (nm)	1.2	0.5	1.2
Wavelength (nm)	232.0	213.9	228.8
Fuel flow rate (mL/h)	55	50	50
Burner height (mm)	5–12	4–10	4–12

Notes: Regression equations: Ni(II): $A = 0.02688\ C + (0.00079)$ $R^2 = 0.99692$.
Zn(II): $A = 0.10919\ C + (-0.00082)$ $R^2 = 0.99202$.
Cd(II): $A = 0.12272\ C + (0.0017)$ $R^2 = 0.99995$.

(10.0 μg mL^{-1}) was prepared daily by appropriate dilution from the stock solutions. The pH adjustments were made by 0.1 mol L^{-1} HCl or NaOH solutions (Adwic, Egypt). Commercial open-cell polyether type PUF sheet with density of 20 kg m^{-3} was kindly provided from a local company (Cairo, Egypt) and used for synthesis of AT–PUF sorbent. The sheet was cut with metallic slicer into similar plugs (1 cm length and 50 mm diameter), washed with 1.0 mol L^{-1} of HCl solution, DDW, and finally ethanol. Then, they were squeezed between clean sheets of filter paper and dried in air.

2.3. Preparation of AT–PUF chelating sorbent

One gram of PUF plugs was soaked in 50% (v/v) HCl for 5.0 h to release the maximum number of free NH_2 groups via hydrolysis of residual isocyanate and some urethane groups. Thereafter, the plugs were washed with DDW and submerged into a 100 mL of 0.1 mol L^{-1} HCl solution and then cooled in an ice bath. Diazotization of PUF was affected by the dropwise addition of 1.0 mol L^{-1} sodium nitrite solution to the cooled mixture with vigorous stirring. The PUF plugs attained the yellow color due to the formation of diazonium salt [21]. Completion of diazotization reaction was identified by the appearance of blue color when testing the mixture with starch–iodide paper as an evidence for excess nitrite. Further, the mixture was cooled below 3°C for 1.0 h. The diazotized PUF plugs were filtered, washed with ice-cold water and rapidly transferred into the AT solution prepared by dissolving 4.2 g AT in 100 mL of 1.0 mol L^{-1} sodium acetate in ethanol 50% (w/v), and the final mixture was left in the fridge for 24 h [18]. The resulting reddish brown plugs from the newly formed AT–PUF sorbent were washed with ethanol followed by DDW and then dried at ambient temperature and stored in a dark glass bottle.

2.4. General procedures

2.4.1. Batch procedure

A 20 mL model solution containing individual metal ion at a concentration of 1.0 μg mL^{-1}, was shaken for 1 h with 100 mg of AT–PUF plugs at room temperature. The sample pH was examined in the range 2–9. After extraction, the retained metal ions in the plugs were desorbed by shaking the sorbent with 10 mL of 0.4 mol L^{-1} hydrochloric acid solution and the amount of metal ion in eluate was determined by FAAS. The shaking time was tested at different time intervals ranging from 2 to 60 min.

2.4.2. Column procedure

A 1.0 g plug from AT–PUF sorbent was packed into a glass column (20 cm length and 1.0 cm i.d) plugged with a stopcock by applying gentle pressure with a glass rod. The packed sorbent was about 2.0 cm bed height and it was permanently immersed in the solution to avoid the formation of any bubbles or channels within the bed. The packed column was used repeatedly after washing it with 0.1 mol L^{-1} HCl solution followed by DDW till the effluent was neutral. A 20 mL aliquot containing 20 μg of each metal ion was adjusted to pH 6.0 and percolated through the column at a flow rate of 3.0 mL min^{-1}. The adsorbed metal ions were eluted by passing 10 mL of 0.4 mol L^{-1} HCl solution at the same flow rate and the content of each metal ion in the eluate was quantified by FAAS.

2.5. Sample preparation

2.5.1. Lake and tap water

Lake water sample was collected from Qaroun Lake at Fayoum City, while tap water was taken from our research laboratory at chemistry department in Fayoum University. Tap water was analyzed without further purification while lake water was filtered to remove any suspended particulates. The pH of lake water was found to be 7.9. The collected samples were acidified to pH 2.0 with nitric acid in order to prevent precipitation of metal ions, and then kept in clean polyethylene bottles. Analysis was performed by spiking 100 mL of water sample with each metal ion to concentration level of 1.0 μg mL^{-1} and adjusted to pH 6.0. The final solution was immediately percolated through AT–PUF column at flow rate of 3.0 mL min^{-1}. The retained metal ions were eluted by 10 mL of 0.4 mol L^{-1} HCl solution and then measured by FAAS. The experiment was performed in triplicate. The recovery percentage (*R*%) and relative standard deviation (RSD%) were calculated.

