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OFF-LINE SOLID PHASE SELECTIVE SEPARATION AND PRECONCENTRATION OF Cu, Zn, Pb AND Cd IN DRINKING WATER BY SOLID-PHASE EXTRACTION USING 4´-(2-HYDROXYPHENYLAZO)-3´-METHYL-1´-PHENYL-2´-PYRAZOLIN-5´-ONE FUNCTIONALIZED AMBERLITE XAD-2

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OFF-LINE SOLID PHASE SELECTIVE SEPARATION AND PRECONCENTRATION OF Cu, Zn, Pb AND Cd IN DRINKING WATER BY SOLID-PHASE EXTRACTION USING 4´-(2-HYDROXYPHENYLAZO)-3´-METHYL-1´-PHENYL-2´-PYRAZOLIN-5´-ONE FUNCTIONALIZED AMBERLITE XAD-2

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Abstract

A new solid – phase extraction sorbent is developed based on stepwise anchoring of two ligand molecules for the determination of copper, zinc, lead and cadmium in drinking water by flame AAS. Amberlite XAD-2 functionalized with 4´-(2-hydroxyphenylazo)-3´-methyl-1´-phenyl-2´-pyrazolin-5´-one (HPAPyr) was utilized for preconcentration/separation of these elements. The sorbent was prepared by two successive azo coupling reactions. Firstly, 2-aminophenol was anchored to the amino groups in the resin resulted from nitration followed by reduction. Then, the resulted 2-aminophenol functionalized resin was further diazotized and coupled to pyrazolone compound and the final product HPAPyr-XAD-2 was characterized by IR and elemental analysis. The optimum pH range for sorption, shaking time, exchange capacity, sample flow rate, preconcentration factor and interference from co-existing ions are investigated. All metal ions are quantitatively desorbed from the resin by 4.5 mol l^{-1} nitric acid solution. The sorbent provides limit of detection within the range 0.9 – 3.3 µg l^{-1} and concentration factor up to 250. The procedure is validated by analysis of certified material NIST-SRM 1577b. Application to drinking water showed satisfactory results with relative standard deviation RSD ≤ 8.5 %.

***Keywords**:4´-(2-hydroxyphenylazo)-3´-methyl-1´-phenyl-2´-pyrazolin-5´-one, Amberlite XAD-2, Preconcentration, Drinking water*

Introduction

The use of a preconcentration/separation technique is a necessity in the determination of trace metal elements by atomic absorption spectrometer when the concentration of the element is too low to be determined directly and/or when interference matrix cannot be eliminated [1,2]. The most important and widely used preconcentration and separation technique is the sorption of trace elements on an exchanger, silica gel, activated carbon with or without chelating groups. Chelating resins have also been used for this purpose [3-6]. The advantages of the column solid phase extraction over the applied liquid –liquid extraction are the higher concentration factor, the ability to handle larger volume samples in a closed system, and the possibility of combination with different modern analytical techniques such as atomic absorption spectrometry AAS permitting in this way simultaneous multi-element determination [7,8].

Solid-phase extraction has been performed by using several solid materials, such as polyurethane foam [9], silica-gel [10], styrene-divinylbenzene [11,12], chitosan [13] and other sorbents [14]. Styrene-divinylbenzene is commercially available as Amberlite XAD resin series. Many ligands were covalently coupled with a polymer backbone, such as 4,5-dihydroxy-1,3-benzenedisulfonic acid [15], pyrocatechol violet [16], *o*-aminobenzoic acid [17], and 3,4 dihydroxybenzoic acid [18,19].

Amberlite XAD-2 was modified by different chelating agents such as *o*-vanilline thiosemicarbazone [20] , dimethylglyoxal bis(4-phenyl-3-thio-semicarbazone), salicylic acid [21], alizarin red-S [22], aminophosphonic and dithiocarbamate group containing polyacrylonitrile [23].

