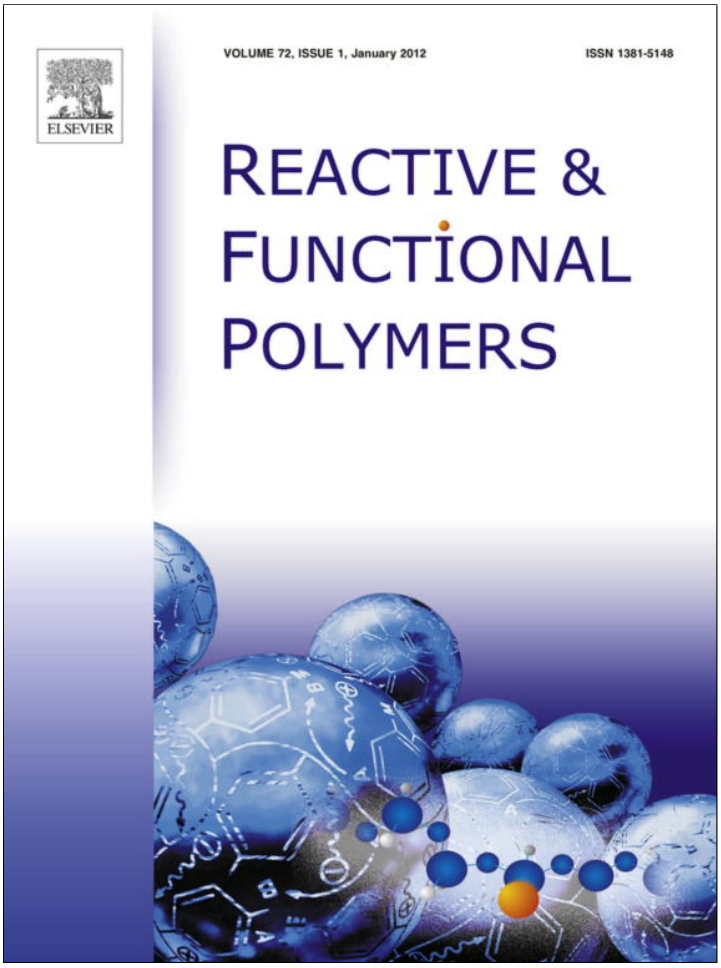

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Acetylacetone phenylhydrazone functionalized polyurethane foam: Determination of copper, zinc and manganese in environmental samples and pharmaceutics using flame atomic absorption spectrometry

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A B S T R A C T

In the present work, acetylacetone phenylhydrazone (AAPH) was chemically anchored to polyurethane foam (PUF) via azo coupling of the toluidine —NH_2 in PUF to active —CH_2— in acetylacetone (AA) and further reaction to phenylhydrazine to give new solid phase extraction (SPE) sorbent for determination of Cu(II), Zn(II) and Mn(II) in natural and pharmaceutical samples. The AAPH–PUF was characterized by UV–VIS, IR, H^1 NMR, elemental and TGA analysis. Optimal experimental conditions were at pH 5–6, shaking time 20 min, sample flow rate 1.0 mL min^{-1}, and desorption by 10 mL from 0.5 mol L^{-1} hydrochloric acid. The limit of detection (3σ) was found to be 0.10, 0.12 and 0.19 μg L^{-1} for Cu(II), Zn(II) and Mn(II), respectively. A preconcentration factor of 100 has been achieved for all elements. Precision (RSD%) was found to be 6.3%, 5.3% and 3.2% ($n = 5$), respectively. Successful application was achieved for environmental samples (tap water, olive leaves, and fish liver) and pharmaceutical formulation. The obtained recovery varied between 90.8% and 96.8% and RSD was under 6.7%.

1. Introduction

Heavy metal pollution is a quickly growing problem for environment in the areas with intensive industry [1] due to waste residue, waste water and exhaust gas from industry and traffic [2]. The toxic metals are generally present in trace concentrations in environmental samples, for example, copper is essential for human beings in trace quantity [3]. Adverse effect is manifested when these levels exceed a threshold level; higher level of essential traces metals in our body is creating health risk. Due to these reasons, the accurate and precise determination of trace metal ions important for analytical chemists [4].

Various analytical techniques have been using such as atomic absorption spectroscopy (AAS), inductively coupled plasma and plasma emission spectroscopy [5]. In trace element analysis, preconcentration and separation step is needed to enhance the sensitivity and precision of the determination. The presence of trace heavy metals lower than the detection limits of instrumental techniques is one of the main problems at these low levels. Therefore, preconcentration techniques including liquid–liquid extraction, cloud point extraction, electro-deposition, co-precipitation, membrane filtration and solid phase extraction (SPE) are generally used by the researchers around the world [3,6,7]. SPE is an attractive technique based on the use of solid sorbent that retains the analytes [8]. It is preferentially used mainly due to its simplicity, low cost, contaminant free and adaptation to flow injection techniques [3].

Polyurethane foam is among many solid sorbents that have been successfully used for the preconcentration, separation and sensitive determination of trace metal ions. For example, grafting Nile blue A into PUF for preconcentration of several metal ions has been reported [9]. Other grafted PUFs were prepared by coupling polyether polyol, toluene diisocyanate and basic dyestuff such as methylene blue, rhodamine B and brilliant green [10]. Penicillins (penicillin G, amoxicillin, and ampicillin) were precocentrated on a mincolumn packed with methylene blue grafted PUF [11].

o-Aminophenol and its azo derivatives with ß-Naphthol, acetylacetone and pyrazolone were anchored to PUF and used as solid phase extractor for metal ions [12].

The action of sodium nitrite on the terminal primary aromatic amine groups of PUF in presence of 0.1 mol L^{-1} HCl leads to a yellow color attributed to the formation of the diazonium chloride in the foam [13]. Another way for reagent bonding to PUF was via —N=N—NH— linkage like in case of 2-aminoacetylthiophenol [14]. Physical immobilization of organic reagents to PUF is well known such as TAC (2-(2-thiazolylazo)-p-cresol) for determination of cobalt in water samples [15], 2-(2-benzothiazolylazo)-2-p-cresol

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(BTAC) for enrichment and determination of lead [16]. Quantitative and/or semiquantitative determination of submicrogram amounts of nitrite could be done by treatement of PUF with hydrochloric acid, sodium nitrite and subsequent coupling to α-naphthylamine, α-naphthol, β-naphthol, 8-hydroxyquinoline, resorcinol, or catechol to give purple azo dye [9].

Acetylacetone (AA)-hydrazone complexes with metal ions are well studied in coordination chemistry, which are also explained by their unique physico-chemical properties and physiological activity [17]. In its enolic form, it can produce the OH radical as a photofragment after the π–π^* transition induced by UV irradiation [4]. Condensation product between AA and primary amines to give hydrazones with the formula $R_2C{=}NR$ are well known ligands that form stable complexes with metals ions [18].