2.5.2. Black tea, spinach, and parsley leaves

Black tea and fresh leaves from spinach and parsley were obtained from nearby market at Fayoum City. The samples were washed with DDW and then dried in an oven at 85°C for 24 h. Afterwards, they were ground into fine powder using porcelain mortar. Each dry sample was digested using the reported procedure [22]. An accurately weighed portion of 0.2 g of the dry sample was put into a Teflon cup, and 4.0 mL of 50% (v/v) nitric acid solution was mixed to the powdered sample; then acid digestion was performed by heating the bomb in a stove at 150˚C for 5.0 h. After cooling at room temperature, the bomb was opened carefully in a fume cupboard. The pH of the final digests was neutralized by suitable addition of a 10% (w/v) sodium hydroxide solution and the resulting mixture was adjusted to pH 6, made up to 25 mL by DDW, and then percolated through AT–PUF columns at the optimum sorption conditions. The amount of metal ion in sample Q (μg g^{-1}) was calculated as follow: $Q = (C_f \times V_0)/m$, where C_f, V_0, and m are the concentration (μg mL^{-1}), volume (mL), and dry weight (g) of sample, respectively.

3. Results and discussion

3.1. Characterization of AT–PUF

The density of untreated PUF and AT–PUF were found to be 20 and 37 kg m^{-3}, respectively. The higher density of AT–PUF sorbent than PUF might be attributed to the inter-bonding between the AT ligand and the PUF backbone via NH_2 groups resulted from the hydrolysis of terminal isocyanate (–NCO) and urethane (–NHCOO–) groups [23].

Elemental analysis data for the PUF and AT–PUF materials were compared. For PUF material, it was found that: C, 62.09; H, 8.9; and N, 4.65%; calculated for the chemical formula $C_{78}H_{134}N_5O_{23}$: C, 62.07; H, 8.89; and N, 4.64%. However, for AT-PUF sorbent, it was found that: C, 61.86; H, 7.94; N, 6.52%; and S, 0.51; calculated for $C_{81}H_{135}N_8O_{23}S$: C, 60.04; H, 8.34; N, 6.92; and S, 1.98%. Obviously, the analysis data of PUF and AT–PUF are in good agreement with the calculated values by presuming the stoichiometry of their repeat units in PUF. The deviation was in the range of 0.01–0.25 and 0.4–1.82%, respectively. Additionally, the content of sulfur in AT–PUF was found to be 0.51%. Thus, the number of anchored AT groups to PUF was found to be 0.159 mmol g^{-1}.

The UV–visible spectra were performed by using thin films from PUF and AT–PUF materials with an average dimension of 0.5 cm × 1.0 cm. The film was placed in quartz cell and dimethyl formamide was added as a blank. The recorded spectrum for PUF showed weak absorption peak at wavelengths less than 280 nm. Controversially, the AT–PUF gave a new absorption peak at 481 nm which confirmed the attainment of reddish brown color by the developed sorbent.

The FTIR spectrum of AT–PUF is presented in Fig. 1. Characteristic peaks were observed at 1,545.67, 1,653.66, and 874.02 cm^{-1} assigned for –N=N–, –N=C, and C–S stretching vibrations, respectively. Also, the broad peaks of –NH and–CO in the urethane (–NHCOO–) group were shifted to 3,366.14 cm^{-1} and 1,713.44 cm^{-1}, respectively, in the spectrum of AT–PUF. Moreover, the peak belongs to the isocyanate (–NCO) groups in PUF appearing at 2,100 cm^{-1} was disappeared in the AT–PUF spectrum. Therefore, the appearance of these new peaks confirmed the coupling between diazotized PUF and AT ligand through –N=N–NH– group. Finally, the proposed chemical structure of AT–PUF sorbent is presented in Fig. 2.

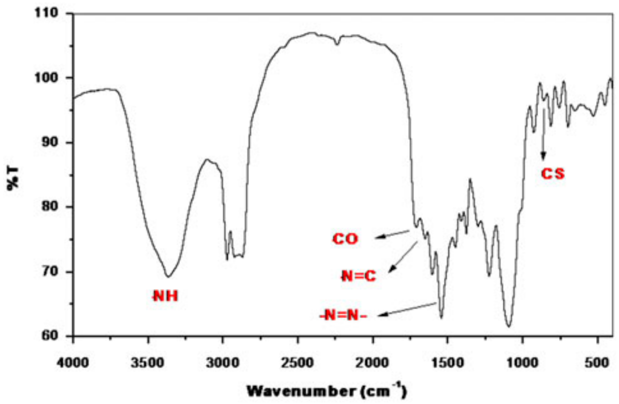

Fig. 1. Infrared spectrum of 2-AT–PUF sorbent.