The coupling of a ligand with a polymer backbone through a spacer arm, generally –N=N– or $–CH_2–$ group was investigated. This strategy renders the rugged system free from ligand leaching problems. However, the exchange capacity of these materials may be increased by an extensive functionalization of an appropriately cross-linked polymer. It is easily possible if ligand molecules of small size are chosen [24]. This is the main reason for carrying out stepwise synthesis of the proposed sorbent in this work to avoid steric hinderance that might originates from anchoring of large size ligands to this cross-linked polymer.

Edaravone (3-methyl-1-phenyl-2-pyrazolin-5-one), a strong novel free radical scavenger, is used for treatment of patients with acute brain infarction. Edaravone has preventive effects on myocardial injury following ischemia and reperfusion in patients with acute myocardial infarction. Antioxidant actions of edaravone include enhancement of prostacyclin production, inhibition of lipoxygenase metabolism of arachidonic acid by trapping hydroxyl radicals, inhibition of alloxan-induced lipid peroxidation, and quenching of active oxygen, leading to protection of various cells, such as endothelial cells, against damage by reactive oxygen species (ROS) [25]. Many pyrazolone derivatives have been used to preconcentrate metal ions such as 3-Methyl-1 -phenyl-4-stearoyl-5-pyrazolone loaded on silica gel for preconcentration of Copper, Cobalt and Nickel [26] and cadmium [27] and Mn (II) [28] by cloud point extraction preconcentration.

This paper proposes the stepwise synthesis of HPAPyr-XAD-2 sorbent and its utilization in an off-line solid-phase extraction (SPE) procedure for preconcentration/separation of trace elements in drinking water at Fayoum City. The principle interest is the use of this chelating resin in trace analysis depends on the simplicity and low cost of the method for separation and preconcentration of the studied metal ions. The main advantages of the proposed method are the low detection limit, high preconcentration factor, short analysis time and high selectivity.

Experimental

Apparatus

Flame atomic absorption spectrometer (FAAS, AAS5 FL, Carl – Zeiss, Germany) equipped with air–acetylene flame (Fuel 1.08 L/min, burner height 4-12 mm, and 1.2 nm slit) was used for the determination of copper (324.8 nm, 3 mA), zinc (213.9 nm, 4 mA) lead (217.0 nm, 3 mA) and Cadmium (228.8 nm, 2 mA) under the conditions recommended by the manufacturer. Infrared (IR) analysis (4000 – 400 cm^{-1}) was recorded on a Nicolet (USA) 5DX Fourier transform IR spectrometer. The pH adjustment was made with microprocessor pH meter equipped with a glass electrode BT. 500 BOECO (Germany), and calibrated with two standard buffer solutions at pH 4 and 7, and mechanical shaker provided with water bath.

Reagents

Doubly distilled water (DDW) was used for all preparations and for washing glassware. The laboratory glassware was kept overnight in chromic acid solution. Afterwards, it was rinsed thoroughly with DDW and dried in a dust-free environment. Standard solutions (1000 µg ml^{-1}) of copper, zinc, lead and cadmium were prepared by appropriate dilutions from Standard atomic absorption solutions (1000 mg ml^{-1}, Merck) and the working solutions were prepared immediately before use. All other chemicals used were of analytical grade. 2-aminophenol (Aldrich, UAS), 3-methyl-1-phenyl-2-pyrazolin-5-one (Fluka, Switzerland), sodium nitrite (Fluka) and nitric acid (Merck) were used without any further purification. Polystyrene divinyl benzene copolymer (amberlite XAD – 2) with 20-60 mesh and 4% cross linking was delivered from Aldrich.

