

APPLICATION OF AMBERLITE XAD-2 FUNCTIONALIZED WITH 8-HYDROXYQUINOLINE IN AN ONLINE SYSTEM FOR DETERMINATION OF COPPER IN WATER BY FAAS

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ABSTRACT

A simple, sensitive and low cost, flow injection time-based method was developed for on-line preconcentration and determination of copper at $\mu\text{g L}^{-1}$ levels in water sample. Amberlite XAD-2 functionalized with 8-Hydroxyquinoline packed in a minicolumn was used as sorbent material. The sample acidity is adjusted over a pH of 4.0 for effective retention of Cu (II) on the resin. The chelating resin can be reused for 300 cycles of sorption-desorption without any significant change in its activity. The enrichment factors were 17, 36 and 68 for preconcentration time of 60, 120 and 180 s and the detection limits are 3.6, 1.3, 0.72 $\mu\text{g L}^{-1}$ respectively. This resin offers better precision and the corresponding relative standard deviation (R.S.D.) values for seven successive determinations were 2.7 and 2.0 % for 50 and 100 $\mu\text{g L}^{-1}$ respectively. The sample throughput was 30 h⁻¹ for 5 mL of sample. To test the accuracy of the developed on-line FI-FAAS procedure, Standard Reference Material (SRM 1643e, Trace elements in water) supplied by National Institute of Standard and Technology (NIST), was analysed. Spiked recovery studies in water samples were performed using a NIST certified copper nitrate solution to confirm the accuracy of the proposed preconcentration procedure.

Keywords: Amberlite XAD-2, Flame Atomic Absorption Spectrometry, Flow-Injection, 8-Hydroxyquinoline, Solid-Phase Extraction, Water Samples.

1 INTRODUCTION

The effect of heavy metals toxicity on the environment and on human health has received considerable attention due to their persistent and bioaccumulative characteristics. Moreover, the toxicological and biological properties of most elements depend to a large extent on their chemical forms. Copper is an essential element not only for life in mammals but also for plants and lower forms of organisms. It has many biological effects as an essential element as well as a toxic one. The World Health Organization (WHO) decides the permissible limits for copper in drinking water which is 1.5 mg L⁻¹ [1]. Thus, even low copper levels in the human body may cause gastrointestinal diseases, such as diarrhea, stomach aches, vomiting and dizziness and high levels, associated with long-term exposure, may cause kidney or liver damages and mental disorders, such as Alzheimer's disease.

People that suffer from Wilson's disease should avoid the ingestion of drinking water and food containing copper. It is not yet confirmed whether copper is carcinogenic, and therefore, more estimates of high inhalation and ingestion exposures need to be analyzed to achieve more accurate responses [2].

There are some analytical techniques of detection, such as flame atomic absorption spectrometry (FAAS) [3], inductively coupled plasma atomic emission spectroscopy [4], inductively coupled plasma mass spectrometry [5,6], electro thermal atomization (ETAAS) [7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8] and X-ray fluorescence [9]. These techniques have no sufficient sensitivity for certain determinations, so these techniques require the use of a preconcentration step in order to reach an appropriate detection. Several enrichment procedures have been developed for the determination of metal traces involving different separation techniques such as co-precipitation [10,11], liquid-liquid extraction [12], cloud-point extraction [13] and solid phase extraction [14,15]. The process based on SPE has received more acceptances due to a number of possible advantages including availability and easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation and enrichment. These procedures generally avoid the use of organic solvents, which may be toxic.

In this context, flow injection analysis (FIA) systems have been successfully coupled with solid-phase extraction (SPE) for preconcentration and determinations of copper. Some of these are carbon nanotubes [16], polyurethane foam [17], silica-gel [18], chitosan [19] and alumina [20]. Another approach employed in on-line SPE systems is the application of functionalized polymeric resins. In this case, some functionalized polymeric solid supports such as polystyrene-divinylbenzene (PS-DVB) polymer commercially available as Amberlite XAD resin. These are o-amino benzoic acid functionalized with Amberlite XAD-4[21], Salicylic acid functionalized with Amberlite XAD-2 [22] and Xylenol orange functionalized with Amberlite XAD-2 [23, 24].