Chemical stability of AT–PUF was examined in different solvents to investigate the possible leaching of AT reagent. In batch mode, 100 mg of AT–PUF was immersed in 25 mL of the tested solvent and shaken for 1.0 h. The sorbent was filtered and the leached AT was determined by spectrophotometry. Several solvents were tested such as 1.0–6.0 mol L^{-1} H_2SO_4 and HCl, 2.0–4.0 mol L^{-1} of NaOH, and organic solvents such as ethanol, methanol, isopropyl alcohol, diethyl ether, and acetone. Results showed that no ligand was detected in effluent which indicates good chemical stability of AT–PUF sorbent.

3.2. Batch procedures

3.2.1. Influence of solution pH

The pH of the solution plays significant role in the sorption of metal ions, because H$^+$ can protonate binding sites in the chelating compound. Also, the OH$^-$ in

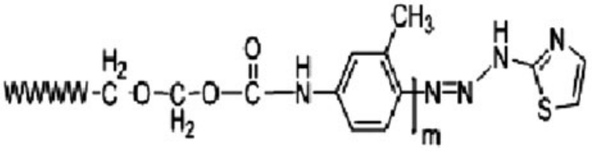

Fig. 2. Proposed chemical structure of 2-AT–PUF sorbent.

basic medium may complex with or precipitates the metal ions [24–26]. Therefore, the influence of initial pH of solution on the sorption was investigated within the range of 2.0–9.0. The obtained results are shown in Fig. 3. Sorption (%) of each metal ion was gradually increased with rising pH from 2 to 4. Maximum sorption was reached at pH 5.0–6.0 with values of 93, 91, and 98%, respectively. Lower sorption at low pH than 4 might be due to the competition of H^+ to the active sites at N and S atoms, which become no longer available to adsorb metal ions. The data reveal maximum sorption (%) at pH range 5.0–6.0 could be attributed to the presence of lone pair of electrons on active sites in sorbent, making them suitable for coordination with metal ions. The sorbent surface becomes more electron donor; thus, increasing the attraction between the metal ions and sorbent. At pH higher than 6, the sorption decreases because of the possible precipitation of metal hydroxides. The high sorption of metal ions indicates good interaction between metal ion and attached ligand in the sorbent. Finally, all subsequent experiments were carried out at sample pH 6.0.

3.2.2. Sorption kinetics

Different shaking intervals ranging from 2 to 60 min were tested at room temperature. Sorption (%) of metal ions was increased with increasing the shaking time and reached equilibrium state after 25 min. In the early shaking time intervals, low sorption (%) was observed which might be due to less contact time between solid sorbent and metal ion. By extrapolating the shaking intervals, the sorption (%) was increased due to the sufficient contact time where equilibrium state was reached after 25 min. This fast equilibration time conveys the diffusion of these metal ions throughout the sorbent might be via hypothetical film or hydrodynamic boundary [27]. Thus, a 30 min shaking interval was found suitable for attaining the equilibrium state.

The kinetic mechanism which might control the sorption process was investigated. The pseudo-first-order model [17] was examined to fit the experimental results and it can be represented by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{1}$$

where q_t and q_e are the adsorbed amount (μg g^{-1}) of metal ion at any time t and at equilibrium, respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}). The obtained linear plots are presented in Fig. 4. The calculated k_1 values were found to be 0.095, 0.156, and 0.099 min^{-1}, and the correlation coefficient (R^2) values were 0.996, 0.983, and 0.993 for Ni(II), Zn(II), and Cd(II), respectively. The obtained values of R^2 showed that the experimental data could be successfully described by pseudo-first-order mechanism. Also, the values of half-life time ($t_{1/2}$) of the pseudo-first-order mechanism are 7.3, 4.4, and 7.1 min, respectively. This short time period confirms the rapid transfer of metal ions into the sorbent during the early shaking stages. Additionally, the practical utility of the developed sorbent might be feasible for dynamic sorption which requires fast rate of sorption. The difference in values of k_1 revealed that the rate of sorption is mainly depending on the chelation reaction

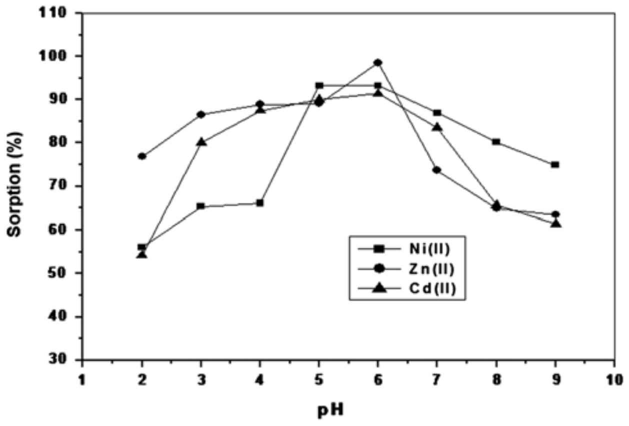

Fig. 3. Effect of pH on the extraction of Ni(II), Zn(II), and Cd(II) by 2-AT–PUF sorbent (20 mL sample, concentration of each metal ion of 1.0 μg mL^{-1}, and 100 mg sorbent).