Copper is well known to form stable chelate compounds with a series of new derivatives of mandelic hydrazones [19]. Hydrazones have effective extraction properties towards transition metal ions, two new macrocyclic hydrazone were synthesized by reaction of succindihydrazide and adipdihydrazide with AA. Hydrazones have been used for liquid–liquid extraction of some s-metal ions e.g. Li^+, Na^+ and K^+ and d-metal ions such as Cu^{2+} and Cr^{3+} [20].

The presence of oxygen and nitrogen as donor atoms in hydrazones provide the ability to coordinate hard as well as soft transition metal ions via p_π–d_π and the stability of the chelates is highly affected by the nature of the donor atoms and the medium of the reaction [21,22].

Hydrazones have been intensively investigated mostly because of their potential applications as anticancer, antiviral, antibacterial, and antifungal agents may be due to the presence of an azomethine —NHN=CH— proton. Therefore, many researchers have evaluated their biological activities [21]. The most significant reactivity is the nucleophilicity of hydrazones carbon atom where hard nucleophiles attack preferentially nitrogen atom, while soft ones attack preferentially at carbon atom [23].

In this work, acetylacetone phenylhydrazone (AAPH) is chemically anchored to the terminal amino groups in PUF to give AAPH–PUF. The synthesized sorbent is attained chelating sites accessible for selective extraction of the studied metal ions. Upon separation and preconcentration by the developed sorbent, the determination of these elements in natural samples by FAAS would be possible with high accuracy.

2. Experimental

2.1. Instrumentations

Unicom-Solaar MKI 969 flame atomic absorption spectrometer (England) was used for determination of Cu, Zn, and Mn. The operational conditions for FAAS are depicted in Table 1. UV-1601 spectrophotometer (Shimadzu, Japan) was used to record the absorption spectra of the new sorbent. The pH measurements were carried out on Inolab WTW720 pH meter with a combined glass electrode (Ltd., Dover Kent, UK). Wrist Action mechanical shaker was purchased from Burrel-El75 (PA, USA). Vario ELIII Elemental analyzer (Hanau, Germany) was used for CHN analysis. Varian NMR mercury-300bb “NMR300” spectrometer (USA) was employed for ^1H-spectra using dimethylsulfoxide as solvent. Thermo scientific Nicolet FT-IR model 6700 (Illinois, USA) was used to record the infrared spectra in the range 400–4000 cm^{-1}. Shimadzu TGA analyzer model TGA-50H (Rash, Japan) was utilized.

2.2. Reagents

Unless otherwise stated all reagents were of analytical-reagent grade. Distilled water was used to prepare the solutions. Acetylacetone (AA) and phenylhydrazine were obtained from Sigma–Aldrich (USA) and Prolabo, Rue palee, (Paris, France), respectively. Mineral acids used were obtained from Merck (Darmstadt, Germany). Standard metal ion solutions (1000 mg L^{-1}) were prepared by dissolving an appropriate amount of $CuSO_4{\cdot}5H_2O$ (Adwic, El-Nasr, Egypt), $ZnSO_4$ (Merck), and $MnSO_4{\cdot}4H_2O$ (Adwic) in distilled water and completed into 1L solution containing 1 mL concentrated sulfuric acid. Working solution 10 μg mL^{-1} was freshly prepared by dilution from the standards with distilled water. Commercial PUF, open-cell polyether type, was supplied from the Egyptian Company for Foam Production (Cairo, Egypt). The PUF was cut into similar cubes (50 mm dimension), washed by 0.1 mol L^{-1} solution of HCl, followed by distilled water and ethanol and then squeezed between clean sheets of filter paper, dried in a stove at 80 °C for 1.0 h and stored in a dark bottle.

2.3. Synthesis of AAPH–PUF

For the coupling of the diazotized PUF to AA, 1-g PUF cubes were soaked in HCl (50% (w/v)) for 6 h to liberate the maximum number of free NH_2 groups by the hydrolysis of residual isocyanate and some urethane groups. Thereafter, the cubes were washed with distilled water, placed into a 0.1 mol L^{-1} HCl solution (100 mL) and cooled in an ice bath. Diazotization was affected by the dropwise addition of 1.0 mol L^{-1} of sodium nitrite to the cold mixture, and stirred vigorously until the yellow color appeared in PUF due to the formation of diazonium salt. The mixture was thermostatic for 1 h at a temperature below 3 °C. After that, the cubes were transferred to mixture containing of 5 ml (AA), 1 mol L^{-1} sodium acetate in 50% (w/v) ethanol and stirred. A canary yellow material from acetlyacetone-PUF was obtained and kept in a fridge for 24 h. Finally, the cubes were washed subsequently with 0.1 mol L^{-1} HCl, distilled water and ethanol then dried. Phenyl hydrazinum chloride (5.0 g) was dissolved in 100 mL absolute ethanol then adds to 1.0 g acetylacetone-PUF and heated in reflux condenser for 4.0 h. Orange color cubes from AAPH–PUF were separated, washed by ethanol, distilled water then dried at ambient conditions and stored for further use.

2.4. General procedures

2.4.1. Batch procedure

A 10 mL aqueous solution, containing of each Cu(II), Zn(II) and Mn(II) at concentration 0.5 μg mL^{-1}, was shaken for 1.0 h with 0.1 g of AAPH–PUF sorbent at room temperature. The sample pH

Table 1
Operational conditions for flame AAS determination of Cu, Zn and Mn.

Property	Cu(II)	Zn(II)	Mn(II)
HC lamp current (mA)	10	5	12
Slit width (nm)	0.5	0.5	0.2
Wavelength (nm)	213.9	324.8	279.5
Fuel flow rate (L min^{-1})	0.9–1.2	0.8–1.1	0.9–1.2
Burner height (mm)	2.0	2.0	2.0
Regression equation	$A = 0.084C + 0.0055$	$A = 0.162C + 0.02$	$A = 0.053C + 0.0078$
R^2	0.999	0.997	0.999

was examined in the range 3–8. Shaking time was tested at 5, 10, 15, 25 and 30 min. After extraction, the retained elements were desorbed by shaking with 10 mL from 0.1 mol L^{-1} hydrochloric acid solution and the desorbed metal ions were determined by flame AAS.

2.4.2. Column procedure

A 1.0 g AAPH–PUF was packed by applying gentle pressure with a glass rod into a glass column (20 cm length and 1 cm i.d) plugged with stopcock at the end. The packed sorbent, about 2 cm bed height, was permanently immersed in solution to avoid bubble or channel formation. The column was used repeatedly after washing with 0.1 mol L^{-1} HCl solution followed by distilled water till the effluent was acid free.

A 10 mL aliquot containing 10 μg each metal ion was taken and adjusted to pH 5 then passed through the column at flow rate 1.0 mL min^{-1}. The adsorbed metal ions were eluted by passing 10 mL from 0.1 mol L^{-1} hydrochloric acid solution at the same flow rate. The metal ion content in the eluate was quantified by flame AAS.

2.5. Sample preparation

2.5.1. Certified sample

Certified atomic absorption reference solutions 1000 mg L^{-1} of Cu, Zn and Mn were obtained from Merck (Darmstadt, Germany) and used to assess the accuracy of the method. For this purpose, an aliquot from the standard solution was adjusted to pH 5.0 and diluted up to 100 mL by distilled water to final concentration 0.5 μg mL^{-1} of each element. The sample was passed into the preconcentration column at flow rate1.0 mL min^{-1}. The retained metal ions were stripped out and determined by flame AAS.

