

Design, synthesis, and application of chelating polymers for separation and determination of trace and toxic metal ions. A green analytical method*

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Abstract: A green analytical method was developed for separation and preconcentration of trace amounts of copper from aqueous samples using aurin tricarboxylic acid-immobilized silica gel (ATA-SG). This was done by determining chemical speciation and stability constant of Cu-ATA complex. The pH-metric studies indicate strong complexation of Cu with ATA ($\log \beta_{\text{Cu}_2\text{ATA}} = 19.56$). Species distribution curve for Cu-ATA complex indicates almost 100% complexation of copper, with ATA forming Cu_2ATA as the predominant species. Considering the selectivity and strong interaction of ATA toward copper, ATA was immobilized on the polymeric matrix of silica gel, and the conditions were optimized for the uptake of copper from the aqueous solutions. The uptake of Cu ions by ATA-SG was studied both by batch and column methods. The method was developed for the estimation of trace amounts of copper in various samples. Molecular modeling studies were also performed on ATA-immobilized silica gel for gaining an insight into the active structure of ATA on the silica surface.

INTRODUCTION

Accurate analysis of metal ions, especially at trace levels, is one of the most difficult and complicated analytical tasks, since it requires the rigorous requirement of versatility, specificity, sensitivity and accuracy in the analysis. For determination of trace metal ions present in various samples like natural and waste water, biological and alloy samples, direct determination using various instrumental methods is not possible owing to matrix effects and low concentration of metal ions in these samples. Thus, the need of separation and preconcentration arises. This results in simplification of the sample matrix and enhances the concentration of the sample to be analyzed. For this purpose, various techniques are available. These include liquid–liquid extraction, precipitation technique, carbon adsorption, distillation, evaporation, electrolytic concentration, capillary zone electrophoresis, and use of chelating resins. However, the solid-phase extraction of metal ions has gained rapid acceptance because of various advantages over other methods [1]. The extraction of metal ions using chelating resins is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid–liquid extraction technique or other methods.

Chelating solid phases can be tailor made by immobilizing appropriate chelating agents on the support matrices for selective trace-metal analysis. Many solid supports are available for this purpose [2,3], but silica-based chelating resins are most commonly used since immobilization reactions on silica surface relatively simple and reproducible [4], especially when compared to immobilization on organic polymers, which involve complicated multi-step reactions. Silica-based chelating resins show fast metal ion-exchange kinetics, the lack of which precludes the use of many organic-based polymers

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[5–7]. Silica has good mechanical strength and swelling stability required for its use in solid-phase extraction [8, 9].

In the present paper, we report the design, synthesis, and application of aurin tricarboxylic acid-immobilized silica gel (ATA-SG) for the uptake of trace amounts of copper.

EXPERIMENTAL

Aurin tricarboxylic acid (ATA) was prepared as discussed in the literature [10]. Its purity was checked by thin-layer chromatography (TLC) and melting point. All other chemicals used were of analytical grade. Copper sulphate solution was standardized by conventional methods as described by Vogel [11]. pH of metal ion solution was maintained using sodium acetate–acetic acid buffer.

Determination of stability constant of Cu_2 -ATA complex

The pH-metric method is used in the present study for the determination of stability constants, as described by Bjerrum and Calvin and modified by Irving and Rossotti. The titration method has been described earlier [12]. The stability constant for Cu_2 -ATA complex was calculated using program BEST [13], and species curves were plotted using SPE program.

Preparation of aurin tricarboxylic acid-immobilized silica gel (ATA-SG)

Immobilization of ATA on silica gel was carried out in two steps, as reported earlier [14].

- 50 g of activated silica gel was suspended in 200 ml 10% (v/v) 3-aminopropyltriethoxysilane in dry toluene. The mixture was refluxed for 12 h in nitrogen atmosphere with constant stirring. The resulting, aminopropyl silica gel (APSG) was filtered washed consecutively with toluene, ethanol, and acetone and was heated at 75 °C for 10 h in vacuum line.
- 10 g of APSG was reacted with 10 g of ATA in anhydrous ethanol with constant stirring for 8 h. The mixture was filtered, washed, and the immobilized silica was heated for 8 h at 55 °C in a vacuum line, the coupling reaction was confirmed by IR spectroscopy.

Procedure for separation of metal ions

Two types of experiments have been performed for separation and preconcentration of metal ions. These two experiments are:

- *Batch experiment:* Immobilized silica gel was equilibrated with a suitable amount of copper ion solution for a fixed period of time, and the unreacted copper was determined in the supernatant atomic absorption spectroscopy (AAS).
- *Column experiment:* For the column experiment, the immobilized silica gel (ATA-SG) was packed in the glass column, and the copper ion solution at a definite pH (between 3.0–9.0) was percolated at a flow rate of 2 ml min⁻¹. The copper ion adsorbed on the resin was eluted from the column using 0.1 N HCl and determined by atomic absorption spectroscopy (AAS). Each metal experiment was carried out in triplicate in order to determine the precision of the method.