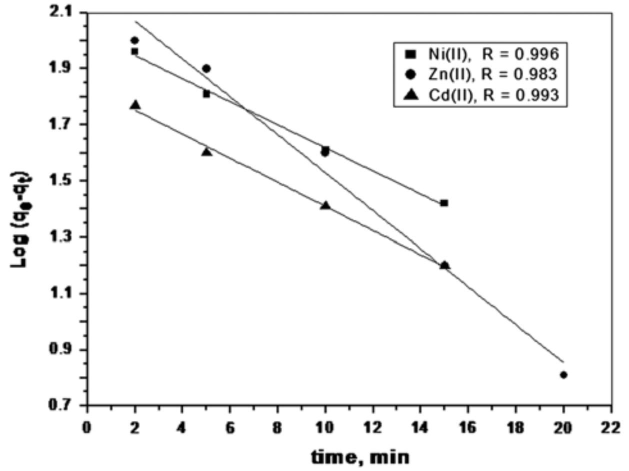

Fig. 4. Lagergren plottings for pseudo-first-order model of Ni(II), Zn(II), and Cd(II) with 2-AT–PUF sorbent.

between the anchored chelating ligand and the tested metal ion.

Pseudo-second-order model suggested by Ho and co-workers [28], represented in Eq. (2), has been also examined to fit the experimental results.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{2}$$

where k_2 is the pseudo-second-order rate constant (g μg^{-1} min^{-1}). The obtained values of R^2 were 0.887, 0.947, and 0.908, respectively, which are less than those obtained by the pseudo-first-order model. Thus, this kinetic model is inconvenient for interpretation of the experimental kinetics data. Finally, the sorption process was found to follow the first-order kinetics.

Intra-particle diffusion behavior was examined by testing the Morris–Weber model [29], represented in the following equation:

$$q_t = R_d \quad t^{1/2} \tag{3}$$

where R_d is the rate constant of intra-particle diffusion with dimension of μg g^{-1} min$^{-1/2}$.

Noteworthy, the PUF material is highly porous with spherical and symmetrical macropores and micropores. The macropores are relatively large compared with the molecular size of the solute and readily accessible to the solute. Sorption into the macropores is rapid and characteristic of film diffusion. In contrast, the micropores are similar in size to the solute molecule. Diffusion in such pores would be severely hindered due to steric interaction, so that the subsequent slow approach to equilibrium would be characteristic of an intra-particle diffusion process.

Fig. 5 shows the plotting of intra-particle diffusion model. It could be seen that the data were linear with a regression coefficient (R^2) of 0.988, 0.959, and 0.978, and the values of R_d were 28.9, 35.2, and 16.8 μg g^{-1} min$^{-1/2}$, respectively. However, the data plot did not pass through the origin, thereby, indicating that a film-diffusion process also occurred during the initial sorption stage. This behavior indicated that although intra-particle diffusion still contributes to the control of the sorption rate, the film diffusion process can also play an important role during this period of time. Thus, the bulk sorption of metal ions onto AT–PUF was governed by intra-particle diffusion in the microporous regions of PUF. Finally, the metal ion sorption onto AT–PUF follows diffusion-controlled kinetics, while pseudo-first-order model may be the rate limiting step.

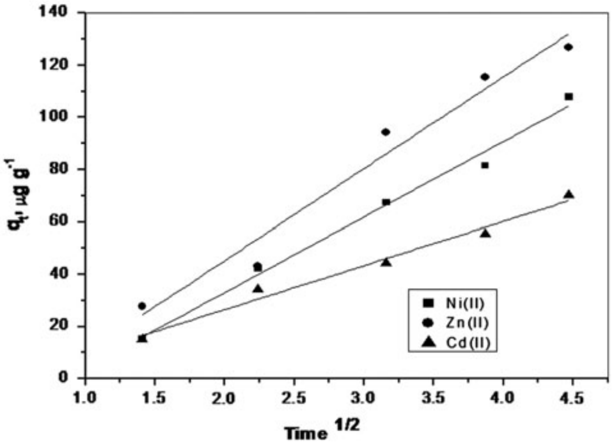

Fig. 5. Intra-particle diffusion profile depicted as variation of sorbed amount of Ni(II), Zn(II), and Cd(II), 1.0 μg mL^{-1} from 20 mL sample, pH 6.0, and 100 mg of 2-AT–PUF sorbent.

3.2.3. Effect of sorbent amount

The influence of sorbent amount was tested by shaking 20 mL solution containing 1.0 μg mL^{-1} of metal ion with variable amount of sorbent in the range of 25–250 mg for 1 h. The sorption increased with increasing the amount of sorbent, and reached maximum value of 94, 91, and 97% for Ni (II), Zn (II), and Cd (II), respectively, when sorbent weight exceeded 50 mg. So, a 100 mg of sorbent was used in all subsequent batch experiments.