2.5.2. Olive leaves and fish liver

Olive leaves and fish liver (Makrel fish), were obtained from a local market in Cairo City. The green leaves were washed many times with distilled water to remove any dust and cut into small pieces then dried in oven at 80 °C for 10 h till constant weight. After that, the dried leaves were ground in porcelain mortar. The liver sample was transferred into clean and dry glass beaker then dried in oven at 105 °C for 24.0 h. Next, the dry sample was put into a clean and dry porcelain ignition crucible and heated for 2.0 h in a muffle furnace at 200 °C, 400 °C and finally at 600 °C, respectively. The dried leaves or liver samples was digested by taking an accurately weighed 0.50 g from the dry sample and mixing to 20 mL of 14 mol L^{-1} concentrated nitric acid solution then heated till nearly dryness. After cooling, the final digest was neutralized using 2.5 mol L^{-1} sodium hydroxide solution, diluted to 50 mL and adjusted pH 5 then passed through the AAPH–PUF column [24].

2.5.3. Tap water

Tap water sample was collected from our research laboratory at chemistry department (Ain-Shams University). It was filtered to remove any suspended particulates, adjusted to pH 6.5 with 0.01 mol L^{-1} nitric acid and immediately analyzed by passing 100 mL sample through the column at flow rate 1.0 mL min^{-1}. The retained metal ions were eluted by 10 mL from 0.1 mol L^{-1} HCl and measured by FAAS.

2.5.4. Pharmaceutical sample

Kerovit is a pharmaceutical preparation which is widely receipted for activity, vitality and memory improvement. It is produced by Amoun pharmaceutical Company (El-Obour City, Cairo, Egypt). Each capsule contains trace elements (7.5 mg) Zn, (2.0 mg) each of Cu and Mn in addition to multivitamins and supplements. Analysis was carried out according to the reported method [25]. The powder in one capsule was mixed to 20 mL concentrated 65% (w/w) HNO_3 and heated for about 30 min until dissolving all constitutes of the sample then adjusted to pH 5.0 and diluted to 1000 mL. A 50 mL aliquot from the final solution was analyzed according to the proposed methodology.

3. Results and discussion

3.1. Characterization of AAPH–PUF

The IR spectral data of the untreated PUF (A) and AAPH–PUF (B) materials were compared as presented in Fig. 1. In the spectrum of AAPH–PUF, characteristic absorption band has appeared at 1657 cm^{-1} which could be attributed to C=N group confirming the condensation reaction between phenylhydrazine and carbonyl group in acetylacetone anchored to the PUF. In addition, a broad band has been observed in the spectrum of AAPH–PUF, extending

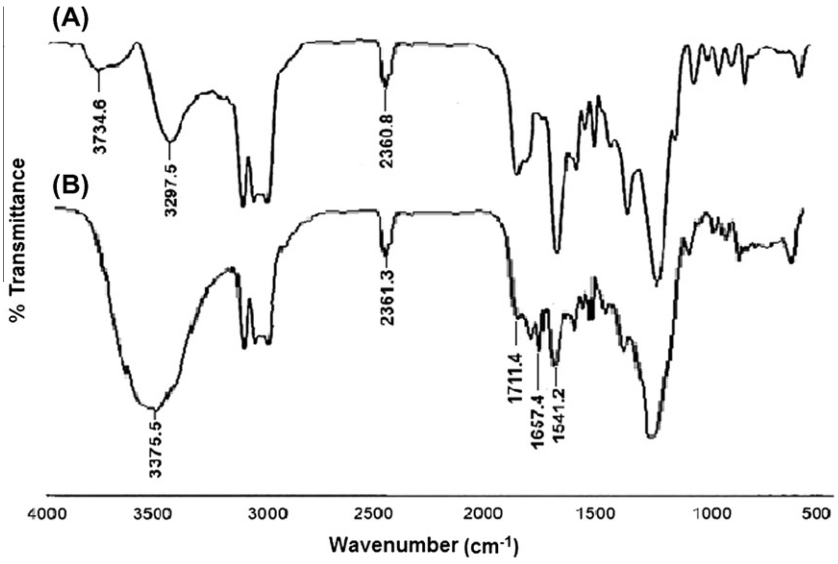

Fig. 1. IR spectra of the PUF (A) and AAPH–PUF (B).

from 3550 to 3100 cm^{-1}, which might be resulted from both of NH group in phenylhydrazine and OH group in AA. Finally, this confirmed the anchoring of acetylacetone phenylhydrazone to PUF.

The elemental analysis data for untreated PUF was found to be: C, 56.3; H, 7.71; N, 5.25%; calculated for $C_{78}H_{126}N_6O_{30}$: C, 57.6; H, 7.74; N, 5.16%. Also, for AAPH–PUF it was found to be: C, 61.06; H, 6.09; N, 6.31%; calculated for $C_{89}H_{137}N_9O_{31}$: C, 58.86; H, 7.49; N, 6.89%. Obviously, there is good agreement between the experimental and calculated data for AAPH–PUF, the deviation in the range 0.58–2.2%. Also, the nitrogen content has been increased by 1.73% due to the incorporation of AAPH to PUF which is equivalent to 1.235 mmol g^{-1}. Therefore, the AAPH moiety could be calculated as 0.412 mmol g^{-1}. Furthermore, the calculated average empirical formula for AAPH–PUF indicated that phenylhydrazine is coupled to acetylacetone by 1:1 M ratio as presented in Fig. 2.

Thermogravimetric analysis curves of control PUF and AAPH–PUF are presented in Fig. 3. The decomposition of untreated PUF was found to occur in single step, starting at 245 °C, which can be due to the decomposition of the urethane group since the decomposition of polyether chain takes place within the range of 250–320 °C [26]. For AAPH–PUF material, a mass loss of 4.8% was observed between 220 °C and 310 °C corresponding to molecular mass of 87.6 g mol^{-1}. As can be seen from the structure in Fig. 2, the molecular mass of phenylhydrazine is 106 g mol^{-1} which compromise about 5.5% mass of AAPH–PUF. Hence, this mass loss it is more likely attributed to decomposition of anchored phenylhydrazine moiety. A third mass loss of 5.2% beginning at 352 °C up to 420 °C that corresponding to molecular mass of 95 g mol^{-1} which is approximately due to decomposition of acetylacetone moiety. Finally, the residue at around 430 °C is higher in case of AAPH–PUF than untreated PUF which might be due to the use of sodium acetate in the azo coupling of acetylacetone and the possibility that sodium is remained as residue.

