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# Solid Phase Selective Separation and Green Preconcentration of Cu, Zn, Pb and Cd in Drinking Water by Using Novel Functionalized Resin

**Research Article**

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**Abstract:** A new solid – phase extraction sorbent was 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. First, 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 the 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 were investigated. All metal ions were 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 $\mu$g $L^{-1}$ and concentration factor up to 250. The procedure was validated by analysis of certified material NIST-SRM 1577b. Application to drinking water showed satisfactory results with relative standard deviation RSD ≤ 8.5%.

**Keywords:** *Pyrazolone • Amberlite XAD-2 • Heavy metals • Preconcentration*



## 1. Introduction

The contamination by heavy metal ions from various environmental sources including natural waters is a great concern today. Water pollution by heavy metal ions is causing serious ecological problems in many parts of the world. Flame atomic absorption spectrometry, FAAS, is among the most widely used method for the determination of the heavy metals at trace levels, but the sensitivity and selectivity of FAAS is usually insufficient for the determination of heavy metals at trace concentration in complex matrix environmental samples [1,2]. In the trace analysis, therefore, preconcentration or separation of trace elements from the matrix is frequently necessary in order to improve their detection and selectivity by FAAS. The main advantages of preconcentration procedures are increased detection sensitivity at lower analyte concentration and avoidance of the matrix effect due to effective separation of the analyte from interfering matrix components.

Chelating resins have previously 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

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possibility of combination with different modern analytical techniques such as AAS which permit simultaneous multi-element determination [7,8].

Solid-phase extraction has been performed using several solid materials, such as polyurethane foam [9-12], silica-gel [13], styrene-divinylbenzene [14,15], chitosan [16] and other sorbents [17]. Styrene-divinylbenzene is commercially available in the Amberlite XAD resin series. Many ligands were covalently coupled with a polymer backbone, such as 4,5-dihydroxy-1,3-benzenedisulfonic acid [18], pyrocatechol violet [19], *o*-aminobenzoic acid [20], or 3,4 dihydroxybenzoic acid [21,22].

Amberlite XAD-2 was modified by different chelating agents such as *o*-vanilline thiosemicarbazone [23], dimethylglyoxal bis(4-phenyl-3-thio-semicarbazone), salicylic acid [24], alizarin red-S [25], aminophosphonic or dithiocarbamate group containing polyacrylonitrile [26].

The coupling of a ligand with a polymer backbone through a spacer arm, generally a methylene or azo group, was investigated. This technique has been used for enhancing the selectivity of the analytical system. However, the exchange capacity of these materials may be increased by extensive functionalization of an appropriately cross-linked polymer which is easily performed if ligand molecules of small size are chosen [27]. The main reason for carrying out stepwise synthesis of the proposed sorbent in this work is to avoid steric hindrance that 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 which provides protection of various cells, such as endothelial cells, from damage by reactive oxygen species (ROS) [28]. Many pyrazolone derivatives have been used to preconcentrate metal ions such as copper, cobalt and nickel [29], cadmium [30] and manganese [31] using 3-Methyl-1-phenyl-4-stearoyl-5-pyrazolone loaded on silica gel 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 of using this chelating resin in trace analysis is based 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.

# 2. Experimental procedure

## 2.1. Apparatus

Flame atomic absorption spectrometer (FAAS, AAS5 FL, Carl – Zeiss, Germany) equipped with air–acetylene flame (Fuel 1.08 L $min^{-1}$, burner height 4-12 mm, and 1.2 nm slit) was used for the determination of copper (324.8 nm), zinc (213.9 nm), lead (217.0 nm) and cadmium (228.8 nm) 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 using a microprocessor pH meter equipped with a glass electrode BT. 500 BOECO (Germany), and calibrated with two standard buffer solutions at pH 4 and 7, placed on a mechanical shaker equipped with a water bath.