Synthesis and characterization of HPAPyr-XAD-2

The method previously published by *Kumar et al.* [24] was applied after some modifications for preparation of 2-aminophenol functionalized amberlite XAD-2 as follow: amberlite XAD-2 beads (20 g) was nitrated by treatment with 10 ml concentrated HNO_3 and 25 ml of concentrated H_2SO_4 and the mixture was stirred at 60°C for 1 h in water bath. Thereafter, the reaction mixture was poured into an ice-water mixture. The nitrated resin was filtered, washed repeatedly with water until it is free from any acid. Then, it was treated with a reducing mixture consists of 40 g of $SnCl_2$, 45 ml of concentrated HCl and 50 ml of ethanol. The mixture was refluxed for 12 h at 90°C. After this, the solid precipitate was filtered, washed with water then 2 mol l^{-1}NaOH solution in order to release the amminated resin (R–NH_2) from $(RNH_3)_2.SnCl_6$ (where R refers to the resin matrix). The amino resin was firstly washed with 2 mol l^{-1}HCl and finally with distilled water to remove the excess acid. For diazotization and coupling, the amino resin was suspended in an ice-water mixture (350 ml), treated with 1 mol l^{-1} HCl and 1 mol $l^{-1}$$NaNO_2$ (added portion wisely) until the reaction mixture showed a permanent dark blue color with starch–iodide paper. The diazotized resin was filtered, washed with ice-cold water and reacted with 2-aminophenol (10.9 g in 100 ml 10% NaOH solution) at temperature less than 3°C for 24 h. The resulting brown colored beads of 2-aminophenol – XAD-2 were filtered, washed with doubly distilled water and dried in air. Coupling of 2-aminophenol – XAD-2 sorbent to pyrazolone was carried out as follows: Five grams from 2-aminophenol – XAD-2 was diazotized by the same procedure previously described and reacted to 3.60 g pyrazolone (in 100 ml ethanol containing 20 g sodium acetate) for 24h. The resulted orange-yellow product from 4´-(2-Hydroxyphenylazo)-3´-Methyl-1´-Phenyl-2´-Pyrazolin-5´-one functionalized amberlite XAD-2 (HPAPyr – XAD-2) was washed by DDW and dried at room temperature.

The data obtained from IR spectra of HPAPyr-XAD-2 sorbent indicate the existence of several additional bands in the modified resin compared to the untreated one. The sorbent has showed four additional bands corresponding to stretching vibration of: O-H (3653 cm^{-1}), C=O (1714 cm^{-1}), C – N (1515 cm^{-1}) and –N=N– (1598 cm^{-1}). The data for elemental analysis have showed good correlation between the experimental and calculated (in parenthesis) values. It was found to be 61.0% C (60.3%), 4.5 % H (5.2%) and 16.8% N (17.6%). The obtained results satisfy the repetitive unit $C_{24}H_{19}N_6O_2.3H_2O$ where three water molecules are added to balance the stiochiometry which might be adsorbed into the polymer matrix. The chemical structure of the repetitive unit in new resin is shown in Fig.1.

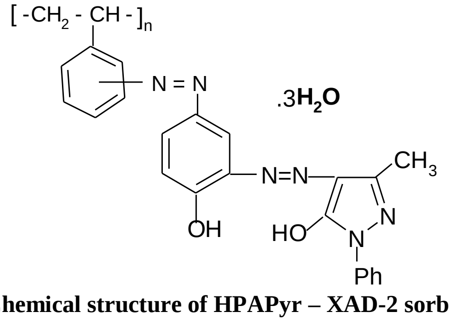

Fig.1. Chemical structure of HPAPyr – XAD-2 sorbent unit

Sample preparation

Reference Material

Certified reference material NIST-SRM 1577b Bovine liver was analyzed by the proposed SPE sorbents. Decomposition of this material was carried out according to the method reported [29]: Accurately weighed 0.4 g from the material was treated with 4.0 ml of 1:1 (v/v) nitric acid solution and kept in a clean glass vessel. Afterwards, the vessel was closed and left for digestion for 72 h. The thermal heating was carried out in a stove at 170°C for 16 h. After cooling at room temperature, the residue was diluted with Millipore water and adjusted to pH 7.0 with a 10% (w/v) sodium hydroxide solution. Finally, the volume was made up to 25 ml by Millipore water.