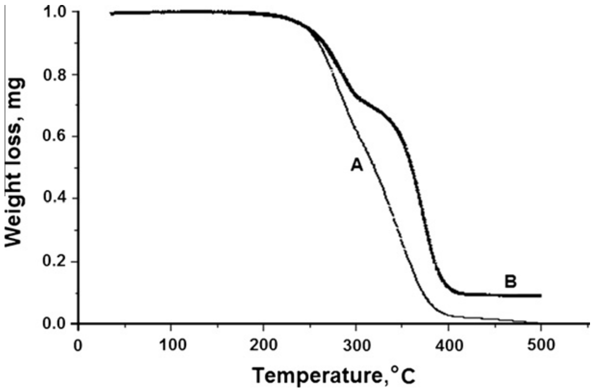

Fig. 3. TGA curves for untreated PUF (A) and AAPH–PUF (B).

^{1}H NMR spectroscopic analysis was performed for structure elucidation of the AAPH–PUF material. It was done by dissolution of the material in dimethylsulfoxide after addition of few drops from triflouroacetic acid to increase the solubility of the AAPH–PUF polymer. Fig. 4 showed the ^{1}H-NMR spectra of AAPH–PUF. The important peaks in PUF are characterized to CH_3-1.5 ppm, CH_2-1.9–2.0 ppm, CH-3.5–3.7 ppm, aliphatic OH-3.9 ppm, The CH_2 proton is appeared at 2.3 ppm. A sharp peak at 2.7 ppm is depicted to the $=CH_2$. The characteristic peaks observed at 8.5 and 9.42 ppm were assigned for the chemical —NH in PUF and in phenylhydrazine moiety, respectively as shown in inserted spectrum (B). Furthermore, in spectrum (B), two multiples in the region 7.0–7.3 and at 7.5 ppm were appeared which imply the H of aryl protons (Ar—H) in benzene ring of toluidine part in PUF and phenyl group in hydrazine compound, respectively. This confirmed anchoring of phenylhydrazone compound to PUF.

Finally, the UV–Vis spectra of PUF and AAPH–PUF were recorded to confirm the chemical modification. A thin film from the foam material was placed in DMF as blank in quartz cell and the absorbance was recorded (Fig. 5). The untreated PUF showed

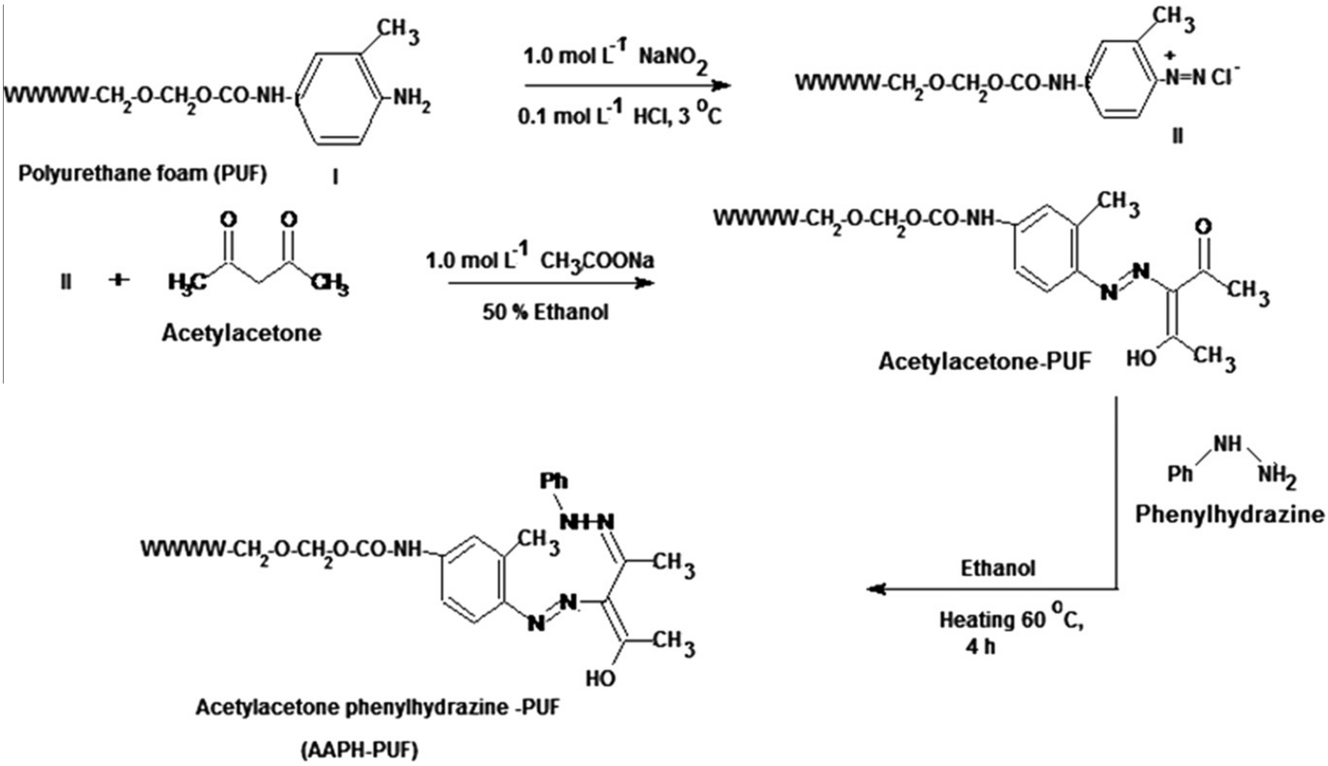

Fig. 2. Schematic diagram for the synthesis of AAPH–PUF sorbent.

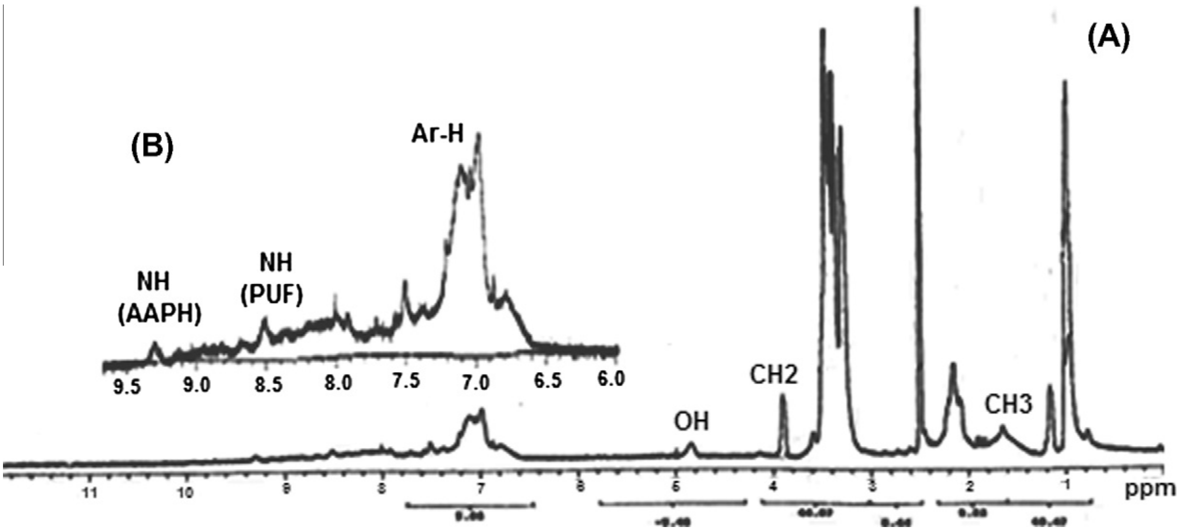

Fig. 4. ^{1}H NMR spectra for AAPH–PUF (A) and insert showing magnification the region of aromatic protons (B).