## 2.2. 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 of copper, zinc, lead and cadmium were prepared by appropriate dilutions from Standard atomic absorption solutions (1000 mg $mL^{-1}$, Merck, Germany) 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, Switzerland) and nitric acid (Merck, Germany) were used without any further purification. Polystyrene divinyl benzene copolymer (amberlite XAD-2) with 20-60 mesh and 4% cross linking was obtained from Aldrich, UAS.

## 2.3. Chemicals and solutions

### *2.3.1 Synthesis and characterization of HPAPyr-XAD-2*

The method previously published by Kumar *et al.* [27] was applied after some modifications for the preparation of o-aminophenol (o-AP) functionalized amberlite XAD-2 as follows: amberlite XAD-2 beads (20 g) were nitrated by treatment with 10 mL concentrated $HNO_3$ and 25 mL of concentrated $H_2SO_4$ and the mixture was stirred for 1 h in a water bath at 60°C. Then, the reaction mixture was poured into an ice-water mixture.

The nitrated resin was filtered and washed repeatedly with water until it is free from any acid. Then, the resin was treated with a reducing mixture consisting of 40 g of $SnCl_2$, 45 mL of concentrated HCl and 50 mL of ethanol which was refluxed for 12 h at 90°C. After this, the solid precipitate was filtered, washed with water followed by 2 mol $L^{-1}$ NaOH solution in order to release the amminated resin (R–$NH_2$) from $(RNH_3)_2SnCl_6$ (where R refers to the resin matrix). The released amino resin was washed with 2 mol $L^{-1}$ HCl and finally with distilled water to remove any excess acid.

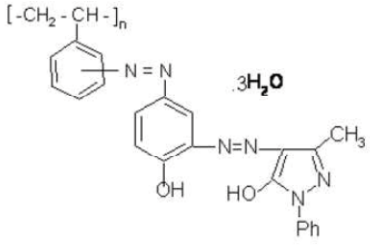
For diazotization and coupling, the amino resin was suspended in an ice-water mixture (350 ml), treated with 1 mol $L^{-1}$ HCl and 1 mol $L^{-1}$ $NaNO_2$ (added portion wisely) until the reaction mixture showed a permanent dark blue color with starch–iodide paper. The diazotized resin was filtered, washed with ice-cold water and reacted with o-aminophenol (10.9 g in 100 mL of a 10% NaOH solution) at temperatures less than 3°C for 24 h. The resulting brown colored beads of o-aminophenol – XAD-2 were filtered, washed with doubly distilled water and dried in air. Coupling of o-aminophenol – XAD-2 sorbent to pyrazolone was carried out as follows: Five grams of o-aminophenol – XAD-2 was diazotized by the same procedure previously described and reacted to 3.60 g pyrazolone pyr (in 100 mL ethanol containing 20 g sodium acetate) for 24h. The resulting orange-yellow product, 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 indicated the existence of several additional bands in the modified resins compared to the untreated one. The sorbent 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 $cm^{-1}$) (see Fig. 1). The data for elemental analysis 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, $C_{24}H_{19}N_6O_2 \cdot 3H_2O$, where three water molecules are added to balance the stoichiometry which might be adsorbed into the polymer matrix. The chemical structure of the repetitive unit in the new resin is shown in Scheme 1.

## 2.4. Recommended Procedure

### 2.4.1. Batch experiments

The influence of the sample pH on the removal efficiency of the resin toward Cu(II), Zn(II), Pb(II) and Cd(II) was




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

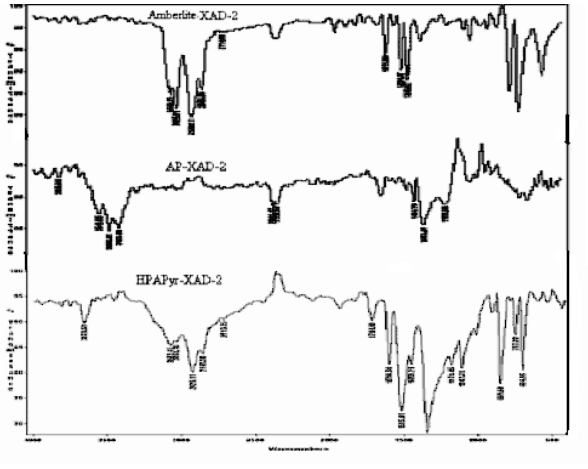



**Figure 1.** IR spectra of Amberlite XAD-2, AP-XAD-2 and HPAPyr-XAD-2 materials

determined under static conditions. 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 sample was studied in the pH range 2.0–9.0 after adjustment by nitric acid or sodium hydroxide. 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.