In the present work, 8-Hydroxyquinoline was functionalized onto Amberlite XAD-2 for the first time in on-line flow injection column preconcentration system for the determination of copper by FAAS. All analytical parameters such as pH, concentration of elution solution, sample and elution solution flow rates, and also the effect of matrix components were studied. Furthermore, the proposed method is applicable for the determination Cu (II) in different water samples.

II EXPERIMENTAL SECTION

2.1 Instrumentation

A PerkinElmer (Shelton, CT, USA) Model AAnalyst™ 400 flame atomic absorption spectrometer, coupled with the FIAS™ 400 flow injection system [22], was used for the automatic processing of the method and operated in the preconcentration mode. The whole system was controlled by a personal computer and Winlab32™ (Version 6.5.0.0266) application software. The flow injection system (FIAS 400) was coupled to the nebulizer system of the spectrometer. It comprises of two peristaltic pumps, two positional valves, and a preconcentration column. Two Tygon® R3607 tubes (i.d.1.14 mm) were applied for both pumps. The pH measurements were made with a Model LI614 pH meter (Elico Ltd., India). An IR spectrum was recorded on a PerkinElmer Model Spectrum

RX-1. CHNS was carried out on a Model Varo EL-III Elementor. Thermal analysis (TGA) was performed with a PerkinElmer Model Diamond DSC. SEM (Scanning Electron Microscopy) was carried out using the Scanning Electron Microscope Model FEI Quanta 200F (ICON, THE Netherlands).

2.2 Reagents and Chemicals

A 1000 mg L⁻¹ stock solution of copper was prepared from analytical reagent grade Cu (II) nitrate in doubly distilled water and standardized titrimetrically with EDTA before use. The standard solutions were prepared by dilution of the stock solutions with doubly distilled water. The pH adjustments were made with 0.1M HCl and 0.1 M NaOH. All laboratory glassware's were kept overnight in a 10% (v/v) nitric acid solution and washed before use with doubly distilled water. Amberlite XAD-2 resin (Sigma-Aldrich) has a surface area of approximately 300 m²/g, moisture holding capacity of 54–60%, particle size of 20–60 mesh, pore diameter of 90 Å (mean pore size), and a pore volume of 0.65 mL/g. 8-Hydroxyquinoline used was of analytical reagent grade. All analytical reagents were procured from either E. Merck (Darmstadt, Germany) or Thomas Baker (India). Certified Cu (II) nitrate solution, traceable to NIST, was procured from E. Merck. The standard reference material SRM-1643e Trace Elements in Water was obtained from National Institute of Standards and Technology, Gaithersburg, MD, USA (NIST). The water samples were collected from three different places Noida (U.P), Naryana and Mayapuri, Delhi, India.

2.3 Synthesis of Amberlite XAD-2 Functionalized with 8-Hydroxyquinoline (AXAD2-HQ) Chelating Resin

The Amberlite XAD-2 (styrene-divinylbenzene copolymer) was modified according to the procedure reported in the literature [24]. The synthesis involves nitration of XAD-2, followed by the reduction to form an aromatic amine. This amine facilitates the formation of a stable diazonium salt. Thereafter, the diazotized polymer was filtered, washed with cold water and reacted at 0–3 °C for 24 h with 2g of Hydroxyquinoline, dissolved in 400 mL of water and 200 mL of glacial acetic acid. The dark brown coloured beads were filtered washed with 4 mol L⁻¹ HCl and water successively and dried in air. The structure of AXAD2-HQ resin is shown in Fig.1.

