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An Agarose-Schiff's Base Chelating Adsorbent for Preconcentration and Flame Atomic Absorption Spectrophotometric Determination of Cu(II) in Water Samples

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A recently synthesized naphthol derivative Schiff's base, 2,2′-[1,2-ethanediyl-bis(1-nitrilopropylidyne)]bis(1-naphthalene), was covalently bonded to an epoxy activated agarose (Novarose) bead. Adsorption properties of the new adsorbent and effects of various parameters on the separation and column preconcentration of Cu^{2+} prior to its determination by flame atomic absorption spectrophotometric method were carefully studied. The optimum pH range for quantitative accumulation of copper was 5.7–7.0 and the binding capacity was calculated to be 14.4 (±0.4) mg Cu^{2+} per mL of the packed adsorbent. The analyte can be eluted with 2 mL of a 0.075 mol L^{-1} HCl solution. The lowest adsorbent volume (packed in a 6 mm i.d. column) for achievement of a quantitative recovery was 0.2 mL. Using this volume, sample flow rates up to 7.5 mL min^{-1} could be applied. Electrolyte, $NaNO_3$, concentrations up to about 0.5 mol L^{-1} was tolerated by a 0.5 mL column. Enrichment of the analyte was quantitative in presence of Na^+, K^+, Mg^{2+} and Ca^{2+} concentrations of 40, 40, 3.3 and 8.2 g L^{-1}, respectively. Pb^{2+}, Ni^{2+}, Fe^{3+}, Cr^{3+} and Zn^{2+} with concentrations of 15 to 20 mg L^{-1} also had no effect on the analyte's signal. The maximum preconcentration factor obtained was 350, corresponding to an enrichment volume of 700 mL. A detection limit of 0.62 μg L^{-1} was obtained. The method was successfully applied to the determination of copper in river and tap water samples.

Key Words: Agarose, Schiff base, Preconcentration, Copper(II), Flame atomic absorption spectrophotometer.

INTRODUCTION

Determination of metal ions at trace level is very important from the viewpoint of environmental protection, water pollution studies, food and agricultural chemistry and high purity material development. To carry out such measurements in a complex matrix by a simple technique, *e.g.*, flame atomic absorption spectrophotometric, separation and preconcentration of the metal ion is essential most of the time. The use of different methods including normal and ion-pair

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chromatography[1, 2], ion-exchange[3] and sorption extraction[4, 5], supported liquid membrane[6] and solid phase extraction[7, 8] for such procedures, have been substantially increased in recent years. Metal chelating adsorbents with chemically bonded chelates[9–11] are good choices for separation and preconcentration of metal ions, as they usually offer superior stability and selectivity and easier use in an automated flow system. Therefore, design of new types of such resins with various selectivities for different elements is important.

The Schiff bases are stable imines containing an aryl group attached to a carbon or nitrogen atom. A group of them called "salens" are multidentate ligands known as stable chelating agents[12, 13]. They are formed by a condensed reaction between salicylaldehyde and ethylendiamine. Salens with four active donor sites, with oxygen and nitrogen donor atoms, make stable complexes with ions such as cobalt[14], manganese[15], lead[16], nickel[17] and copper[12]. Salen complexes have found applications in both homogeneous and heterogeneous forms as bio- and chemical sensors[18], electrocatalysts[19] and epoxidation agents[20], but their analytical applications have been rarely reported. They have been, however, used for determination of metal ions by spectrophotometric[21], ion selective electrode[22], membrane sensor[16, 23] and column preconcentration[24] techniques. Shamsipur *et al.*[12] reported the use of a naphthol derivative salen, 2,2′-[1,2-ethanediyl-bis(1-nitrilo-ethylidyne)]bis(1-naphthalene), to the selective preconcentration of copper(II) from aqueous media on a modified octadecyl silica membrane disk. The method, however, requires the use of some organic solvents and since the salen is not chemically bonded to the disc, it is necessary to repeat the modification procedure of the disc before enrichment of each sample.

In previous works[9, 10, 25], the use of Novarose (a highly crosslinked agarose) as a promising neutral matrix for the design of chelating resins was reported. In comparison to commercial resins, the Novarose based adsorbents showed superior kinetic properties. The aim of this study is to chemically link 2,2′-[1,2-ethanediyl bis(1-nitrilopropylidyne)]bis(1-naphthalene), to the Novarose bead in order to make a stable, selective and highly efficient adsorbent for simple and efficient column preconcentration of copper(II) in natural waters.