The rate by which the metal ions were sorbed by HPAPyr-XAD-2 was investigated by the batch procedure. The 100 mg of resin beads was shaken for different time intervals with 20 mL of sample solution containing 1.0 μg $mL^{-1}$ of each element at the optimum pH. The concentration of the 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.

The maximum capacity of HPAPyr-XAD-2 was determined by shaking 20 mL of Cu, Zn, Pb and Cd solution of different concentrations (0.5-100 μg $mL^{-1}$) with 100 mg resin for 60 min at pH 7, followed by the filtration of the resin and the concentration of the sorbed metal ion determined by flame AAS. The capacity was calculated based on the difference between the original and unsorbed concentration.

To assess the usefulness of the proposed method, the effect of diverse ions on the trace level determination of the metal ions has been investigated. A 20 mL solution containing 20 μg of Cu, Zn, Pb and Cd with 100 mg resin and foreign ions at various concentrations was prepared. Then, the procedure was performed under the optimal conditions and the recoveries of the studied metal ions were calculated. The interfering ions considered are those normally present in water.

The reproducibility of the proposed method for the removal and determination of Cu, Zn, Pb and Cd was investigated for 10 replicate measurements. The sample solutions were prepared identically using 20 mL solution containing the metal ions (1 μg $mL^{-1}$) adjusted to the optimum conditions. The uptake and the accuracy measured as RSD% was calculated for each metal.

#### 2.4.2. Dynamic procedure

For the preconcentration experiments, a minicolumn was fabricated by using a glass tube of 100 mm length and 10 mm *i.d*. The sorbent beads (1.0 g) were 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 sample was passed through the column after adjusting its pH and flow rate to the optimum value. 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. The concentration factor was calculated from the ratio of the initial volume of the sample to its final volume.

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. A 50 mL solution was studied at flow rates from 1 up to 9 mL $min^{-1}$. Beyond 9 mL $min^{-1}$ of eluent solution the recovery values of the metal ions were not quantitative.

The limit of detection of the proposed method for the determination of Cu, Zn, Pb and Cd was studied under the optimal experimental conditions. Blank samples of 500 mL were passed into the column then eluted with 4.5 mol $mL^{-1}$ nitric acid. Then, the ions in the eluate were determined by FAAS. This experiment was performed three times and the standard deviation of the results was calculated.

### 2.5. Sample preparation

Certified reference material NIST-SRM 1577b Bovine liver was analyzed by the proposed procedure. Decomposition of this material was carried out according to the method reported [32]. Accurately weighed 0.4 g of the material was treated with 4.0 mL of 1:1 (v/v) nitric acid solution and kept in a clean glass vessel. Afterward, the vessel was closed and left for digestion for 72 h. 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 and the metal ions were measured by the recommended method.

Ten liters of 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 to pH 7 and the preconcentration/separation procedure was applied. After this, the sorbed elements in the column were eluted by 4.5 mol $L^{-1}$ nitric acid solution. The metal ions in the collected eluate were measured by FAAS for triplicate experiments.

## 3. Results and discussion

### 3.1. Chemical and hydrodynamic optimizations

The pH is an important parameter to obtain quantitative recovery for heavy metal ions. Maximum sorption for all the examined elements was observed in the pH range

6–8 (except for Zn(II)). In addition, it was found that the uptake is increased by raising the sample pH until reaching a limiting value then leveling off within a certain range of pH which is usually followed by a decrease. The decrease in sorption higher than pH 8 may be attributed to the low solubility of the studied ions at this pH value. 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. All subsequent experiments were performed at pH 7.