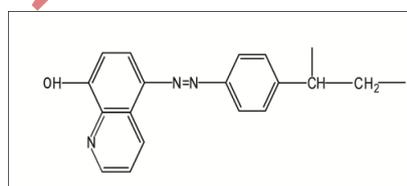


Fig.1 Structure of AXAD2-HQ resin

2.4 Mini-column preparation

The synthesized AXAD2-HQ resin (150 mg) was packed in a mini glass column (3.0 cm length and 3.0 mm internal diameter), both the two ends of the column were sealed with cotton. The minicolumn was treated with 2.0 mol L⁻¹ HNO₃ and washed with doubly distilled water until the resin was free from acid. A suitable volume

of the solution containing copper in the concentration range of 0–120 $\mu\text{g L}^{-1}$ was passed through this column after adjusting its pH to an optimum value. The column had a constant performance during all experiments and there was no need for any regeneration or repacking.

2.5 On-line Flow injection – Flame Atomic Absorption Spectrometry (FI-FAAS) determination of copper

The on-line FI-FAAS system used involved two simple preconcentration and elution steps. Flow Injection analysis program was controlled by a computer program which includes: pre-filling, filling, and loading and elution steps [22]. In the preconcentration step, the injection valve is in the 'load' position and the sample was typically pumped by Pump1 through the AXAD2-HQ minicolumn. During the elution step, the above valve is in the 'injection' position, and the elution solution, nitric acid is propelled by pump 2 through the column in order to elute the sorbed complex and transport directly into the nebulizer of the spectrometer. Signals were recorded as absorbance using the instrument software. The sampling rate achieved was 30 samples per hour for a preconcentration time of 60 s and an elution time of 30 s.

III RESULTS AND DISCUSSION

3.1 Characterization of the Amberlite XAD-2 functionalized with 8-Hydroxyquinoline (AXAD2-HQ) chelating resin

3.1.1 FT-IR spectrum -The chelating resin shows bands (Fig. 2) of Amberlite XAD-2 and chelating agent, 8-Hydroxyquinoline which shows that chelating agent has been loaded on resin. AXAD2-HQ resin has bands at 3421 cm^{-1} (O-H stretching), 2924 cm^{-1} (C-H stretching), 1615 cm^{-1} (C=N), 1346 cm^{-1} (C-N), 1109 cm^{-1} (C-O) and 1515 cm^{-1} (-N=N-), which did not appear in the IR spectrum of AXAD-2. This supports the loading of 8-Hydroxyquinoline resin onto Amberlite XAD-2 with diazotized (N=N) coupling.

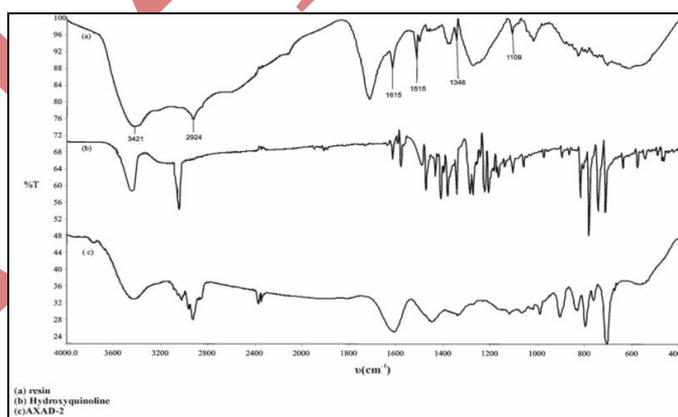


Fig.2 Infrared spectra of Amberlite XAD-2 functionalized with 8-Hydroxyquinoline resin.

3.1.2 Thermogravimetric analysis (TGA) - The thermogravimetric analysis (TGA) curve of freshly prepared AXAD2-HQ resin showed a very slow but steady weight loss up to 600 °c. The observed weight loss is 6.9% up

to 120 °c. This is due to physisorbed water on the resin, which supported the presence of only one water molecule per repeat unit of chelating resin. It should be assume that with each ring one dye molecule is covalently bonded to an azo group and it occupies a para position to the -CH-CH₂- group.