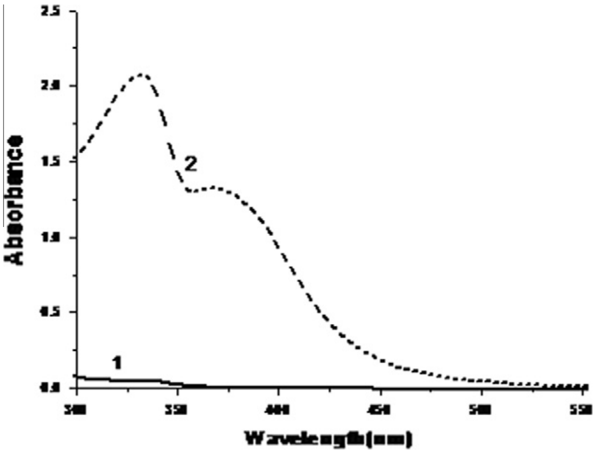

Fig. 5. UV–Vis absorption spectra of untreated-PUF (1) and AAPH–PUF (2).

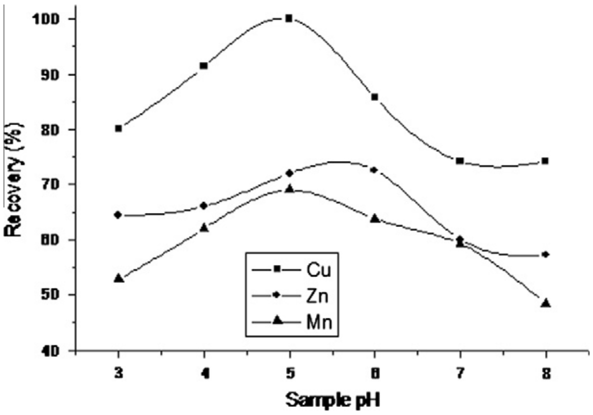

Fig. 6. Influence of sample pH on the recovery of metal ions (0.5 μg mL^{-1}, 10 mL sample) and 0.1 g AAPH–PUF sorbent.

no absorption peaks in the estimated wavelength range from 550 to 300 nm. In the spectra of AAPH–PUF, two strong absorption bands were observed with maxima at about 375 and 335 nm which could be due to easy electronic transition of in the incorporated N=N, C=N and C=O groups in AAPH moiety which do not exist in PUF. This confirmed the orange color attained by AAPH–PUF.

3.2. Batch method

3.2.1. Influence of solution pH

The careful optimization of solution pH is a pivotal point. The influence of pH on extraction was investigated in the range 3–8. The results are presented in Fig. 6. Maximum recovery for copper and manganese was achieved at pH 5.0 and for zinc at pH 6.0. The ligand has indicated high recovery of copper (100%) and low recovery (68%) for manganese at pH 5 but the recovery of zinc was found to be 73% at pH 6.0. In case of samples containing mixture of these elements, the solution was adjusted to pH 5.0 since there is no significant difference in the recovery of zinc than pH 6.0. An explanation could be due to the different binding affinity of the active groups in hydrazone moiety immobilized in AAPH–PUF. The sorbent contains two nitrogen atoms from the phenylhydrazine residue which could be represented by Ph—NH—N= group, the oxygen atom of the remaining carbonyl group in acetylacetone, and two azo nitrogen atoms which link the acetylacetone to PUF backbone. Therefore, the improvement in sorption characteristics for copper and zinc than manganese might be due to the chelating nitrogen atoms. Copper and zinc are well known to have good affinity to nitrogen containing compounds [27,14]. On the other hand, manganese ions form more stable complexes with oxygen atoms than nitrogen. Thus, anchoring of phenylhydarzine has consumed the oxygen atoms of the carbonyl groups which resulted in less stability of manganese complex to AAPH–PUF. Generally, recovery decreases by decreasing pH which might be due to protonation of the chelating groups. Also, all elements showed a decrease in recovery at pH $\geqslant 7$ which could be due to precipitation of metal hydroxides.

3.3. Sorption kinetics

The effect of shaking time on the uptake of these metal ions by the proposed sorbent was investigated in the selected shaking intervals 5, 10, 15, 20, 25 and 30 min. This parameter is important to envisage the minimum time period necessary to achieve maximum uptake. Results showed in Fig. 7 indicated that, copper reached equilibrium after 15 min while zinc and manganese required 20 min to attain equilibrium. This fast sorption is indicative

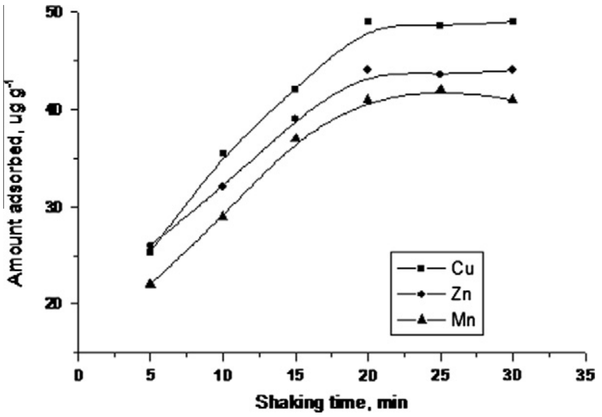

Fig. 7. Effect of shaking time on adsorption of metal ions by AAPH–PUF: metal ion concentration 0.5 μg mL^{-1}, sample volume (10 mL) and pH 5, weight of sorbent 0.1 g and temperature 25 °C.

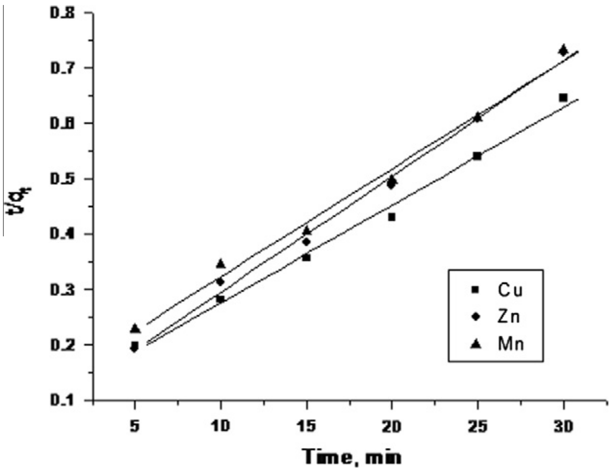

Fig. 8. Pseudo-second order plotting for adsorption of metal ions at concentration 0.5 μg mL^{-1}, pH 5, 10 mL volume of sample, weight of sorbent 0.1 g and temperature 25 °C.

of diffusion of metal ions throughout a hypothetical film or hydrodynamic boundary [28]. Therefore, the best enhancement was observed for Cu(II) uptake which conveys higher selectivity and accessibility for Cu(II) than Zn(II) and Mn(II) under the operating conditions.