To study the equilibrium established in a liquid-solid system, it is important to determine the distribution of the ions between the solid and liquid phases. The results showed that the rate of metal removal is found to be very rapid during the initial 10 min, and thereafter, the rate of ion uptake reached equilibrium as indicated in Fig. 3. The sorption half time $t_{1/2}$ needed for 50% metal ion removal of their initial concentration has been estimated to be 3-5 min. This rapid sorption indicates that the new resin is a suitable extractor for the preconcentration of Cu, Zn, Pb and Cd from trace solutions. Also, the surface is readily accessible to the ions in the solution. The rate at which the studied ions are removed from dilute aqueous solution by the new resin is a significant factor for the application in water quality control. Also, the position at which equilibrium is attained determines the useful life of the resin.

The capacity values along with their 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 that 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 the natural aqueous sample.

**Table 1.** Total exchange capacity of HPAPyr – XAD-2 modified resin with Cu, Zn, Pb and Cdd

| 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 |

Three important factors which influence the quantitative recoveries of metal ions on solid – phase extraction procedures are the flow rates of the sample and the volume and concentration of the eluent solutions. The maximum flow rate at which quantitative retention obtained estimates the range allowed for sorption of 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 $min^{-1}$ for all elements except for Zn(II) which is 1 - 4 mL $min^{-1}$. At flow rate greater than the highest estimated limit, the retention efficiency strongly decreases due to insufficient phase contact between the analyte and the resin as indicated in Fig 4. Flow rate 3 mL $min^{-1}$ was chosen for all experiments.

Elution of the metal ions from the resin column is expected to be achieved by application of mineral acid