Drinking water

Ten liters from drinking water were collected in a glass container from our research laboratory in Faculty of Science at Fayoum City. The water sample was adjusted to pH 3.0 by nitric acid solution. Then, it was neutralized by sodium hydroxide solution and buffered to pH 6.5 with acetic/acetate buffer and the preconcentration/separation procedure column method was applied. After this, the sorbed elements in the column were eluted by nitric acid solution with suitable concentration. The metal ions Cu (II), Zn (II), Pb (II) and Cd (II) in the collected eluate are measured by FAAS for triplicate experiments.

Recommended Procedure

The influence of the sample pH on the extraction efficiency of the resin toward Cu (II), Zn (II), Pb (II) and Cd(II) was determined under static conditions in the batch mode. For this purpose, 100 mg of the sorbent was added to 20 ml, 1 µg ml^{-1} metal ion solution at different pH values. The mixture was mechanically shaken for 60 min at room temperature to attain equilibrium. The sorbent was separated, washed with DDW and the unextracted metal ion in the filtrate was determined by FAAS. For the preconcentration experiments, a minicolumn was fabricated by using glass tube 100 mm length and 10 mm i.d. The solid sorbent (1.0 g) was packed into the minicolumn. The minicolumn was treated with 4.5 mol l^{-1} nitric acid solution then washed by doubly distilled water until the effluent is free from any acid. A suitable aliquot of the drinking water sample was passed through the column after adjusting its pH to the optimum value and at a flow rate at 1.5 ml min^{-1}. The column was washed with DDW to remove unbounded metal ions and the sorbed metal ions were stripped off from the resin column with nitric acid. The recovered amounts of the metal ions in the eluate were measured by FAAS.

Results and discussion

Chemical and hydrodynamic optimizations

The sample pH was studied in the range 2.0–9.0 after adjustment by nitric acid or sodium hydroxide solution and stirred for 1.0 h with 100 mg of the modified resin by the batch procedure. Generally, maximum sorption for all the examined elements was observed in the pH range 6–8 (except Zn (II)) by this modified resin. In addition, it was found the uptake is increased by increasing the sample pH till reaching a limiting value then leveling off in certain range of pH which is usually might appear followed by a decrease. The decrease in sorption higher than pH 8 may be attributed to the possible precipitation of metal hydroxides. The optimum pH range for sorption is 6-8, 7-9, 5-7 and 6-8 for Cu (II), Zn (II), Pb (II) and Cd (II), respectively as shown in Fig. 2.

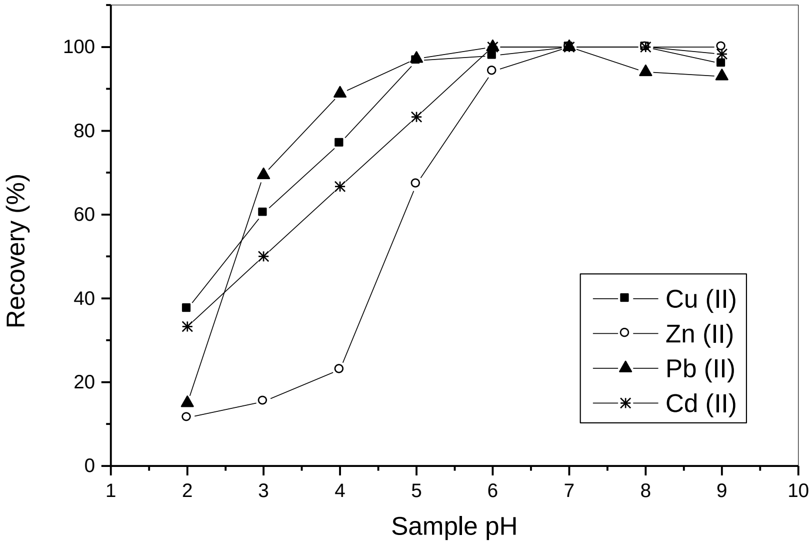

Fig. 2: Influence of sample pH on the retention of metal ions (1.0 µg /ml each) by 100 mg HPAPyr- XAD-2

The rate by which the metal ions are sorbed to HPAPyr-XAD-2 was investigated by batch procedure. The 100 mg of resin beads is stirred for different time intervals with 10 ml sample solution containing 1.0 µg/ml each element at the optimum pH 7.0. The concentration of metal ions in the supernatant solution was determined by the recommended method and the amount of metal ions sorbed on the resin phase was calculated from the difference. It was found that 10 min is enough shaking time to reach the maximum uptake for all elements as indicated in Fig. 3.