3.4. Kinetic models

The kinetic mechanism controlling the adsorption of the metal ion was investigated by applying the pseudo first-order, pseudo-second order and intra-particle diffusion models to fit the experimental results.

For the pseudo-first order, the correlation coefficients (R^2) were in the range 0.958–0.971 and the calculated q_e values 0.27–0.30 μg g^{-1}, respectively. Comparing to the experimental q_e values, a large difference was observed which proves the pseudo first-order model is inconvenient for an interpretation of the adsorption kinetics data.

The pseudo-second order equation reported by Ho and coworkers [29] could be expressed as:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t$$

where k_2 is the pseudo-second-order rate constant (g μg^{-1} min^{-1}). As presented in Fig. 8 and Table 2, the obtained R^2 values are higher than those obtained by the pseudo-first order model they are between 0.995 and 0.997. Also, the calculated q_e values were very close to the experimental q_e values which show the pseudo-second-order described the experimental data well, indicating the possibility of chemisorptions forces between the AAPH–PUF surface and the studied metal ions.

The intra-particle diffusion model, put by Morris–Weber equation [30] represented by $q_t = k_{id}t^{1/2}$, is usually investigated for porous sorbents such as PUF. Non-linear plots were obtained in the initial stages and the correlation coefficients R^2 were found to be 0.934, 0.948 and 0.957 for Cu, Zn and Mn, respectively indicating the metal ion sorption did not follow diffusion-controlled kinetics and the intra-particle diffusion may not the rate limiting step.

3.5. Sorption isotherms

The sorption isotherm of the studied metal ions by AAPH–PUF was examined by shaking 0.1 g sorbent with solutions contain individual metal ion within concentration range 50–1250 μg L^{-1}. The obtained results are shown in Fig. 9. The sorption of metal ions increased with concentration and reached the maximum sorption at concentration 1000 μg L^{-1} for Cu and 500 μg L^{-1} for both of Zn and Mn. The capacity of AAPH–PUF was found to be 800, 490 and 325 μg g^{-1} for Cu, Zn and Mn, respectively. These results demonstrated the sorption capacity for Cu(II) is much higher than those for other two elements which imply the better accessibility of the chelating groups towards Cu than Zn or Mn. Also, the capacity difference may be attributed to their different ionic sizes, degree of hydration and the value of their binding constant with the adsorbent [31,32].

The Langmuir isotherm was used to model sorption equilibrium data [33] which can be described by the equation:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max}$$

where $q_{\max}$ (μg g^{-1}) is the maximum amount of metal ion per weight to form a complete monolayer equilibrium metal ion concentration C_e (μg L^{-1}) and K_L is the Langmuir constant related to the affinity of binding sites. The plot of Langmuir model is presented in Fig. 10 and the corresponding parameters are listed in Table 3. The Langmuir model described the experimental data well based on the high correlation coefficients (R^2). Also, the maximum sorption capacity values calculated from the Langmuir isotherm were in good agreement to the experimental values.

The Freundlich isotherm was also tested and the calculated parameters are compromised in Table 3. The results proved the correlation coefficients were stronger with respect to Langmuir model than Freundlich model. This finding indicates the adsorption of these metal ions by AAPH–PUF is possibility proceeds via formation of monolayer coverage at the sorbent interface within the initial concentration range due to the accessibility of donor atoms, i.e. the availability of the electron in the sorbent towards the metal ions in the aqueous phase.

3.6. Sample flow rate

Sample flow rate is a measure of the contact time between the metal ion in the liquid phase and the solid sorbent. The lower the flow rates the longer the contact time and the larger extent of metal binding. A vacuum pump was connected to the end of the column tap to adjust the flow rate. An aliquot of 5 mL at concentration 0.5 μg mL^{-1} from individual metal ion was adjusted at pH 5 and introduced into the column at varying rates from 0.25 to 3 mL min^{-1}. The results showed similar behaviour for the three elements. At flow rate variations in the range from 0.25 to 2 mL min^{-1}, the recovery was approximately constant and quantitative. At flow rates higher than 2 mL min^{-1}, the recovery de-

Table 2
Adsorption kinetic data obtained from pseudo-first order and pseudo-second-order models at 25 °C.

Metal ion	$q_{e(\mathrm{exp})}$ (µg g^{-1})	Pesudo first-order			Second-order		
		q_e (µg g^{-1})	K_1 (min^{-1})	R^2	q_e (µg g^{-1})	K_2 (g µg^{-1} min^{-1})	R^2
Cu(II)	49	0.300	0.2427	0.9585	56	0.003	0.9965
Zn(II)	44	0.286	0.2639	0.9674	47	0.005	0.9973
Mn(II)	42	0.271	0.0669	0.9717	51	0.0029	0.9954

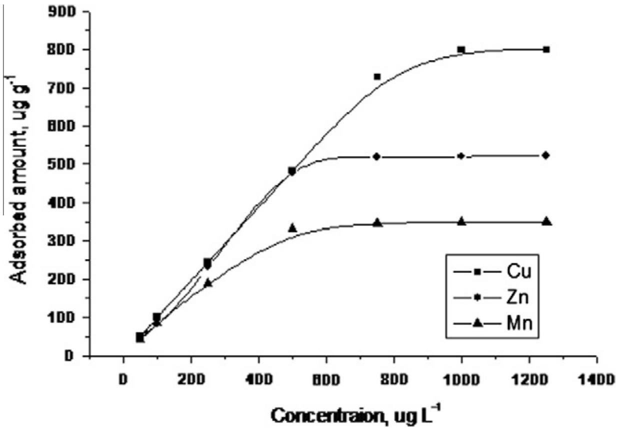

Fig. 9. Extraction isotherm of the studied metal ions with AAPH–PUF sorbent (pH = 5, volume of sample10 mL, weight of sorbent 0.1 g).

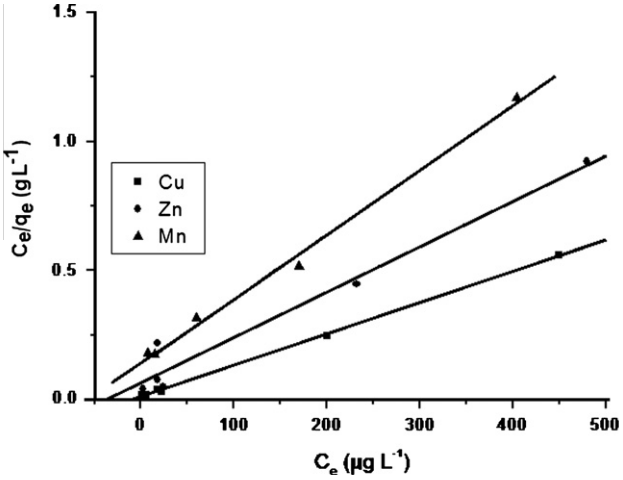

Fig. 10. Langmiur model of copper, zinc and manganese with AAPH–PUF.