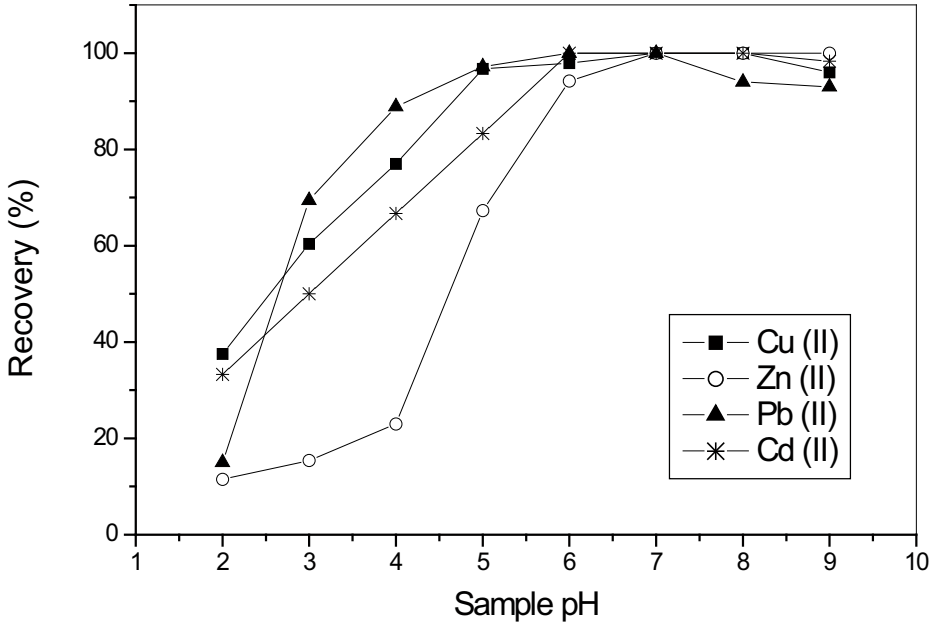



**Figure 2.** Influence of sample pH on the recovery of metal ions (1.0 $\mu$g $mL^{-1}$ each) by 100 mg HPAPyr- XAD-2

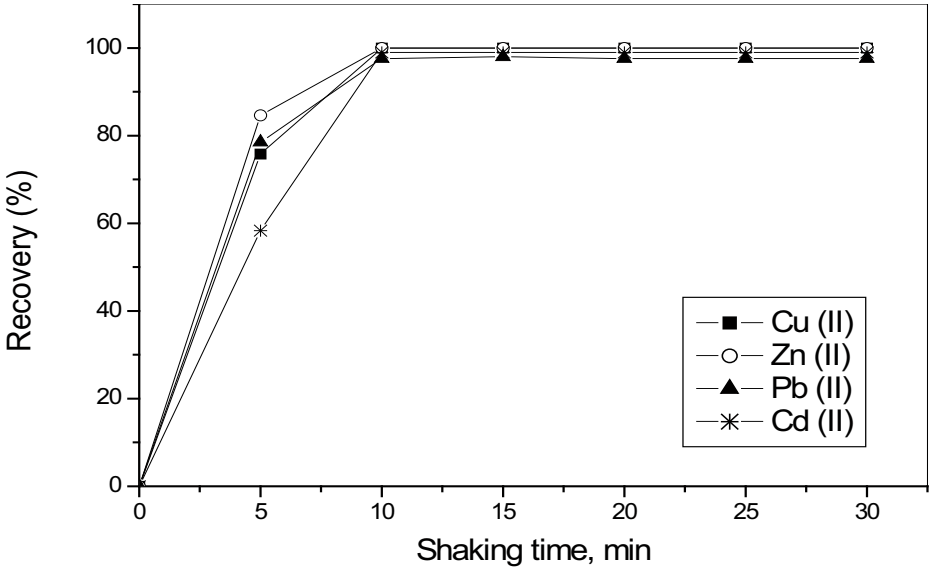



**Figure 3.** Influence of shaking time on the rocovery of metal ions (1.0 $\mu$g mL$^{-1}$ each) by 100 mg HPAPyr-XAD-2 at pH 7.0

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 quantitative recovery of the retained elements, the column procedure was applied using 50 mL samples prepared identically. The retained elements were stripped using 25 mL nitric acid solutions of varying concentrations in the range 1-6 mol L$^{-1}$ at 3 mL min$^{-1}$ flow rate. The obtained results are displayed in Fig. 5. The recovery was found to be quantitative at nitric acid concentration ≥4.0 mol L$^{-1}$. Therefore, the 4.5 mol L$^{-1}$ of the acid was selected for further desorption experiments. At acid concentrations less than 4.0 mol L$^{-1}$, the recovery percentage strongly decreases.

Preconcentration of the investigated elements from synthetic solutions was studied using columns 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) as shown in 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 at various volumes using

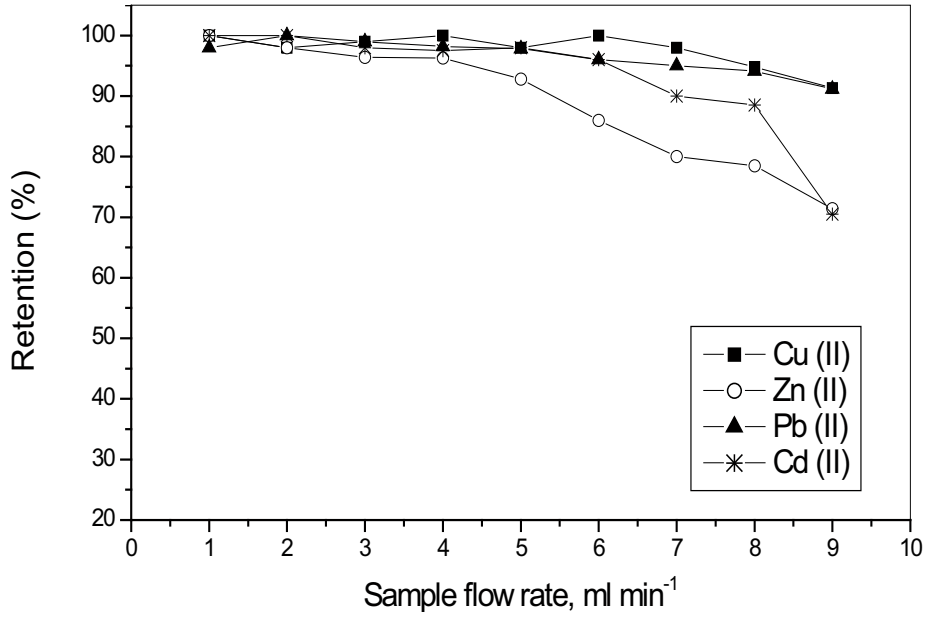



**Figure 4.** Effect of sample flow rate on the retention of metal ions 1.0 g HPAPyr - XAD-2 column at pH 7; 50 mL; 1 $\mu$g mL$^{-1}$ sample