RESULTS AND DISCUSSION

The IR spectrum of ATA-SG shows a band at 1580 cm⁻¹ which is characteristic of $\nu_{\text{C=N}}$. However, the bands between 1560–1400 cm⁻¹ may be assigned to benzene ring vibrations and deformation modes of -CH₂ group.

Stability constant and chemical speciation

Stability constant of Cu_2ATA complex was found to be 19.56. Using stability constant and pH-metric titration data, chemical speciation curve was drawn (Fig. 1). Both stability constant and chemical speciation curve indicate strong complexation of ATA with copper.

Optimization of conditions for separation of copper from aqueous samples

The pH dependency of the adsorption of copper ion by the ATA-modified silica gel has been investigated by column experiment. Copper has been quantitatively retained from the aqueous solution in the pH range 4.5–6.8 with a recovery of 95%. Further studies were carried out with metal ion solution maintained between this pH range of maximum complexation.

The time required for the solid–liquid system to attain equilibrium condition is of considerable importance. It was determined by batch experiment. It was found that the time required for copper ions to reach the equilibrium was about 3 min, thus indicating fast metal ion exchange kinetics. The influence of temperature on the adsorption of copper ions by immobilized silica gel was studied by batch experiment. Copper ion solution, maintained at the pH of maximum complexation was equilibrated with ATA-SG at different temperatures (between 15–55 °C). The percent adsorption of Cu^{2+} was found to be constant and maximum up to 40 °C, but the adsorption of metal ions decreases after these temperatures.

The effect of flow rate on the adsorption of copper solution by chelating silica gel was investigated by column experiment. The flow rates being varied between 0.5–5.0 ml min^{-1} . Adsorption was quantitative and reproducible in this range. However, for farther studies, a flow rate of 2 ml min^{-1} was maintained.

Adsorption isotherm

The adsorption isotherms for copper was obtained by batch technique at 25 °C. Metal ion solutions in concentration range 0.03×10^{-3} to 1.6×10^{-3} mmol ml^{-1} maintained at pH of maximum complexation, were stirred with 0.05 g of modified silica gel. The metal content in the supernatant was determined by means of AAS. Amount of metal adsorbed was calculated with the help of following equation.

$$N_f = (x - y)/z$$

where N_f is the amount of metal adsorbed per g of modified silica gel (in mmol g^{-1}), x and y are the initial and final amount of metal ions (in mmol) and z is the amount of modified silica gel (in g). The aver-

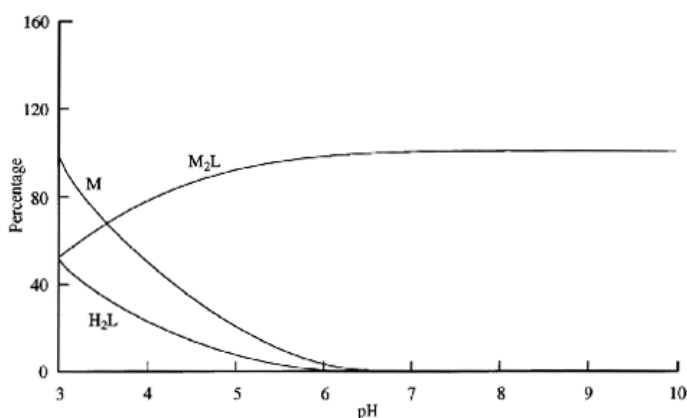


Fig. 1 Species distribution curve for Cu_2ATA .

age values of the distribution coefficients, D , where $D = N_p/C$, calculated (in ml g^{-1}) have been found to be, Cu^{2+} : 3.46×10^2 .

Preconcentration and recovery of copper

To carry out this study, 100 ml solution of copper ion was percolated through a column packed with 0.5 g of ATA-SG at a flow rate of 2 ml min^{-1} . The adsorbed metal was eluted with 10 ml of 0.1 N HCl, and the metal content in it was determined by AAS. The experiment was performed in triplicate in order to determine the reproducibility and precision of the method. The recovery of copper was found to be 95% with a standard deviation of 0.06. It is quite evident from the results that copper can be quantitatively preconcentrated from a column of ATA-SG, and the low value of standard deviation indicates that the method is precise.

Determination of copper in medicines

The contents of a capsule or powdered tablet, to be analyzed, were placed in a 400-ml beaker and were treated with 10 ml of conc. HNO_3 on a hot plate at a low temperature to avoid violent flashing. The residue was cooled, and again HNO_3 was added. The temperature of the hot plate was raised to 400°C . It was heated to dryness. The process was repeated 3–4 times until all the carbonaceous matter was removed. The beaker was cooled. The residue was dissolved in minimum amount of water. It was transferred to a 500-ml volumetric flask and was buffered with sodium acetate–acetic acid buffer (pH 5.9) and the volume was made up to the mark. 10.0 ml of the above solution of tablet/capsule was passed through a column packed with ATA-SG. The adsorbed metal ions were eluted from the column with 10.0 ml of 0.1 N HCl. The copper in eluent was determined with AAS technique. Results are given in Table 1.