3.2.4. Sorption isotherms

Sorption isotherm of the studied metal ions was examined using 100 mg sorbent and 20 mL solution containing varying concentration of metal ion in the range 0.5–6.0 μg mL^{-1}. The sorbed amount of metal ions increased with increasing the initial metal concentration and reached maximum sorption at concentration level of 3.5, 3.0, and 2.5 μg mL^{-1} for Ni(II), Zn(II), and Cd(II), respectively. The maximum capacity was found to be 461 ± 1.4, 341 ± 1.3, and 435 ± 2.4 μg g^{-1}, respectively. The increase in sorption with increasing initial concentration may be due to higher probability of collision between metal ions and sorbent surface, in addition to higher concentration gradient which increases rate of mass transfer [30]. The capacity followed the order Ni(II) > Cd(II) > Zn(II). The higher capacity for Ni and Cd than Zn implies the better accessibility of the chelating groups towards these two elements than Zn(II). Variation of capacity with type of element may be attributed to the difference in ionic size, degree of hydration, and the binding strength to sorbent [31]. Furthermore, the calculated average empirical formula for AT–PUF has indicated that AT is coupled to PUF by a ratio of 1:1. It is too difficult to predict the repetitive unit of the ligands in the modified sorbent due to the complex structure of PUF material. The obtained value of capacity was found to be 0.008, 0.005, and 0.004 mmol g^{-1}, respectively, which is less than the mmoles of the anchored AT ligand. This might be attributed to some of the active sites in AT ligand, which did not participate in sorption of metal ions under equilibrium condition established at the solid–liquid interface.

Since the transfer of metal ions from the bulk of solution to the outer surface of sorbent, and subsequently to the interior surface for ultimate sorption is governed by sorption process. As a consequence, the isotherm data were treated with Freundlich model represented by the following equation:

$$\ln Q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \quad (4)$$

where Q_e is the sorbed amount of metal ion (μg g^{-1}), C_e is the remaining concentration of metal ion in solution (μg mL^{-1}) at equilibrium, and K_F and $1/n$ are constants. The plot of ln Q_e vs. ln C_e was linear as shown in Fig. 6 and the R^2 values were found to be 0.983, 0.999, and 0.979, respectively. The sorption capacity K_F was found to be 457.2, 336.2, and 434.5 μg g^{-1}, respectively, which is comparable to total sorption capacity. The values of n were found to be 0.983, 0.999, and 0.979, respectively, which are low ($n < 1$), indicating that sorption capacity was slightly reduced at lower equilibrium concentrations. Also, it should be noted that Freundlich isotherm provides an expression which encompasses both surface heterogeneity and exponential distribution of energy sites on AT–PUF.

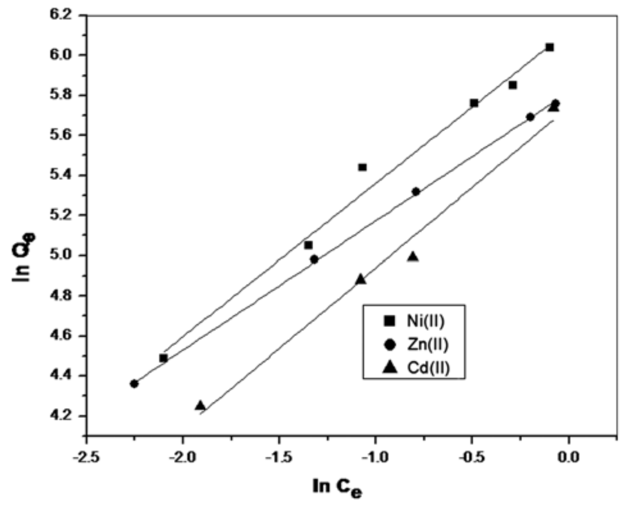

Fig. 6. Freundlich isotherm plottings of Ni(II), Zn(II), and Cd(II) ions on 2-AT–PUF sorbent.

Langmuir isotherm [29] was also tested to fit the experimental results which can be described by the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L} \quad (5)$$

where $q_{\max}$ is the maximum sorbed amount of metal ion (μg g^{-1}) to form a complete monolayer, C_e is the equilibrium concentration of metal ion (μg L^{-1}), and K_L is the Langmuir constant related to the affinity of binding sites to metal ions. The obtained values of Langmuir correlation coefficients (R^2) were found to be 0.884, 0.758, and 0.588 which are weaker than those obtained by Freundlich model. This finding indicates that the sorption mechanism might be proceeding via formation of multilayer coverage at the sorbent interface within the initial concentration range and the experimental results are well described by Freundlich model.