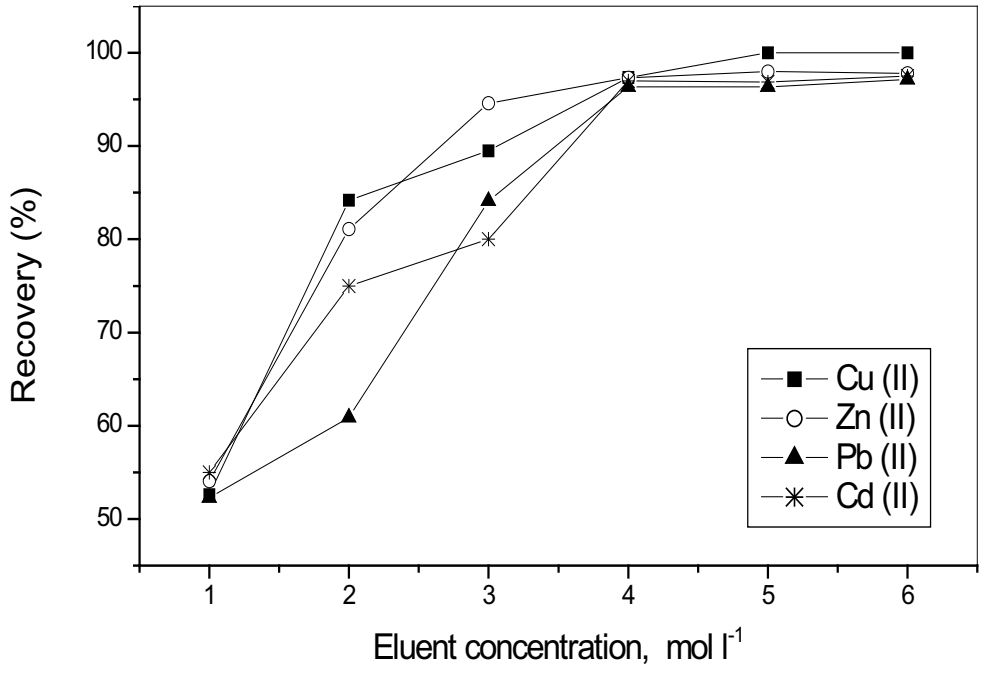



**Figure 5.** Effect of nitric acid concentration on the desportion of Cu, Zn, Pb and Cd with HPAPyr - XAD-2 resin by column method

**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 |

4.5 mol $L^{-1}$ nitric acid solution. The eluent volume was designated from desorption breakthrough experiments at ≥95% recovery. It was found that 14, 16, 12 and 10 mL of 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 results show that the tested metal ions can be concentrated effectively from large volume 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.

## 3.2. Interference

The influence of common co-existing ions present in drinking water on the recovery of the studied metal ions was investigated. The metal ion under investigation was mixed with diverse ions in the same sample. Thus, a competitive sorption would take place among all the ions present for the available ligand sites. The results indicated little interference effect on the recovery of these elements up to the concentration designated. The foreign ion is recognized as interfering if the recovery percentage for the element decreases by ≥5% from the value obtained in the absence of these ions. It was found that the sorbent can extract the elements in the presence of $Na^{+}$ (1500 mg $L^{-1}$), $K^{+}$ (1000 mg $L^{-1}$), $Ca^{2+}$ (50 mg $L^{-1}$), $Mg^{2+}$ (50 mg $L^{-1}$), $Fe^{3+}$ (0.3 mg $L^{-1}$), $Mn^{2+}$ (0.1 mg $L^{-1}$), $Cl^{-}$ (1500 mg $L^{-1}$), $Br^{-}$ (100 mg $L^{-1}$), $I^{-}$ (100 mg $L^{-1}$), $SO_4^{2-}$(500 mg $L^{-1}$), $NO_3^{-}$ (1000 mg $L^{-1}$) and $PO_4^{2-}$ (150 mg $L^{-1}$).

