# Designing and Synthesis of Chelating Resin 2,2-Dipyridyl Ketone(dpk) immobilized on Silica Gel for Separation and Preconcentration of Trace Cu(II) Metal Ion

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**ABSTRACT**

The presence of toxic metal ions in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. Copper is largely used in electrical machinery and for electroplating. The determination of metal ions at trace levels is very important in the context of environmental protection, food, agriculture chemistry, and high purity materials. In the present research work we have done the removal of Cu (II) metal ion at trace level using 2,2'-dipyridyl ketone immobilized aminopropyl silica gel (dpk-APSG). The present study deals with removal, recovery or enrichment/preconcentration, prior to the determination of copper metal ion from aqueous sample.

**Keywords:** Chelating Resin, 2,2-Dipyridyl Ketone, Silica Gel, recovery, Trace, Cu(II).

## 1. INTRODUCTION

The removal of toxic and polluting metal ions has received much attention in recent years [1]. Metals such as Cu, Hg, Cr, Pb, Ni, Cd and Zn are usually associated with toxicity. Analytical chemistry is towards the elaboration of simple, ecologically safe, sensitive, and selective methods for the determination of these metal ions in the environment at trace level from the aqueous solution which is the most difficult and complicated analytical task [2]. To obtain the reliable data, the best technique is to separate the analyte of interest from the matrix constituents and determine them in an isolated state. This results in greater sensitivity but calls for elegant separation and concentration technique. Various method used for this purpose are liquid-liquid extraction [3-4], precipitation technique [5], freezing-based concentration methods [6], carbon adsorption [7], distillation [8], sublimation [9], evaporation [10-12] and the use of ion exchange resins [13-16]. Among all of these, ion-exchange resins and chelating resins are the most suited for trace analysis. These are of several types, such as cation exchangers, anion exchangers, and chelating resins [17-22]. In recent years, the use of chelating resins has increased extensively because the chelating resins behave more selectively than plain ion exchangers [23]. A covalent complex is

Formed between the metal atom and the donor atoms (O, N, S) of ligand [24-27].

## 2. Experimental

All the chemicals used were of AR grade, and were procured from Aldrich. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard spectroscopic grade.

### 2.1. Physical measurements

The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. IR spectra (KBr) were recorded on a Perkin Elmer FTIR spectrum BX-II spectrophotometer. Thermo gravimetric analysis is carried out in dynamic nitrogen atmosphere (30 mL/min) with a heating rate of $10^0C$/min using a Schimadzu TGA-50H thermal analyzer. The Elico LI 120 model digital pH meter was used for adjustment of the pH values of various solutions. Lab India Atomic Absorption Spectrophotometer (LabIndia AA7000)

### 2.2. Synthesis of 2,2-Dipyridyl Ketone Modified Silica Gel

Immobilization of the 2,2-dipyridyl ketone onto modified silica gel was carried out as follow: 10g of activated silica gel was suspended in 40mL of 3-aminopropyltriethoxysilane in dry toluene. The mixture was refluxed for 24 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 $75^0C$ for 10 h in vacuum line (Figure 1). 5g of APSG was

reacted with 5g 2,2-dipyridyl ketone in dry toluene. The mixture was refluxed for 12 h at 110⁰C with constant stirring. The resulting resin was filtered off and washed with dry toluene (Figure 2).
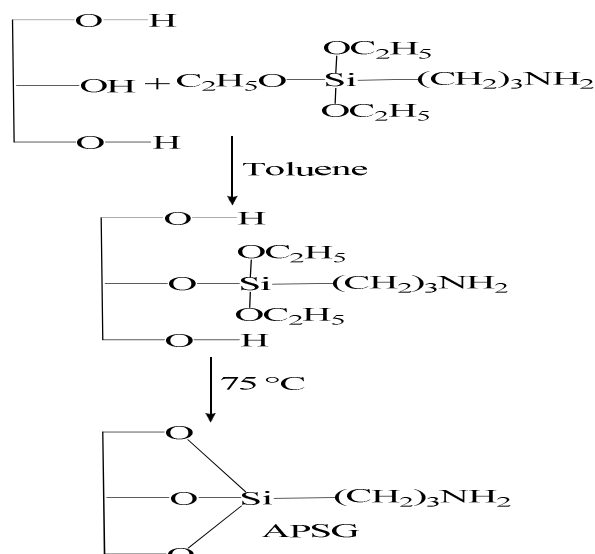


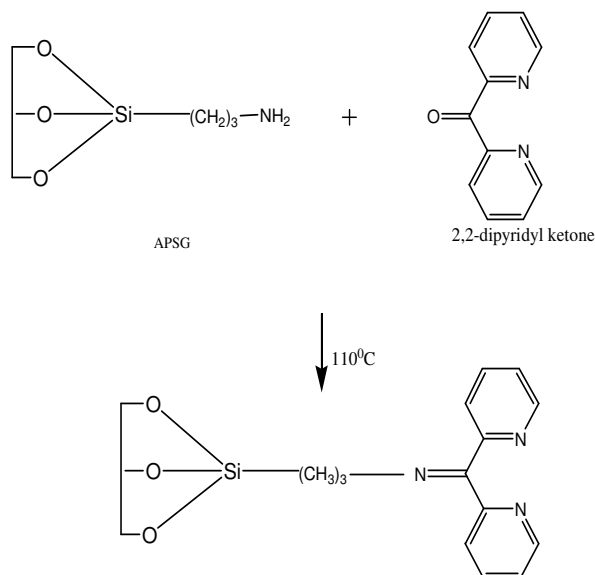**Figure - 1**: Synthesis of Aminopropyl silica Gel (**APSG**).