3.3. Column procedures

3.3.1. Sample flow rate

The sample flow rate should be optimized to ensure quantitative retention of metal ions as well as reducing the time required for sample processing. For this purpose, a 20 mL aliquot containing 1.0 μg mL^{-1} from single metal ion was adjusted to pH 6.0 and passed through the packed column at varying flow rates from 1.0 to 5.0 mL min^{-1} controlled with a peristaltic pump. The results indicated at sample flow rates from 1 to 3 mL min^{-1}; there was no significant effect on the quantitative retention of the elements. At flow rates higher than 3 mL min^{-1}, the retention (%) was gradually decreased which is probably due to the short contact time between the metal ions in the mobile phase and sorption sites in AT–PUF. Flow rates lower than 1 mL min^{-1} were not considered in order to avoid the long time analysis, besides decreasing the sample throughput. Also, high flow rates are also limited by the back pressure produced inside the column. In subsequent experiments, the flow rate was selected at 3 mL min^{-1} as a compromise between efficiency and sample throughput.

3.3.2. Desorption of metal ions

The concentration and volume of eluant used for desorption of the retained metal ions were investigated. Acidic solutions were recommended since they would rapidly change the pH of the medium and displace the metal ions from the adsorption sites. However, the concentration of acid should be as low as possible in order to prevent degradation of the PUF [24]. Hydrochloric acid was tested for desorption at concentration between 0.1 and 0.7 mol L^{-1}. Quantitative elution of all elements was reached at acid concentrations ≥0.4 mol L^{-1}. Also, the volume of eluant was examined in the range of 2–12 mL. Best recovery was achieved when eluant volume was ≥10 mL. Thus, 10 mL of 0.5 mol L^{-1} hydrochloric acid was recommended as eluant.

3.3.3. Breakthrough capacity

The breakthrough capacity is strongly correlated to the chromatographic retention of the analyte onto a specific sorbent. It depends mainly on the nature of sorbent and metal ion, mass of sorbent, and concentration of sample [32]. Dynamic capacity of AT–PUF column was investigated by percolating the metal ion solution with concentration of 5 μg mL^{-1}, pH 6.0, and flow rate of 3.0 mL min^{-1}. The obtained breakthrough curves are shown in Fig. 7. Evidently, the breakthrough point was found at 20, 10, and 15 mL for Ni (II), Zn(II), and Cd(II), respectively, and zero-point sorption was reached after the passing of 40, 30, and 35 mL, respectively. The dynamic capacity could be calculated using the following equation:

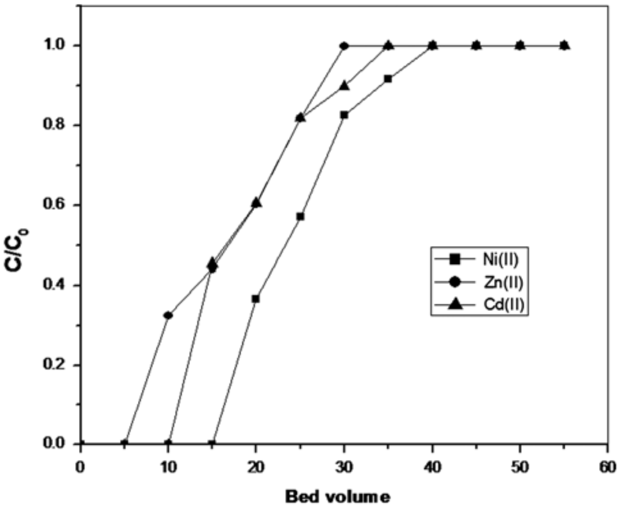

Fig. 7. Breakthrough capacity curves for Ni(II), Zn(II), and Cd(II) with 2-AT–PUF packed column at sample flow rate 3.0 mL min^{-1}, concentration 5.0 μg mL^{-1}, and pH 6.0.

$$C_w = \frac{V_b \, . \, C_0}{m} \tag{6}$$

where C_w is the column dynamic capacity (μg g^{-1}), V_b is the collected volume of effluent (mL) between the first fraction and the breakthrough point, C_0 is the concentration of metal ion in feeding solution (μg mL^{-1}), and m is the sorbent weight (g). The values of dynamic capacity were found to be 200, 150, and 175 μg g^{-1}, respectively, which follow the same order of batch capacity. This revealed good retention of metal ions onto AT–PUF column and predicted good preconcentration capability. Also, the steeping portions in the curves are of higher slopes which reflect strong retention of metal ions to the sorbent.

A plausible explanation for the large difference between the batch and column capacities might be due to the nature of static and dynamic operations. Since the chelating AT groups are attached to the terminal $-NH_2$ groups which initially present in few numbers within PUF; thus, the ultimate number of chelating sites is rather low. The higher value of batch than dynamic capacity might be due to the decrease in concentration gradient with time at the solid–liquid interface of sorption zone. This allows less competition among the metal ions to the chelating sites; thus, enables continuous attraction to the solid phase, thereby, the total amount of adsorbed elements increases. Controversially, the column operation continuously increases concentration gradient at the sorbent–liquid interface during passing of sample through the column and, thereby, the degree of competition to the limited number of adsorption sites increases, leading to leakage of metal ions into the effluent. Moreover, the contact time is short under dynamic flow unlike the batch capacity, where enough contact time between metal ions and sorbent allows high mass transport to the sorbent.