EXPERIMENTAL

A flame atomic absorption spectrometer (Shimadzu AA-670, Japan) employing an air-acetylene flame was used for determination of copper and other elements under the recommended conditions. Hollow-cathode lamps were employed as radiation sources. For pH determinations, a Jeneway (USA) model 3020 with a combined glass electrode was used after calibration against standard Merck buffers. Preconcentration columns were 6 mm i.d. polypropylene tubes with two frits at their bottoms and tops, packed with an adsorbent. A peristaltic pump (EYLA, Japan) was used for pumping solutions through columns.

All chemicals and reagents used were of analytical reagent grade (Merck, Germany) and used as received. Doubly distilled water, prepared by a totally glass Fision (UK) double distiller, was used for all the dilutions. Cross-linked and epoxy activated agarose (Novarose) was a gift from Inovata AB (Stockholm, Sweden) with 40–60 μm particle size. Before use, Novarose was thoroughly washed with 20 mL portions of water, hydrochloric acid (1 mol L^{-1}) and acetate buffer (0.1 mol L^{-1}, pH 5.5), respectively.

Stock copper solutions (1000 mg L^{-1}) were prepared by dissolving required amounts of copper sulfate in 10 mL of concentrated hydrochloric acid and diluted to 250 mL by water. Standard and test copper solutions were prepared by dilution of the stocks. The test solutions were usually buffered with a 0.01 mol L^{-1} acetic acid/ammonium acetate buffer solution and pH adjusted with drops of HCl (0.1 mol L^{-1}) or NaOH (0.1 mol L^{-1}) solutions, before enrichment on a column.

For packing of columns, suspensions of the adsorbent were pipetted into an empty column with a frit at the bottom. A gentle vacuum was applied for faster settling of the particles before mounting the top frit. The column pretreatment was made by its washing by 20 mL double distilled water, 20 mL hydrochloric acid 1 mol L^{-1} and 20 mL acetate buffer 0.1 mol L^{-1} (pH 5.5).

Measurement of capacity for the chelating adsorbent was performed in column mode as reported elsewhere[25]. A 100 mL solution of 100 mg L^{-1} copper at pH 5.4 (0.01 mol L^{-1} acetate buffer) with a flow rate of 0.8 mL min^{-1} was used for saturation of the column. Analysis of the effluent showed that the column was saturated after the passage of *ca.* 90 mL of Cu^{2+} solution. After washing with 5 mL acetate buffer (0.01 mol L^{-1}) to displace non-bound Cu^{2+} from the void volume, the Cu^{2+} was eluted with 10 mL of hydrochloric acid 1 mol L^{-1} and determined by flame atomic absorption sepctrophotometer.

Preconcentration and recovery experiments were performed, usually, by pumping 30 mL of a buffered test solution through a pretreated 0.5 mL column with a flow rate of 2.5 mL min^{-1}. The column was then washed with a few mL acetate buffer 0.01 mol L^{-1} and eluted by 5 mL hydrochloric acid 1 mol L^{-1} (unless otherwise stated). The eluate was collected in small capped vessels and analyzed by flame atomic absorption spectrophotometer against matched standards.

All the field samples were acidified to pH 2 on collection and filtered to remove any particulate matter. These samples were pH adjusted and analyzed with essentially the same method as the test samples. The sample volume was 450 mL in this case.

Preparation of the chelating adsorbent: The Schiff's base, 2,2′-[1,2-ethanediyl-bis)nitriloisopropylidyne]bis(1-naphthalene), was synthesized and purified as described elsewhere[26, 27]. The reaction product was recrystallized from methanol to give the product as yellow crystals, yield 97%, m.p. 196–198°C.

The recommended procedure of the Inovata Company[28] was followed for preparation of the adsorbent. About 1.2 g of the ligand was supersaturated in 20 mL ethanol, filtered and the filtrate was added to a suspension of 1.3 mL activated Novarose in doubly distilled water. A 10 mL portion of a sodium carbonate solution 0.5 mol L^{-1} (pH = 11.6) was added and the mixture was agitated for 24 h. The mixture was then filtered and the adsorbent was washed by 20 mL portions of HCl solution 0.5 mol L^{-1}, water, ethanol and water respectively. Deactivation of the remaining active sites was made by suspension of the adsorbent in 25 mL of a sodium hydroxide solution 0.5 mol L^{-1} and agitation for an extra 24 h. Finally, the adsorbent was washed by water and ethanol and stored at 4°C under 20% ethanol. Fig. 1 represents a possible reaction between the epoxy groups of the activated Novarose and one of the naphthol groups of the Schiff's base.