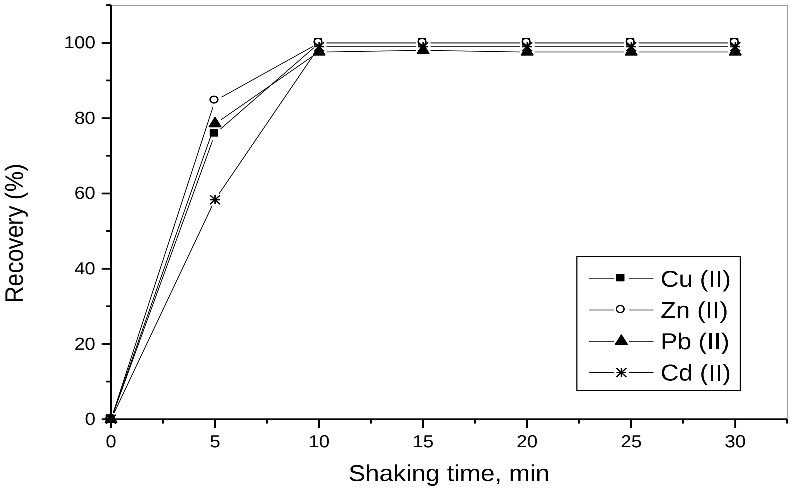

Fig.3: Influence of shaking time on the recovery of metal ions (1.0 µg/ml each) by 100 mg HPAPyr-XAD-2 at pH 7.0.

The exchange capacity of HPAPyr-XAD-2 by shaking excess amount from each element sample adjusted to pH 7.0 with 100 mg sorbent was investigated. The capacity values along with the RSD % after four measurements are listed in Table 1. Obviously, the affinity of the sorbent depends on the stability constant of the metal ion with the immobilized ligand on the resin. The results indicate the retention capacity of the prepared material is in the following order Pb (II) > Cu(II) > Cd (II) > Zn (II). Finally, the sorbent revealed satisfactory exchange capacity and it is sufficient to remove the studied elements from any natural sample.

Table 1: Total exchange capacity of HPAPyr – XAD-2 modified resin with Cu, Zn, Pb and Cd

Capacity (Mean ± S.D. mg g^{-1})			
Cu (II)	*Zn (II)*	*Pb (II)*	*Cd (II)*
4.70±0.09	*3.80±0.05*	*5.35±0.04*	*3.95±0.05*

Two important factors influence the quantitative recoveries and sorption of metal ions on solid – phase extraction studies which are flow rates of sample and eluent solutions. The influence of the sample flow rate on the sorption of the studied metal ions onto the resin column was investigated separately at the optimized pH 7.0. All experiments were performed at flow rates from 1.0 up to 9.0 ml min^{-1}. The maximum flow rate at which quantitative retention obtained (≥95 % recovery) estimates the range allowed for sorption the metal ions onto the column. The results demonstrated optimum range of sample flow rate for the investigated elements with HPAPyr-XAD-2 sorbent are 1 - 6 ml min^{-1} except for Zn (II) which is 1– 4 ml min^{-1}, however at flow rate greater than the estimated higher limit, the retention efficiency extensively decreases due to insufficient phase contact between the analyte and the resin as indicated in Fig 4.