3.1.3 CHN- The CHN elemental analysis provides a mean for the rapid determination of carbon, hydrogen and nitrogen in organic matrices. The C, H and N % in AXAD2-8HQ resin, resin was found to be C: 70.42%, H: 4.86%, N: 15.02%, while calculated for C₁₇H₁₄N₃0.1H₂O was C: 69.38%, H: 4.76%, N: 14.28%. It further confirmed one water molecule per repeat unit of chelating resin.

3.1.4 SEM- A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The micrographs of the pure resin had a smooth and flat surface, while the modified chelating resin shows dense microstructures and granular grains. This signifies that the ligand loads onto the support. The substrate surface was changed after functionalization with 8-Hydroxyquinoline. They are agglomerated polymeric materials with irregular shapes and sizes vary from 30 µm to 500µm.

3.2 Optimization of experimental parameters for online preconcentration of copper

In order to improve the performance of the online preconcentration method for Cu (II) determination, all major chemical and flow variables were examined in detail using the FI-FAAS manifold with standard solution of 100 µg L⁻¹ of copper. The first variable optimized was the sample pH, with a pH range of 2.0–10.0 and it was adjusted with buffer solution. The low absorbance of Cu (II) at high acidity was due to the low complex formation rather than the low retention efficiency of the packing material. Thus, the pH of sample solution for the online preconcentration was adjusted at 4.0 in further experiments as shown in Fig.3.

The elution of Cu (II) from the minicolumn was studied by using HNO₃ solutions at different concentrations (0.01–2.0 mol L⁻¹). The total elution was reached in concentration over 0.5 mol L⁻¹. So, 0.5 mol L⁻¹ HNO₃ solution was selected as eluent for further studies (Fig.4). The time of elution was also studied, because it determines the quantity of acid that passes by minicolumn. It was found that for elution time superior than 30 s the absorbance signal was constant, using 0.5 mol L⁻¹ HNO₃ as eluent solution. So, an elution time of 30 s was chosen for further experiments in order to pass a minimum quantity of acid by the minicolumn and to increase the sample throughput.

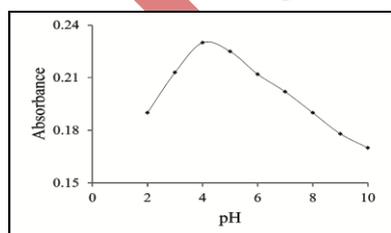


Fig.3 Effect of pH

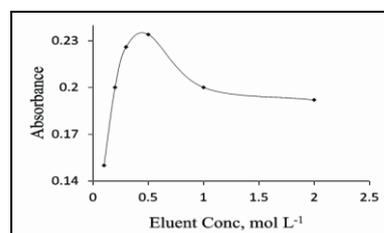


Fig.4 Effect of eluent concentration

The flow rate of the eluent in the elution stage was investigated in the range 2.0–7.0 mL min⁻¹. The analytical signals slowly decreased as flow rate increased. The results obtained showed that the analytical signal is

maximum at eluent flow rate of 6.0 mL min⁻¹ as shown in Fig.5. High flow rates are also limited by the backpressure produced by the column. Otherwise, low flow rates decreases sample throughput resulting in a long time of analysis. The effect of sample flow rate in the preconcentration of Cu (II) was studied at flow rates of 2.0– 7.0 mL min⁻¹. A flow rate of 5.0 mL min⁻¹ was selected (Fig.6) for the preconcentration of the Cu (II) ions, with the aim of obtaining a greater analytical frequency, and this flow rate was used for all of the later experiments.