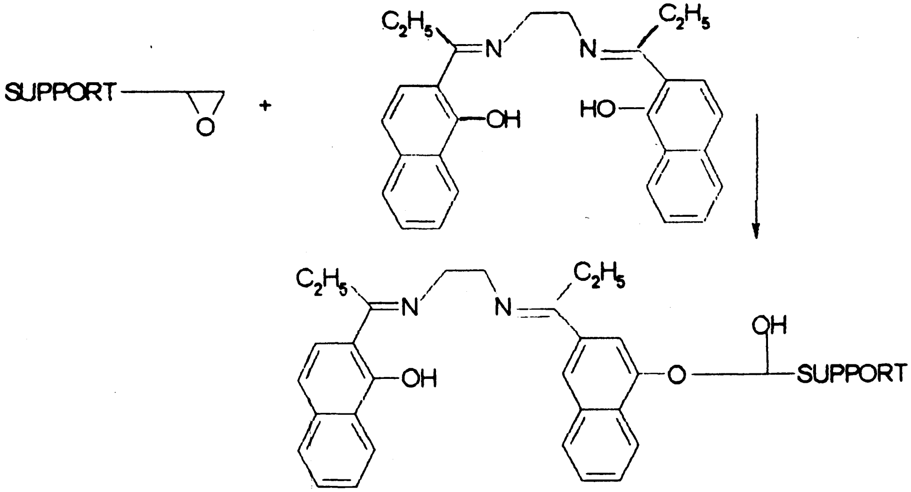

Fig. 1. Schematic representation of the reaction between the activated Novarose and the Schiff's base

RESULTS AND DISCUSSION

Capacity of the adsorbent: The maximum capacity of the synthesized adsorbent was measured to be 14.4 (± μmol Cu^{2+}) per mL of the adsorbent. The capacity for copper could be a measure of total active sites of the new chelating adsorbent. In a previous work[9], the same support was functionalized with iminodiacetic acid (IDA) groups to result in capacities up to about 140 μmol mL^{-1}. It was shown that the final capacity is mainly dependent on the chelating agent's concentration in the reaction media during the synthesis procedure. Since the Schiff's base used in this work is only slightly soluble in water, a saturated solution of it was used to give the mentioned capacity.

Effect of pH on the recovery: The pH is a very important factor for metal-chelate formation and preconcentration process. Therefore, the effect of pH on the retention of copper on the column was studied in the range of 2.5–8. The results are shown in Fig. 2. Quantitative recoveries (> 98) were obtained over a pH range of 5.8–7.0. For subsequent experiments, pH 6–6.5 was chosen as the working pH. Lower pH values are usually preferred because of a risk of analyte hydrolysis in a high pH.

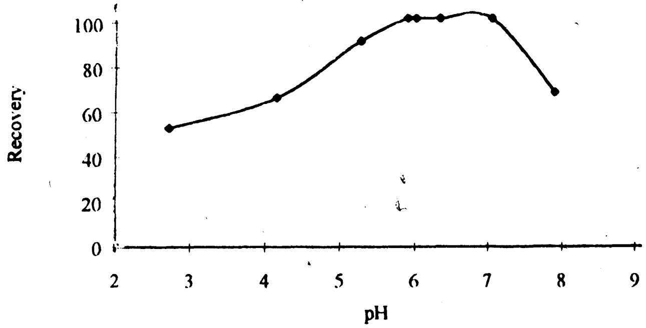

Fig. 2. Effect of pH on the recovery of Cu^{2+} on a 0.5 mL Novarose-Schiff's base column. Eluent, 10 mL HCl (1 mol L^{-1}); sample volume, 30 mL; buffer concentration, 0.01 mol L^{-1}; flow rate, 2.5 mL min^{-1} ; amount of copper, 15 μg.

Effect of type, volume and concentration of eluent: Desorption of copper(II) from the column was tested using various eluent types, volumes and concentrations. A 2 mL portion of hydrochloric acid with a minimum concentration of 0.075 mol L^{-1} was found to be satisfactory for a quantitative elution. Table-1 compares desorption of the analyte by different eluents. The results indicate that HCl and HNO_3 are the most appropriate eluents. Nitric acid, however, was not used further because of its oxidizing effects.

TABLE-1
EFFECT OF ELUENT ON THE RECOVERY OF COPPER(II)

Sample volume, 30 mL; eluent concentration, 0.075 eq L^{-1}; eluent volume, 2 mL; amount of Cu^{2+}, 15 μg; pH, 6.3; flow rate, 2.5 mL min^{-1}.