Molecular modeling studies on silica surface chemically modified with aurin tricarboxylic acid

Surface chemistry is a field of increasing importance in various fields like immobilized polymeric resins, heterogeneous catalysis [15], etc. One of the objectives of research in this field is to study elementary steps of reactions on the surface. If a single structure or several closely related structures are formed on the surface, then it becomes possible to use stoichiometric reactions to characterize the reac-

Table 1 Determination of copper in medicine tablets/capsules.

Sample	Certified composition	Cu taken (mg)	Cu found* (mg)	Standard deviation
A	Zn (as ZnO) 15 mg, Cu (as CuO) 2.5 mg, Se (as sod. Selenate) 60 μg , Mn (as MnCl_2) 1.4 mg, Cr (as CrCl_3) 65 μg	2.5	2.4	0.28
B	Zn (as ZnO) 40 mg, Se (as sod. Selenate) 40 μg , Cu (as CuO) 2.0 mg, Mn (as MnSO_4) 2.0 mg	2.0	1.88	0.11
C	CuSO_4 3.39 mg (Cu = 1.35 mg), ZnSO_4 2.20 mg, Sod. Molybdate 0.25 mg, Sod. Borate 0.88 mg	1.35	1.21	0.13

* Mean of three determinations

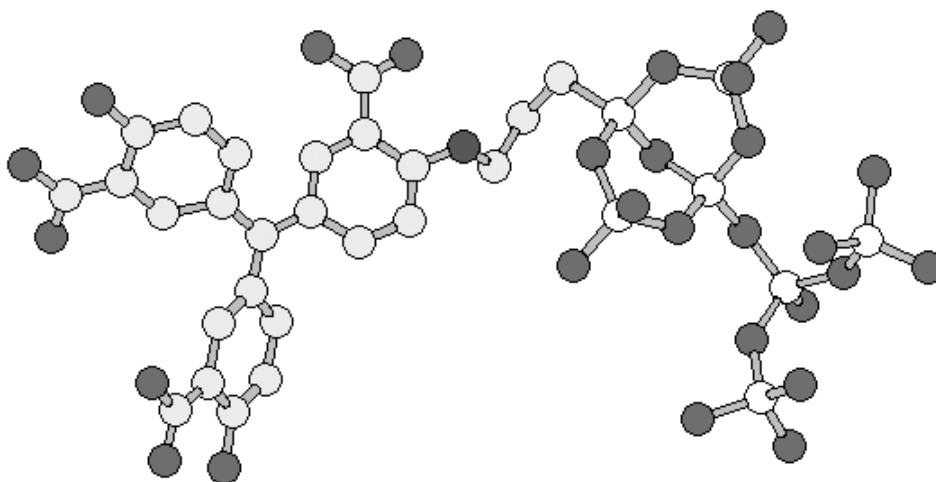


Fig. 2 Energy-minimized structure of ATA-SG.

tivity of these surface species. By studying these immobilized polymeric surfaces, we can gain insight about the reactivity and the “working site” of the immobilized chelating agent on the surface.

The molecular mechanics calculations on ATA-immobilized on silica surface were carried out with HyperChem, release 5.1, professional version, an interactive graphic program that allows for rapid structure building, geometry optimization, and molecular display [16]. First of all, the structure of ATA was minimized. This ATA was then bonded to the modeled aminopropyl silica gel (APSG), through a C=N bond, which was predicted on the basis of IR spectroscopy. Figure 2 shows the modeled structure of ATA on silica surface. All the unbonded contact distances between surface atoms and ATA were calculated in order to determine if ATA could be reasonably well accommodated on the local surface sites. If the unbonded contact distances between ATA atoms and surface atoms are larger than the sum of their van der Waals radii, we concluded that the ATA could be immobilized on that site.

This approach indicates that there is no steric hindrance around the immobilized ATA. So ATA could easily form chelate with metal ions and this accounts for the high uptake of metal ions by ATA-SG.

CONCLUSION

The silica-immobilized aurin tricarboxylic acid (ATA-SG) offers a great potential for the enrichment of metal ions from water. The preparation of the polymeric solid phase (ATA-SG) is easy and inexpensive. The working conditions are easy to manipulate, and the adsorption of metal ions by ATA-SG is quantitative and reproducible. The metal uptake takes place faster, and there is less flow resistance for column applications. This chelating resin has been successfully employed for the determination of metal ions present in various samples. Since the method does not involve the use of toxic chlorinated solvents, it offers an eco-friendly way of separation and preconcentration of metal ions from various samples. The modeled surface of ATA-SG indicates that there is no steric hindrance for the uptake of metal ions, and this accounts for the high uptake of metal ions by ATA-SG.

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