Table 3
Langmiur and Freundlich isotherm constants for adsorption of metal ions onto AAPH–PUF at 25 °C.

Metal ion	Langmuir constants			Freundlich constants		
	$q_{\max}$ (µg g^{-1})	K_L (L µg^{-1})	R^2	1/n	K_F (L g^{-1})	R^2
Cu(II)	826	0.089	0.999	0.82	0.23	0.981
Zn(II)	568	0.026	0.982	0.51	0.20	0.819
Mn(II)	401	0.017	0.999	0.64	0.05	0.985

creased very slowly. For achievement of a good precision, the flow rate was set at 1 mL min^{-1} in subsequent experiments. However, higher flow rates up to 2 mL min^{-1} could be employed when the sample concentration is too low to benefit from the decrease in analysis time but on the expense of efficiency.

3.7. Desorption of metal ions

Eluent type can influence the lifetime of sorbent and efficacy of the method. The use of complexing agents like thiourea or EDTA was excluded since it might be sorbed by the PUF, thus causing chemical changes in the nature of its surface leading to irreproducible recovery data. Hydrochloric and nitric acids are presumed to be the most suitable for desorption of the bound metal ions from PUF [34]. The most frequently used is hydrochloric acid because it is suitable with its non-oxidative effect, controversy to nitric acid.

However, at too low acid concentration the amount of protons may be not enough to protonate the chelation site and to make to exchange with the retained metal ion. High acid concentration is not recommended for desorption due to increasing the volume of eluate by neutralisation prior to FAAS determination that would reduce the preconcentration factor or contamination from acid. Therefore, concentration of hydrochloric acid was carefully optimized. For this purpose, the metal ions were eluted from the column with 10 mL of HCl solution at varying concentration between 0.2 and 0.7 mol L^{-1} and 1.0 mL min^{-1} flow rate. The recovery of Cu, Zn and Mn, was quantitative (95–98%) within concentration range 0.3–0.5 mol L^{-1}. At concentration <0.3 mol L^{-1}, low recovery was achieved. Also, at acid concentration more than 0.5 mol L^{-1}, the recovery decreased which could be due to the synergistic effect caused by chloride ion. Accordingly, the 0.4 mol L^{-1} concentration was selected as the optimum eluent concentration in the subsequent experiments to achieve high recovery.

The volume of eluent necessary to quantitatively remove these elements from the sorbent was investigated. It is of great importance to use sufficient volume from the eluent; however, extra volume will adversely affect the value of preconcentration factor. Elution was effected with volumes from 2.5 to 12 mL from 0.4 mol L^{-1} hydrochloric acid. Under the specified experimental conditions, recoveries higher than 98% were obtained by employing 10 mL from the eluent. Less volumes than 10 mL caused decrease in the recovery. Thus, in order to pursue maximum preconcentration and recovery, the 10 mL eluent volume was employed.

3.8. Break through curve

The dynamic capacity of the column was computed by percolating it with metal ion solution with concentration 10 µg mL^{-1} and pH 5 at flow rate 1.0 mL min^{-1}. Breakthrough curves were obtained by measuring the content of metal ions in 5 mL collected fractions from the effluent as shown in Fig. 11. Evidently, the breakthrough point was found at 20, 15 and 10 mL for Cu, Zn, and Mn, respectively. The zero-point sorption was reached after passing of 20 mL for Mn and 25 mL for Cu and Zn. The steeping portions in the curves are of higher slopes, which reflect strong retention of metal ions to the sorbent. The working breakthrough capacity could be calculated by the equation:

$$C_w = (V_b \cdot C_o)/m$$

where C_w is the column working capacity (µg g^{-1}), V_b is the collected volume of effluent between the first fraction and the break-

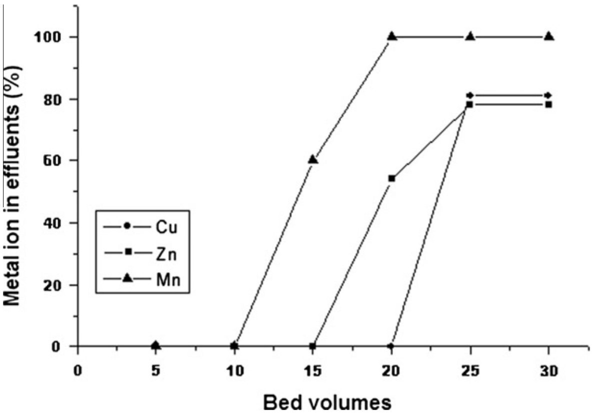

Fig. 11. Breakthrough curve of Cu, Zn, and Mn solution(10 μg ml^{-1}) with AAPH–PUF foams at 1.0 mL min^{-1}, pH 6 and 1 g foam sorbent.

through point (mL), C_o is the initial concentration of metal ion, m is the weight of sorbent (g). The capacity values were found to be 200, 150 and 100 μg g^{-1} respectively. This revealed good retention of the element onto the column and predicted good preconcentration capability and low limit of detection. As a fact, the breakthrough capacity is less than the total capacity determined from the extraction isotherm because the first one is determined under dynamic flow of metal ion solution where the contact time is short unlike the batch capacity where enough contact time between the metal ion and the sorbent allows high mass transport to the solid phase.

A plausible explanation for the large difference between the batch and column capacities can be due to the nature of static and dynamic operations. Since the chelating AAPH groups are attached to the terminal —NH$_2$ initially present in few numbers within PUF, the integrated number of chelating sites is rather low. The higher batch capacity might be due to the decrease in concentration gradient with time at the interface of the adsorption zone which allows less competition among the metal ions to the chelating sites thus enables continuous attraction to the solid phase and the total amount of adsorbed elements increases. Controversy, the column operation continuously increases concentration gradient at the sorbent-liquid interface as it passes 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.

Comparing the values total capacities found by batch and column reveals the former is more than three times the latter. Also, the batch and column capacities follow the same order Cu > Zn > Mn which implies the same trend in sorption affinity.

3.9. Interference effect

The influences of some foreign ions which may interfere with sorption of the studied elements onto AAPH–PUF were investigated in order to identify the method selectivity. For this purpose, 10 mL model solution containing 0.5 μg mL^{-1} Cu, Zn or Mn was mixed with the interfering species and adjusted to optimum pH and passed through the column at flow rate 1.0 mL min^{-1}. The concentration of examined ions were: Na (1000 mg L^{-1}), Ca(II) (100 mg L^{-1}), Mg(II) (100 mg L^{-1}), Fe(IIII) (0.5 mg L^{-1}), Co(II) (0.1 mg L^{-1}), Pb(II) (0.1 mg L^{-1}), chloride(1000 mg L^{-1}), sulphate (500 mg L^{-1}), nitrate (500 mg L^{-1}), and oxalate(100 mg L^{-1}). The obtained results are depicted in Fig. 12. The error analysis corresponding to 5% error in the recovery data is shown by the vertical lines. Comparing the obtained data showed that all results are within the error range 3–4.9%, 4.1–5.5% and 3.5–5.2% for Cu, Zn and Mn, respectively. The strongest interference was found by lead and oxalate on the Zn and Mn determinations, respectively. They are corresponding to error values of 5.5% and 5.2%, respectively. The alkaline and alkaline earth metal ions did not interfere with the extraction. Generally, the majority of the examined foreign ions were found not interfere which confirms the adequate selectivity of AAPH–PUF material and feasibility for quantitative determinations in natural samples with relevant accuracy. Furthermore, the added concentrations of foreign ions were higher than those exist in most natural samples which predict the validity of the developed procedure.