Eluent	H_2SO_4	$HClO_4$	H_3PO_4	CH_3COOH	HNO_3	HCl
Recovery (%)	95.84	99.11	86.89	80.24	99.99	101.90
s (n = 3)	1.44	1.34	3.66	3.90	1.23	1.77

Effect of ionic strength: Effect of ionic strength was studied by using different sodium nitrate concentrations in the sample matrix. It was found that the electrolyte concentration up to about 0.5 mol L^{-1} is tolerable by the column and quantitative adsorption of Cu^{2+} is obtained.

As a complementary study, different acetate buffer concentrations, up to 1 mol L^{-1}, also were tested. As shown in Fig. 3, no significant recovery change is observed for the buffer concentrations up to 0.5 mol L^{-1}. It is hence concluded that the method is well suited for high salt samples. This can be understood by the formation of stable coordination bonds between copper(II) and the Schiff's base rather than a simple ion exchange mechanism.

Effect of column length: The column length or adsorbent volume is another important parameter that may affect the recoveries. A quantitative retention is not obtained when too short a column is used. On the other hand, an excess amount of resin increases the column dead volume and accumulation of matrix ions such as calcium and magnesium. Hence, the column length should be optimized. For

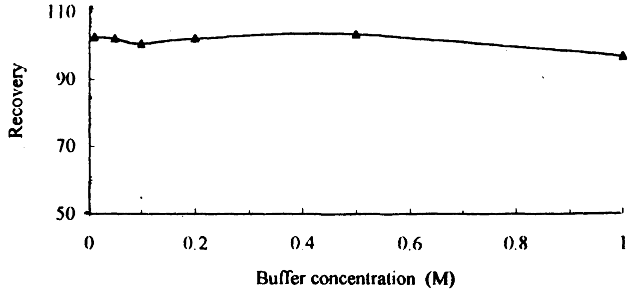

Fig. 3. Effect of buffer concentration on the recovery of Cu^{2+} on a 0.5 mL column. Eluent, 3 mL HCl (0.1 mol L^{-1}); sample volume, 30 mL; flow rate, 2.5 mL min^{-1}; amount of copper, 15 μg.

this purpose, different amounts of the Novarose based adsorbent (0.1–0.6 mL) were examined (Fig. 4). Quantitative recoveries were obtained for adsorbent volumes higher than 0.2 mL (column lengths > 7 mm). Hence, adsorbent volumes between 0.3 to 0.5 mL were used for subsequent experiments.

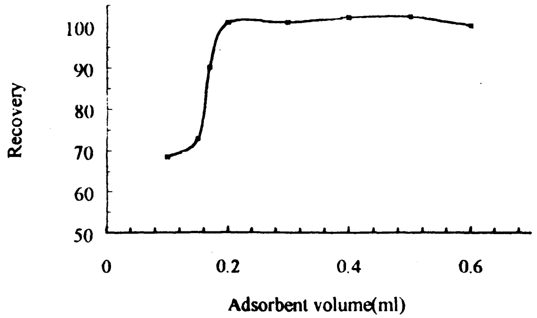

Fig. 4. Effect of adsorbent volume on the recovery of Cu^{2+}. Buffer concentration, 0.01 mol L^{-1}; other conditions are as in Fig. 3.

Effect of enrichment flow rate: Effect of the flow rate of test solutions on copper(II) adsorption was investigated by varying the enrichment flow rate from 2.5 to 16.7 mL min^{-1}. Encountering a high back pressure did not allow using higher flow rates. By the use of a minimum adsorbent volume of 0.2 mL, quantitative recoveries were obtained up to a flow rate of about 8.5 mL min^{-1} (Fig. 5).

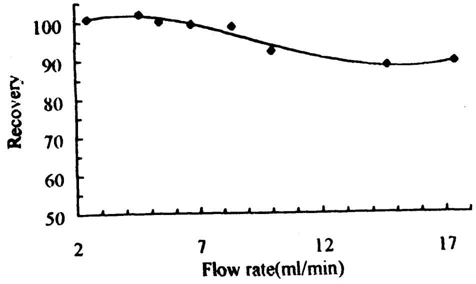

Fig. 5. Effect of enrichment flow rate on the recovery of Cu^{2+} on a 0.2 mL column. Buffer concentration, 0.01 mol L^{-1}; other conditions are as in Fig. 3.