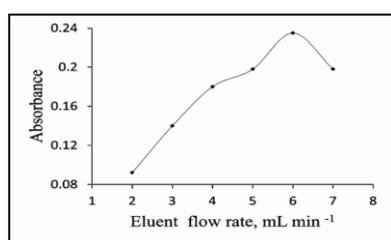


Fig.5 Effect of eluent flow rate

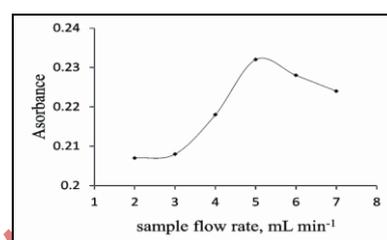


Fig.6 Effect of sample flow rate

3.3. Analytical figures of merit

The proposed procedure can be applied for preconcentration and separation of Cu (II) within the range 0-120 µg L⁻¹ from AXAD-2 resin functionalized with 8-Hydroxyquinoline reagent. The analytical characteristics of the proposed procedure using the parameters previously optimized are summarized in Table 1. The limit of detection (LOD), defined as the absolute mass of metal that gives a response equivalent to three times the standard deviation (s) of the blank was also calculated. The calibration graphs were linear at a preconcentration time of 60,120 and 180 s. The enhancement factors obtained were 17, 36 and 68 by using the pH 4.0 and sample flow rate of 5.0 mL min⁻¹. The experimental enhancement factor was calculated as the ratio of the slopes of the calibration graphs with and without preconcentration. The detection limits (DL) were found to be 3.6, 1.3 and 0.7 µg L⁻¹ at a preconcentration time of 60,120 and 180 s respectively. The precision (RSD) of 2.7 and 2.0% was obtained at 50 and 100 µg L⁻¹ Cu (II). The sample throughput of 30 h⁻¹ was obtained at 60 s preconcentration time. A lower sample throughput of 20 and 15 h⁻¹ were obtained by using longer preconcentration time of 120 and 180 s.

Table 1 Analytical Features of the on-line Cu (II) preconcentration system

Parameter	Optimum Condition		
	60	120	180
Preconcentration Time (PT, s)	60	120	180
Linear range (µg L ⁻¹)	0-120	0-120	0-90
Limit of detection (µg L ⁻¹)	3.6	1.3	0.7
Sample Throughput (h ⁻¹)	30	20	15
Enhancement factor	17	36	68
Regression equation (6 standards, Cu (II) /µg L ⁻¹) (with preconcentration)	$A_{60} = 0.01528 + 0.00263 [\text{Cu (II)}]$ $A_{120} = 0.01144 + 0.00553 [\text{Cu (II)}]$ $A_{180} = 0.04532 + 0.01028 [\text{Cu (II)}]$		

Regression equation (6 standards, Cu (II) / $\mu\text{g L}^{-1}$) (without preconcentration)	A = 0.00086 + 0.00015204 [Cu(II)]		
Correlation coefficient, r	0.993279	0.993926	0.993564
Precision (%)	2.7, [Cu (II)] = 50 $\mu\text{g L}^{-1}$ 2.0, [Cu (II)] =100 $\mu\text{g L}^{-1}$		

3.4. Effect of Foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of interferences on the determination of copper was investigated. The results obtained are shown in Table 2, from which it is clear that copper could be determined in the presence of commonly encountered matrix components such as alkali and alkaline earth elements. Thus, the effect of Na^+ , Cl^- , NO_3^- , SO_4^{2-} , Br^- , Mg^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ca^{2+} , Al^{3+} , K^+ on the sorption efficiency of AXAD2-HQ resin for 100 $\mu\text{g L}^{-1}$ Cu (II) were studied using the recommended flow-injection column method under the optimum conditions. The effect of each species was considered interference when the signal in the presence of the species resulted in an absorbance deviation of more than $\pm 5\%$.

3.5. Determination of copper in water Samples

The on-line pre concentration procedure was applied to the determination of Cu (II) in water samples. These water samples were collected from three different places Noida (U.P.), Naryana and Mayapuri, Delhi, India. All the water samples were filtered through 0.45 μm pore size membrane filter to remove suspended particulate matter. The method validation was made through spike recovery tests with the addition of 20 $\mu\text{g L}^{-1}$ Cu (II) using certified Cu (II) nitrate solution, traceable to NIST. The recoveries from the spiked samples were varied in the range 95-97%. The analytical results along with the recovery are summarized in Table 3.