3.10. Precision and accuracy

The precision was estimated using model solution prepared by dilution of AAS standards to concentration of 1.0 μg mL^{-1} each metal ion then subjected to successive preconcentration-desorption cycles. The precision (RSD%) for five replicates was good (less than 10%) and the RSD varied in the range 5.5–6.2%.

The accuracy of the developed method was evaluated by the add-found test using synthetic solutions containing individual metal ion at 0.5 μg mL^{-1} level. The obtained results are complied in

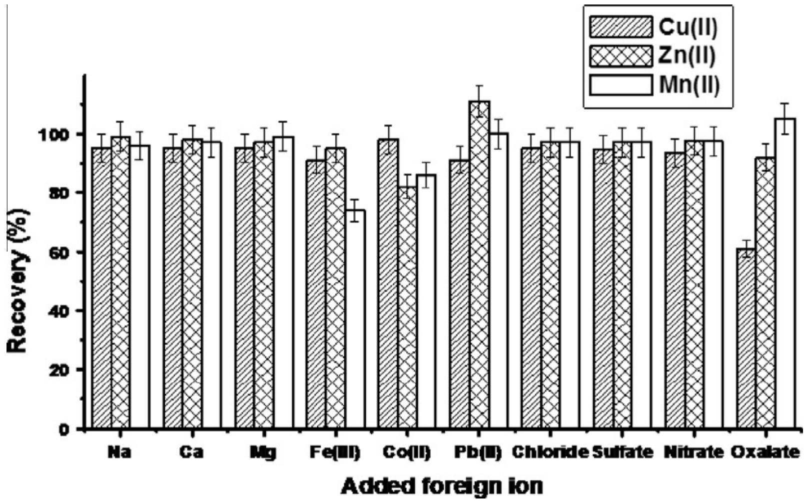

Fig. 12. Interference effect by some cations and anions on the recovery of Cu, Zn and Mn.

Table 4
Preconcentration factors obtained using 1.0 g AAPH–PUF column.

Element	Initial volume (mL)	Concentration ($\mu g\ mL^{-1}$)	Desorption volume (mL)	Recovery (%)	CF
Cu(II)	1000	10	10	93.0	100
Zn(II)	1000	10	10	96.7	100
Mn(II)	1000	10	10	96.0	100

Table 5
Accuracy of the AAPH–PUF method calculated by add-found test.

Element	Added ($\mu g\ mL^{-1}$)	Found[a] ($\mu g\ mL^{-1}$)	Recovery (%)	RSD (%)
Cu(II)	0.5	0.51	102	2.7
Zn(II)	0.5	0.48	96	4.3
Mn(II)	0.5	0.46	92	2.6

[a] Mean value for five measurements.

Table 6
Determination of Cu, Zn and Mn in Kerovit tablets.

Metal ion	Taken (μg)	Found (μg)	Recovery (%)	RSD (%)
Cu(II)	13.0	12.4 ± 0.06	95.3	4.6
Zn(II)	5.0	4.8 ± 0.09	96.0	1.8
Mn(II)	13.0	12.0 ± 0.01	92.3	0.8

Table 7
Determination of metal ions in environmental samples by AAPH–PUF and reference procedures.

Sample	Metal ion	Found[a]	RSD (%)
Fish liver	Cu(II)	27.5	6.3
	Zn(II)	150.0	3.5
	Mn(II)	10.7	6.7
Olive leaves	Cu(II)	20.0	2.8
	Zn(II)	57.0	3.1
	Mn(II)	16.8	6.6
Drinking water	Cu(II)	10.0	5.8
	Zn(II)	80.0	2.9
	Mn(II)	50.0	4.5

[a] Mean value of four replicate measurements ($n = 4$). Fish liver and olive leaves ($\mu g\ g^{-1}$) and drinking water ($\mu g\ L^{-1}$).

Table 5. Quantitative recovery was achieved varying between 92% and 102% and the corresponding RSD values were in the range 2.6–4.3%. The results are in good agreement, showing that the proposed method might be used for metal ion determination, even at low concentrations.

Noteworthy, the capacity of the sorbent was practically constant after its repeated use more than 70 cycles suggesting the multiple use of sorbent without significant loss in analytical its efficiency.

3.11. Preconcentration and recovery

The recovery of 10 μg of each metal ion placed in solutions of varying volumes from 100 to 1000 mL was determined after desorption by 10 mL from 0.4 mol L^{-1} HCl solution. The obtained results are summarized in Table 4. Quantitative recoveries (93–97%) were achieved at sample volumes in the range of 100–1000 mL. Above 1000 mL, the recoveries decreased and were not quantitative which might be attributed to the incomplete retention of metal ions probably by the washing action of the column by the sample itself. The corresponding preconcentration factor (CF) was found to be 100. Therefore, a sample volume $\leqslant$ 1000 mL was recommended for the simultaneous preconcentration of all metal ions in order to ensure good recovery. The detection limit (3σ) was found to be 0.10, 0.12 and 0.19 $\mu g\ L^{-1}$ and the limit of quantification (10σ) was 0.25, 0.32 and 0.39 $\mu g\ L^{-1}$, respectively. Obviously, the limit of detections are less than the concentration of the tested metal ions in the majority of real samples which enables quantification of these elements with sufficient accuracy.

3.12. Analysis of real samples

The applicability of the developed sorbent was evaluated by analysis of several real samples. Firstly, the pharmaceutical preparation, Kerovit tablet, was analyzed. The obtained results are shown in Table 6. Adequate recovery values were obtained in the range 92.3–96.0%. The corresponding RSD values varied in the ranges 0.8–4.6%, which are reasonable. Secondly, the content of metal ions under investigation was determined in fish liver, olive leaves and drinking water. The obtained results are summarized in Table 7. The RSD% values are found to be in the range 2.8–6.7% which is considered relevant (less than 10%) for real samples. The obtained data conferred susceptible accuracy of the developed method based on the satisfactory values of RSD in addition to the reasonably high sensitivity and validity of the proposed method for determination in pharmaceutical and environmental samples.

4. Conclusions

Simple and fast preparation of the AAPH–PUF sorbent was carried out under mild conditions to avoid decomposition of PUF polymer. The prepared sorbent was characterized by various physical tools and it showed fast equilibration with the studied elements and easy regeneration. Recycling the new sorbent is possible for more than 70 times and preconcentration factor 100 was achieved. The developed methods have been successfully applied to determination of metal ions in pharmaceutical and environmental samples. This made the proposed procedure alternative to other reported solid phase extraction methods.

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