Comparing batch to column capacity, it was revealed that the former is more than four, five, and six times greater than the latter. Therefore, batch technique is more efficient than column methodology for removal of these elements when existing at high concentration.

3.4. Interference effect

One of the main problems in FAAS determination of heavy metal ions is the interference by matrix. Also, investigation of matrix components of the real samples

Table 2
Determination of Ni(II), Zn(II), and Cd(II) in tap and Qaroun lake water

Sample	Metal ion	Added (μg mL^{-1})	Found* (μg mL^{-1})	R (%)	RSD (%)
Tap water	Ni(II)	0.0	0.022	–	–
		0.1	0.127 ± 0.007	105	5.5
	Zn(II)	0.0	0.013	–	–
		0.2	0.109 ± 0.002	96	1.8
	Cd(II)	0.0	0.007	–	–
		0.1	0.11 ± 0.006	103	5.5
Qaroun lake water	Ni(II)	0.0	0.023	–	–
		0.1	0.115 ± 0.001	92	0.9
	Zn(II)	0.0	0.029	–	–
		0.1	0.125 ± 0.004	96	3.2
	Cd(II)	0.0	0.075	–	–
		0.1	0.187 ± 0.003	112	1.6

*Mean of three replicate measurements ($n = 3$) ± standard deviation.

is an important point in the preconcentration/separation studies [24]. Influence of foreign species in presence of metal ions is very important from the application point of view. These species might have the ability to interfere with adsorption of metal ions by binding to sorbent; thus, preventing chelation with target metal ion. So, selective sorption of metal ions is of great interest in presence of other species particularly for analysis of real samples.

In order to identify the effect of some matrix ions on the recovey of these metal ions, model solutions containing some foreign cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, and anions such as Cl^-, Br^-, I^-, SO_4^{2-}, and NO_3^- were mixed to metal ion solution at concentration of 1.0 μg mL^{-1}. Results showed that ions normally present in water do not interfere where quantitative recovery (≥95%) was obtained. The tolerance limit is defined as the foreign ion concentration causing a relative error ±5 (%) in the recovery (%). Results showed AT–PUF sorbent possessed reasonably high tolerance limits for most examined foreign ions, especially which commonly exist in fresh water bodies. Therefore, AT–PUF method would be expected successful for determination of these metal ions in real samples containing different cations and anions at mg L^{-1} level.

3.5. Preconcentration and recovery

The influence of the sample volume was investigated by studying the preconcentration of metal ions existing at low concentration in large sample volume. Fixed amount of metal ions at 20 μg was placed in model solutions with varying volumes between 25 and 1,000 mL. The recovery was found to be ≥95% at volumes up to 1,000 mL, and the corresponding concentration of metal ion at 95% recovery could be defined as the lower limit of quantification (LOQ) [33]. Finally, the value of preconcentration factor (CF) was found to be 100 for all metal ions.

3.6. Analytical figures of merits

The values of limit of detection (LOD) and LOQ were calculated based on $3\sigma/m$ and $10\sigma/m$ definition, respectively, where m is the slope of the calibration curve and σ is the standard deviation for three blank measurements. Under the optimized conditions, the value of LOD was found to be 2, 3, and 3 μg L^{-1} and LOQ was 5, 10, and 10 μg L^{-1} for Ni(II), Zn(II), and Cd (II), respectively. Linearity was found in the range of 10–1,500, 5–2,000, and 5–1,500 μg L^{-1}, respectively. The corresponding regression equations are: $A = (0.1475) C + 0.000923$ ($R^2 = 0.9975$), $A = (0.3082) C + 0.000612$

Table 3
Determination of Ni(II), Zn(II), and Cd(II) in black tea and leave samples

Sample	Metal ion	Found* (μg g^{-1})	RSD (%)
Black tea	Ni(II)	2.71 ± 0.06	2.2
	Zn(II)	3.83 ± 0.10	2.6
	Cd(II)	2.77 ± 0.12	4.3
Spinach leaves	Ni(II)	3.06 ± 0.12	3.9
	Zn(II)	7.94 ± 0.31	4.0
	Cd(II)	1.86 ± 0.07	3.7
Parsley leaves	Ni(II)	2.10 ± 0.02	0.9
	Zn(II)	6.40 ± 0.41	6.4
	Cd(II)	1.92 ± 0.04	2.1

*Mean of three replicate measurements ($n = 3$) ± standard deviation.