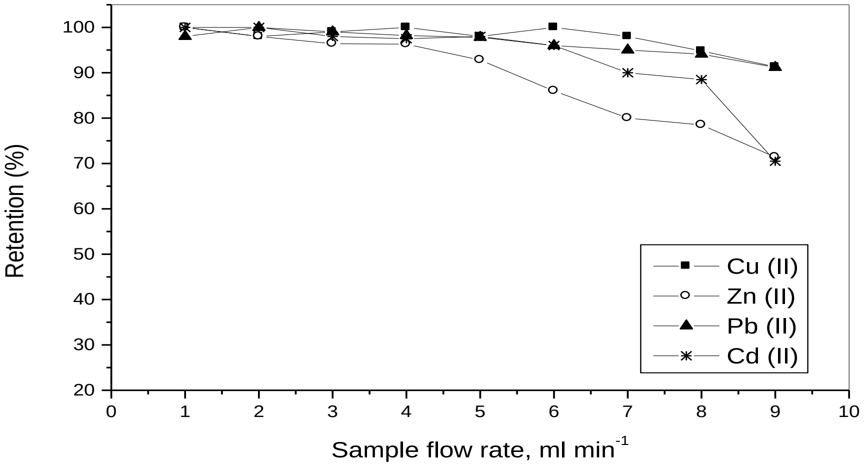

Fig. 4: Effect of sample flow rate on the retention of metal ions on 1.0 g HPAPyr - XAD-2 column at pH 7, 50 ml 1µg /ml sample

Elution of the metal ions from the resin column is expected to be achieved by application of mineral acid as eluent since it can furnish hydrogen protons needed for proton – metal exchange. For investigation of the suitable concentration of nitric acid solution that can provide proper recovery of the retained elements, the column procedure was applied: 50 ml samples were prepared equally. Each aliquot containing 1µg ml^{-1} from each element is adjusted to the optimized sorption pH. The retained elements were stripped using 25 ml nitric acid solution of varying concentrations in the range 1 – 6 mol l^{-1} and 2 ml min^{-1} flow rate. The obtained results are depicted in Fig. 5. The recovery was found to be similar and quantitative (recovery ≥ 95%) at nitric acid concentration ≥ 4.0 mol l^{-1}. Therefore, the 4.5 mol l^{-1} solution of the acid was selected for further desorptions experiments. At acid concentration less than 4.0 mol l^{-1}, the recovery percentage strongly decreases.

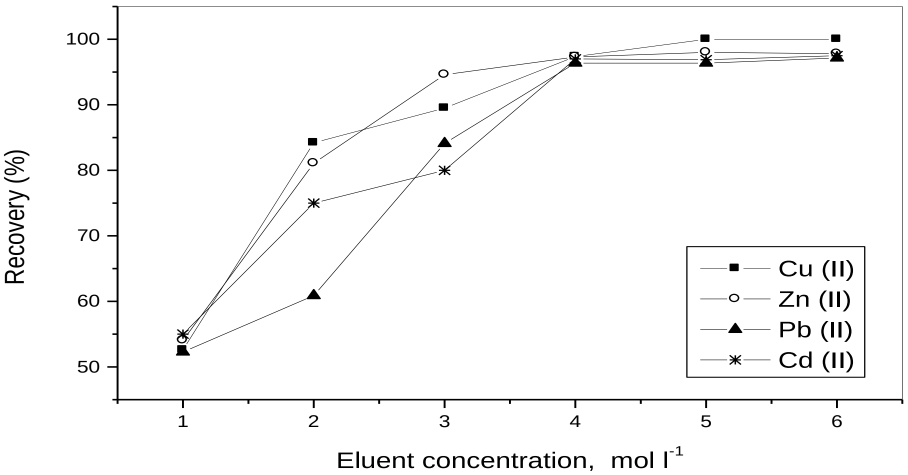

Fig. 5: Effect of nitric acid concentration on the desorption of Cu, Zn, Pb and Cd (50 ml, 1.0 µg /ml solutions) with HPAPyr - XAD-2 resin by column method

