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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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ABSTRACT

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 ^{1}H-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