($R^2 = 0.9945$), and $A = (0.5325)\ C + 0.00481$ ($R^2 = 0.9948$), respectively, where A is the peak high absorbance and C is the metal ion concentration in μg mL^{-1}. Finally, the developed sorbent could be reused more than 30 cycles of sorption–desorption without significant loss in analytical performance.

3.7. Analysis of real samples

3.7.1. Tap and lake water

Spiked water samples were successfully analyzed by the developed AT–PUF procedure. The obtained results are summarized in Table 2. The recovery (%) was found in the range of 96–105% and 92–112%, and the corresponding RSD (%) value was in the range of 1.8–5.5% and 0.9–3.2% for tap and lake water, respectively. These results are considered relevant for analysis of real samples (RSD less than 10%). The adequate RSD (%) values of the present method indicate good accuracy and precision of the method.

3.7.2. Analysis of leave samples

The feasibility of the developed procedure for the determination of these elements in black tea and plant leaves, namely spinach and parsley leaves, was explored. The obtained results based on three replicate measurements are compiled in Table 3. The values of RSD (%) were found to be in the range of 2.2–4.3, 3.7–4.0, and 0.9–6.4% for black tea, spinach, and parsley leaves, respectively. These results indicate successful application of the developed procedure for the selective preconcentration and determination of target elements in complex matrices. Also, the proposed method afforded high accuracy and precision could be used with high repeatability.

Table 4
Comparison of the CF of 2-AT–PUF extractor to other extractors

		CF			
Support	Ligand	Ni(II)	Zn(II)	Cd(II)	Reference
PUF	2-Aminothiazole	100	100	100	This work
	Alizarin complexone	–	100	100	[34]
	2-Aminophenol	–	–	125	[35]
	AAPH	–	100	–	[17]
	4-Hydroxytoluene	–	100	100	[21]
XAD-2	2-Aminophenol	65	40	50	[36]
	Alizarin red S	–	40	40	[37]
	Pyridyl azo naphthol	50	–	–	[38]
Silica gel	Salicyldoxime	40	40	–	[39]
	2, 2´-Dipyridylamine	80	80	–	[40]
XAD-7	Xylenol orange	100	100	50	[41]

Notes: CF: Preconcentration factor.
AAPH: Acetyacetone phenylhydrazone.

Table 5
Comparison of capacity of 2-AT–PUF to other extractors

		Capacity, μg g^{-1}			
Support	Ligand	Ni(II)	Zn(II)	Cd(II)	Reference
PUF	2-Aminothiazole	461.3	341.3	435.4	This work
	Alizarin complexone	–	843.3	562.0	[34]
	2-Aminophenol	–	–	663.2	[35]
	AAPH	–	490.0	–	[17]
	4-Hydroxytoluene	–	256.3	319.2	[21]
XAD-2	2-Aminophenol	3,240.0	2,940.0	3,420.0	[36]
	Alizarin red S	–	510.5	123.6	[37]
Silica gel	Salicyldoxime	2,348.4	2,614.8	–	[39]
XAD-7	Xylenol orange	2,600.9	1,799.6	1,999.6	[41]

4. Comparison to other extractors

A comparison of CF obtained by AT–PUF procedure with other reported procedures is compiled in Table 4. The present sorbent showed CF of 100 which is similar to other PUF based sorbents like alizarin complexone [34], 2-aminophenol [35], and AAPH [17]. Sometimes, it is higher than others such as XAD-2 and silica gel supported sorbents like 2-aminophenol [36], alizarin red S [37], PAN [38], salicyldoxime [39], 2,2´-dipyridylamine [40], and xylenol orange [41]. The comparable CF obtained by AT–PUF method conveys adequacy of the present sorbent.

Comparison of the capacity of the developed sorbent to other sorbents is depicted in Table 5. The present sorbent has greater capacity than other PUF supported sorbents like AAPH [17] and 4-Hydroxytoluene [21]. Although the capacity values of the present sorbent are less than some XAD-2, XAD-7, and silica gel sorbents, AT–PUF sorbent is still sufficient to quantitatively adsorb the studied metal ions from environmental samples since these elements exist at low concentration.

5. Conclusions

The results obtained clearly demonstrated the utility of SPE of Ni, Zn, and Cd using AT–PUF. The determination of these metal ions in water and plant samples by FAAS was successfully performed. The developed method is very simple, sensitive, inexpensive, and eco-friendly, and it shows high tolerance to foreign ions. Sorption behavior of these metal ions onto AT–PUF was found to follow first-order kinetic and Freundlich isotherm models. Also, good analytical performance such as detection limit, enrichment factor and precision were achieved, making it alternative for trace-element analysis. Functionalized PUF sorbents are very promising materials for application in offline preconcentration systems. Compared to cross-linked polymers and silica gel sorbents, the proposed procedure showed adequate CF and capacity values which make popularity of the developed procedure.

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