Preconcentration of the investigated elements from synthetic solutions was studied using column packed with the modified resin. The uptake was quantitative up to 4000 ml for Cu (II), Zn (II) and Pb (II) and up to 3000 ml for Cd (II) Table 2. The recovered amount of the element was found to be linearly proportional to the sample volume up to the recognized limit. The sorbed metal ions were eluted out by various volumes from ml 4.5 mol l^{-1} nitric acid solution. The eluent volume was designated from desorption breakthrough experiment at ≥95 % recovery. It was found that 14, 16, 12 and 10 ml from the eluent is sufficient to achieve ≥95 % recovery from Cu (II), Zn (II), Pb (II) and Cd (II), respectively. In addition, the concentration factor (CF) could be calculated from the ratio of the sample volume of a model solution to the eluate volume. The quantitative recoveries of the present matrixes, faster sorption/desorption and good reusability (more than 17 cycles) and stability of the resin are distinct advantages for this procedure. The results show the tested metal ions can be concentrated effectively from large volumes aqueous solutions, and can be applied for further determinations at trace level by using the modified sorbent. Finally, the results confirm the validity of the proposed method for the preconcentration of the investigated metal ions from drinking water.

Table 2: Preconcentration and recovery of Cu (II), Zn (II), Pb (II), and Cd (II) with HPAPyr-XAD-2 modified resin by column method

Metal ion	*Initial volume, ml*	*Eluent volume, ml*	*CF*
Cu (II)	*4000*	*14*	*285.7*
Zn (II)	*4000*	*16*	*250.0*
Pb (II)	*4000*	*12*	*333.3*
Cd (II)	*3000*	*10*	*300.0*

Interference

The influence of common co-existing ions might present in drinking water on the recovery of the studied metal ions was investigated. The metal ion under investigation was mixed with the diverse ion in the same sample. Thus, a competitive sorption would take place among all present ions for the available ligand sites. The results indicated little interference effect which could take place on the recovery of these elements up to the concentration depicted. The foreign ion is recognized interfering if the recovery percentage for the element decreases by ≥ 5 % from the value obtained in absence of this ion. It was found that the sorbent can extract the elements in the presence of Na^+ (1500 mg l^{-1}), K^+ (1000 mg l^{-1}), Ca^{++} (50 mg l^{-1}), Mg^{++} (50 mg l^{-1}), Fe^{+++} (0.3 mg l^{-1}), Mn^{++} (0.1 mg l^{-1}), Cl^-(1500 mg l^{-1}), Br^- (100 mg l^{-1}), I^- (100 mg l^{-1}), SO_4^{--}(500 mg l^{-1}), NO_3^- (1000 mg l^{-1}) and PO_4^{---} (150 mg l^{-1}).

Analytical Features

The analytical curves obtained from the use of the modified resins were found to be satisfactory since they provide wide range for analytical application and low detection limits. The LOD for the investigated elements are estimated based on three times standard deviation of the blank as can be seen in Table 3. The values of LODs for all metal ions enable the use of this material in collection of these metal ions at a trace concentration prior to their determination with higher sensitivity. This is an advantage since the higher sensitivity is a critical demand in any proposed analytical method. The detection limit obtained is 2.0, 3.3, 2.8 and 0.9 µg l^{-1} for Cu (II), Zn (II), Pb (II) and Cd (II), respectively which indicates good sensitivity of this sorbent. Furthermore, the analytical range of application is quite wide. Therefore, application of this preconcentration procedure is feasible even for natural samples in which large difference in its analyte concentration.

Table 3: Analytical features of HPAPyr- XAD-2 sorbent with Cu (II), Zn (II), Pb (II) and Cd (II)

Metal Ion	*Linear equation*	*Correlation coefficient*	*LOD (µg l^{-1})*	*Linear range (µg l^{-1})*
Cu	*A=(0.094552) C + 0.001244*	*0.99969*	*2.0*	*10-1000*
Zn	*A=(0.066995)C - 0.0020697*	*0.99637*	*3.3*	*10-1250*
Pb	*A=(0.089521) C – 0.001705*	*0.99632*	*2.8*	*3 - 1000*
Cd	*A=(0.094603)C - 0.0003161*	*0.99866*	*0.9*	*2 - 1250*

Accuracy

In order to assist the accuracy of the proposed preconcentration procedure in the determination of these elements in complex matrix, a certified was analyzed. The obtained results are listed in Table 4. The sorbent could retain the elements quantitatively with recovery values in the range of 94 – 106 % and RSD 0.8-6.8%. Therefore, utilization of this method for the determination of the elements under study is expected to be very successful since drinking water is less complex interfering matrix than biological samples.