Effect of matrix ions: The preconcentration procedure for trace metals can be strongly affected by other constituents of samples. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions of the water samples. The interfering elements were added to the model samples as their nitrate, chloride, sulfate and acetate salts. Table-2 shows the effect of the interfering ions on the recovery of the analyte (25 μg Cu^{2+}).

TABLE-2
EFFECT OF MATRIX IONS ON THE RECOVERY OF COPPER(II)

Buffer concentration, 0.01 mol L^{-1}; other conditions are as in Fig. 3. RSD is estimated to be about 3% for the recoveries.

Matrix ion	Na^+	K^+	Ca^{2+}	Mg^{2+}	Pb^{2+}	Fe^{2+}	Ni^{2+}	Zn^{2+}	Cr^{3+}
Marix ion concentration (mg/L)	40000	40000	8200	3320	15	15	20	15	15
Matrix ion/analyte mol ratio	86860	50210	25960	17313	9.2	34	32	122	37
Cu^{2+} recovery (%)	100.5	101.7	105.8	100.5	106.9	99.62	103.4	101.0	101.1

Effect of sample volume: In order to determine the effect of sample volume on the recovery, different volumes (20 to 800 mL) of test solutions containing a fixed amount of the analyte (25 μg of Cu^{2+}) were enriched on the column. The recovery of copper(II) did not decrease significantly when up to 700 mL sample was used. By using 2 mL of the eluent, hence, preconcentration factors up to 350 may be obtained . Results are shown in Fig. 6.

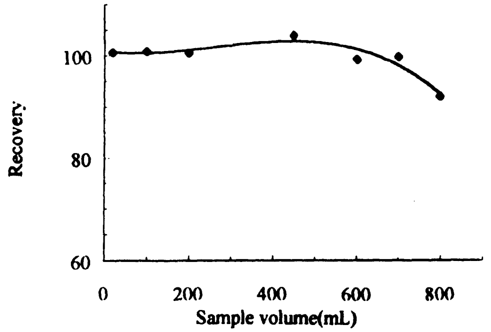

Fig. 6. Effect of sample volume on the recovery of Cu^{2+} on a 0.5 mL column. Buffer concentration, 0.01 mol L^{-1}; other conditions are as in Fig. 3.

The limit of detection based on three times the standard division of blank was 5.55 μg L^{-1} for the direct determination of copper(II) (N = 19). Hence, by applying a preconcentration factor of 350, a detection limit as low as 0.62 μg L^{-1} can be obtained using a flame AAS instrument. It is obvious that by the use of more sensitive methods such as electrothermal AAS, ICP-AES and ICP-MS much lower limits of detection may be obtained.

Application for real samples: The proposed method was applied to the determination of copper(II) ions in the tap water of Khoramabad and Abadan (Iran) and Sarab Robat river water (located in Khoramabad's suburb). A volume of 450 mL of the water samples were enriched on the column at pH 6.3. The results obtained by the proposed method are listed in Table-3 and compared to the reference values obtained by direct determinations with an electrothermal AAS (Shimadzu, AA6650, Japan) instrument. A good agreement between the measured values, by the method, and the reference values was obtained.

TABLE-3
APPLICATION OF THE NOVAROSE-SCHIFF'S BASE ADSORBENT TO SOME NATURAL WATER SAMPLES

Adsorbent volume, 0.5 mL; sample volume, 450 mL; pH, 6.3; flow rate, 2.5 mL min^{-1}; buffer concentration, 0.01 mol L^{-1}; eluent, 5 mL HCl (0.2 mol L^{-1}). Standard deviations (between parentheses) are reported for duplicate measurements.

Sample	Measured value ($\mu g\ L^{-1}\ Cu^{2+}$)	Reference value* ($\mu g\ L^{-1}\ Cu^{2+}$)
Abadan tap water	1.024 (±0.003)	0.9809 (±0.005)
Khoramabad tap water	3.929 (±0.006)	3.361 (±0.007)
River water	20.12 (±0.03)	23.44 (± 0.02)

*Measured directly by electrothermal AAS method.

Conclusions

The study indicates that the prepared Novarose-Schiff's base adsorbent can accumulate copper(II) ions from water samples, efficiently and with a good selectivity. The chemical bond between the chelating ligand and the inert support resulted in a stable adsorbent that is stable in a pH range of 0 to 14. The method doesn't require the use of any organic solvent and the column tolerates high concentrations of naturally occurring matrix and interfering ions in waters. The adsorbent can be used a number of times and for hundreds of enrichment-elution cycles with no significant change in its properties.

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