## 3.3. Analytical Features

The analytical curves obtained from the use of the modified resins were found to be satisfactory since they provide a wide range for analytical application and low limit of detection, LOD. The LOD for the investigated elements was 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 a collection of the studied 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,

**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 | 0.9997 | 2.0 | 10 - 1000 |
| Zn | A=(0.066995) C - 0.0020697 | 0.9964 | 3.3 | 10 - 1250 |
| Pb | A=(0.089521) C - 0.001705 | 0.9963 | 2.8 | 3 - 1000 |
| Cd | A=(0.094603) C - 0.0003161 | 0.9987 | 0.9 | 2 - 1250 |

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 resin. Furthermore, the analytical range of application is quite wide. Therefore, application of this preconcentration procedure is feasible even for natural samples with large differences in analyte concentration.

## 3.4. Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after being regenerated with 10-16 mL of 4.5 mol $L^{-1}$ $HNO_3$ and is stable up to a minimum of 17 adsorption elution cycles without an obvious decrease in the recoveries for the studied metal ions. The quantitative recoveries of the present matrixes, faster sorption/desorption and good reusability of the resin are distinct advantages for this procedure.

## 3.5. Accuracy

In order to assess the accuracy of the proposed preconcentration procedure in the determination of these elements in complex matrix, a certified material 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 a less complex interfering matrix than biological samples.

## 3.6. Analytical Application

In order to evaluate the applicability of this method to real analysis, 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, which proved the applicability of the presented method to the quantitative preconcentration of Cd, Pb, Zn and Cu in the natural samples. The values for RSD% vary within the range of 2.1-8.5% confirms the validity of the applied procedure.

## 3.7. 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 provides confidence in this method. Again, the present procedure finds application to real water samples unlike Amberlite XAD-4 *o*-vanillin semicarbazone which has been tested using only simulated river water samples [33].

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

| Metal Ion | Certified (μg $g^{-1}$) | Found (μg $g^{-1}$) | 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*

**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

**Table 6.** Comparative data of the studied ions on different sorbents

| Elements | Sample | Determination technique | CF** | LOD*** (μg $L^{-1}$) | 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 | 34 |
| 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 | 35 |
| 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 | 36 |
| Pb(II), Cd(II) | Tap and river waters | FAAS | 90 | 0.032-0.096 | Seeds of Sterculia lychnophera Hance Bacillus sphaericus immobilized on | 37 |
| Cu(II), Pb(II), Zn(II), Cd(II) | Tap water | FAAS | 40-50 | 2.0-25.0 | o-Aminophenol functionalized amberlite XAD-2 | 27 |
| Cu(II), Pb(II), Zn(II), Cd(II) | Drinking water | FAAS | 250-333 | 0.9-3.3 | HPAPyr-XAD-2 | This work |

*FAAS - fame atomic absorption spectrometry;
**CF - concentration factor;
***LOD - limit of detection.

## 4. 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, simple and green preconcentration procedure for the determination of Cu, Zn, Pb and Cd using the new modified matrix was successfully employed for the determination of the studied elements in drinking tap water at Fayoum City. The results obtained from the analysis of drinking water prove the reliability of the proposed sorbent and its application to natural samples. This procedure is suitable for the preconcentration and direct determination of the studied ions in real samples with high selective adsorbability, high precision and concentration factor, short analysis time and low detection limit. Moreover, the effect of coexisting interference ions in the determination of the studied metal could be eliminated by the selective adsorption and elution. So this method can be applied to direct determination of heavy metals in environmental samples using a technique with low investment and operation costs.

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