Table 4: Analysis of certified reference material NIST – SRM 1577b (Bovine liver) using amberlite HPAPyr-XAD-2 by column method

Metal Ion	*Certified (µg/g)*	*Found (µg/g)*	*Recovery (%)*	*RSD%**
Cu	*160.0*	*151.0*	*94*	*6.8*
Zn	*127.0*	*123.0*	*97*	*2.9*
Pb	*0.13*	*0.12*	*95*	*4.5*
Cd	*0.50*	*0.53*	*106*	*0.8*

* For three replicate measurements

Analytical Application

In order to evaluate the applicability of this method to real analysis such as drinking water, the preconcentration step was carried out prior to the determination by flame AAS. The present preconcentration method was applied to the determination of the studied ions in drinking water. The results in Table 5 show that determination of the elements by this procedure is satisfactory. The values for RSD % vary within the range of 2.1 – 8.5 % which confirms the validity of the applied procedure. Finally, the method is simple and economical as the matrix can be used several times.

Table 5: Analysis of drinking water at Fayoum City by modified HPAPyr- XAD-2 resin by column method

Metal Ion	*Found (μg l^{-1})*	*RSD (%*)*
Cu	*58.1*	*8.5*
Zn	*128.0*	*2.1*
Pb	*3.9*	*6.6*
Cd	*7.9*	*3.9*

* Based on three times replicates

Comparison to other preconcentration procedures

The concentration factor obtained from the employment of the proposed modified resin as solid phase extractor is comparable to several sorbents reported in literature. The sorbent is capable to achieve higher concentration factor than many reported materials as shown in Table 6. Furthermore, the LOD for the procedure under investigation is close to most of the methods listed below which assess more confidence to this method.

Table 6: Comparative data of the studied ions on different sorbents

Elements	*Sample*	*Determination technique*	*CF*	*LOD μgL^{-1}*	*Separation/preconcentration technique*	*Reference*
Cu(II), Zn(II), Pb(II)	*Waters and vegetables*	*FAAS*	*50*	*1.3–5.8*	P. digitatum *immobilized on pumice stone, column technique*	*[30]*
Cu(II), Zn(II), Cd(II)	*Vegetable and dam, lake and tap waters*	*FAAS*	*50*	*1.14–1.66*	S. carlsbergensis *immobilized on silica gel, column technique*	*[31]*
Cu(II),Pb(II), Zn(II)	*Water, dust and black tea*	*FAAS*	*50*	*0.30–0.72*	A. fumigatus *immobilized on Diaion HP-2MG, column technique*	*[32]*
Pb(II), Cd(II)	*Tap and river waters*	*FAAS*	*90*	*0.032-0.096*	*Seeds of* Sterculia lychnophera *Hance* Bacillus sphaericus *immobilized on*	*[33]*
Cu(II), Pb(II),Zn(II), Cd(II)	*Tap water*	*FAAS*	*40-50*	*2.0-25.0*	*o-Aminophenol functionalized amberlite XAD-2*	*[24]*
Cu(II), Pb(II),Zn(II), Cd(II)	*Drinking water*	*FAAS*	*250-333*	*0.9-3.3*	*HPAPyr-XAD-2*	*This work*

FAAS, Flame atomic absorption spectrometry; CF: concentration factor.

Conclusion

Novel sorbent is developed based on the stepwise linking of ligand molecules to the surface of cross-linked polymer to avoid steric hindrance. A fast and simple preconcentration procedure for determination of Cu, Zn, Pb and Cd using the new modified matrix was successfully employed for the determination of the studied elements in drinking water at Fayoum City. The results obtained from the analysis of drinking water prove the reliability of the proposed sorbent and its application to various natural samples. The procedure showed relevant accuracy for determination of these elements even in the presence of various interfering ions which confer more selectivity of the method.

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