Table 2 Effects of Matrix Ions on the recovery of Cu (II) ions

Interfering ion	Tolerance Limit (mgL^{-1})
Na^+	30,000
Cl^-	25,000
Br^-	15,000
Mg^{2+}	20,000
SO_4^{2-}	10,000
NO_3^-	1500
Cd^{2+}	20
Pb^{2+}	25
Ca^{2+}	18

K ⁺	20
Al ³⁺	10
Zn ⁺²	15

Table 3 Analytical Results Obtained for the Determination of Cu (II) in Water Samples

Sample	Conc. Determined ($\mu\text{g L}^{-1}$)	Conc. Determined by 20 $\mu\text{g L}^{-1}$ Spiked Cu (II) ($\mu\text{g L}^{-1}$)	Recovery (%)
Noida, Industrial Area, U.P	40.44 \pm 2.2	59.39 \pm 2.1	95 %
Nariana, Industrial Area, Delhi	46.59 \pm 2.5	65.72 \pm 2.3	97 %
Mayapuri, Industrial Area, Delhi	15.03 \pm 1.6	33.57 \pm 2.2	96 %

3.6. Accuracy of the method

In order to evaluate the accuracy of the developed on-line preconcentration procedure, it was tested by determining the Cu (II) content in certified standard reference material NIST SRM 1643e Trace elements in water. The analytical results obtained are in good agreement with certified values. The recoveries occur in the range 97-99%.

3.7. Comparison of performance characteristics of newly designed chelating resin with other selected on-line SPE methods

For comparative purposes, the performance characteristics of the proposed method and other selected online solid phase extraction (SPE) preconcentration methods coupled to FAAS for Cu (II) determination reported in the literature are presented in Table 4. The proposed method shows good accuracy, sensitivity and precision with better detection limits than previous works for Cu (II) determination using reasonable preconcentration time as well as sampling frequency.

Table 4 Performance characteristics of the proposed method and other selected online SPE methods for Cu (II) determination with FAAS

Support	Chelating Agent	Eluent	PT (s)	RSD (%)	DL	EF	Ref.
Amberlite XAD-2	Pyrocatechol	HNO ₃	180	3.8	0.3	36	25
Amberlite XAD-2	3,4-dihydroxybenzoic acid	HCl	120	1.1	0.2	33	26

Amberlite XAD-2	2-aminothiophenol (AT-XAD)	HNO ₃	180	-	0.5	35	27
Amberlite XAD-4	3,4-dihydroxy benzoic acid	HCl	60	2.1	2.3	22	28
Amberlite XAD-4	β-nitroso-α-naphthol	HNO ₃	180	2.8	0.4	58	29
Amberlite XAD-4	2,6-dihydroxyphenyl-Diazominoazobenzene	HNO ₃	60	2.7	0.3	28	30
Amberlite XAD-4	Schiff Bases	HNO ₃	60	-	1.2	13.	31
Chitosan bipolymer	5-Sulphonic acid-8-hydroxyquinoline	HNO ₃	90	0.7	0.3	19.	32
Chloromethylated polystyrene	PPDOT	HNO ₃	240	2.0	0.5	41	33
Micelle	HBDAP	HNO ₃	30	-	3.2	-	34
Polyurethane foam	Me-BTANC	HCl	90	2.9	1.2	14.	35
styrene-divinylbenzene	(S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester	HCl	120	1	1.1	42	36
styrene-divinylbenzene	salen-OMe complex	-	60	2.8	1.0	12	37
Amberlite XAD-2	8-Hydroxyquinoline	HNO₃	180	2.0	0.7	68	This Work

IV CONCLUSION

Amberlite XAD-2 functionalized with 8-Hydroxyquinoline was successfully applied to the on-line preconcentration and determination of Cu (II) by FAAS. The on-line preconcentration procedure is simple, rapid, low-cost and sensitive. The Enrichment factors (EF) obtained, for Cu (II), was better than comparable to those presented by other methods described in the literature (Table 4). The low detection limits and high tolerance to interferences from the matrix ions allows the application of the proposed procedure for copper determination in different water samples. The synthesis resulted in a promising and very stable support that does not present problems of leaching. These features allow a long lifetime of the minicolumn packed with the resin, with its use for many cycles being possible.

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