**Figure - 2: Synthesis of 2,2-dipyridyl ketone Aminopropyl Silica Gel (dpk-APSG).**

## 3. RESULTS AND DISCUSSION

### 3.1. IR of Chelating Resin

The infrared spectra of SG, APSG and modified 2,2-dipyridyl ketone onto aminopropyl silica gel (dpk-APSG) are presented in figure 3.4, 3.5, 3.6. The incorporation of 2,-2-dipyridyl ketone onto aminopropyl silica gel was confirmed by comparing the spectra of aminopropyl silica gel with 2, 2-dipyridyl ketone modified aminopropyl silica gel. Band at 3430-3770 cm$^{-1}$ correspond to O-H stretches of silanol groups, bands in the range 2860-2924 cm$^{-1}$ are characteristic bands for C-H

stretching. The bands between 1625-1656 cm$^{-1}$ correspond to angular vibration of water molecules. The band in the range between 1084-1090 cm$^{-1}$ corresponds to the siloxane stretching and the band between 790-805 cm$^{-1}$ Si-O stretching frequency for silanol groups. The shifting from 1643.83 cm$^{-1}$ to 1636.81 cm$^{-1}$ indicates the immobilization of the 2,2-dipyridyl ketone(dpk) onto modified silica gel [Figure 3-5].
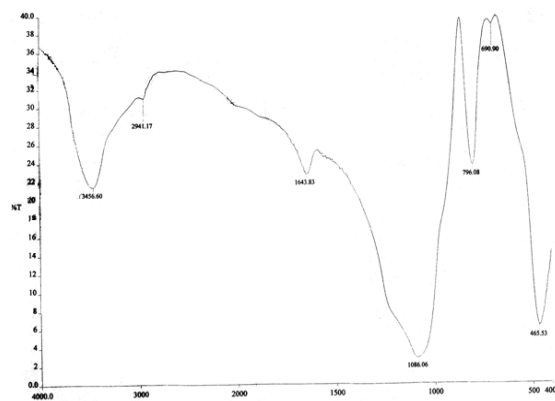


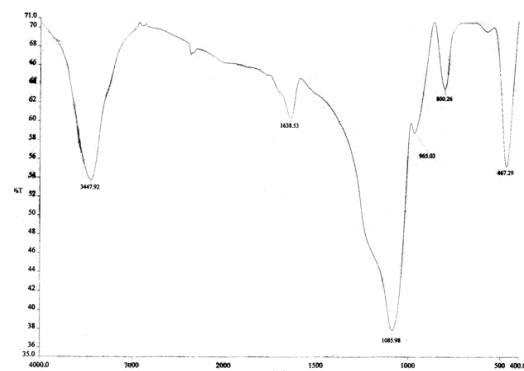**Figure - 3: IR Spectra for Silica Gel (SG).**



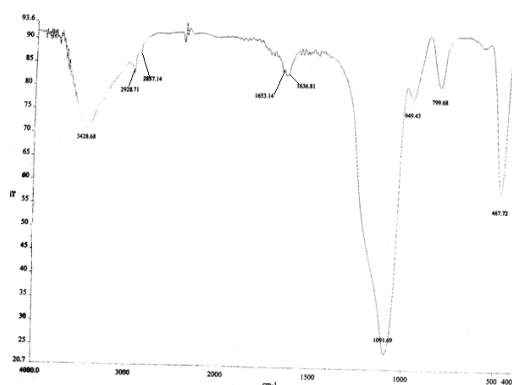**Figure - 4: IR Spectra for Aminopropyl Silica Gel (APSG).**



**Figure - 5: IR Spectra for 2,2-dipyridyl ketone Aminopropyl Silica Gel (dpk-APSG)**

### 3.2. Thermogravimetric curves for SG, APSG and dpk-APSG and CHN Analysis.

The TGA curve of APSG and dpk-APSG are presented in figure 3.7, 3.8. In the first step 3.622% mass loss was observed at temperature

$(39.31\text{-}93.97)^0$C due to physically adsorbed water on the surface of aminopropyl silica gel. In second step a mass loss of 7.637% was observed at the temperature range $(385.24\text{-}573.18)^0$C due to the decomposition of organic moiety (aminopropyl group) covalently bonded on the silica surface. The dpk-APSG shows two step weight losses. The first step appears at temperature $<150^0$C corresponds to the release of water (adsorbed water on the surface). In second step a mass loss of 11.473% was observed at the temperature range $(108.75\text{-}596.41)^0$C due to the loss of organic moieties of chelating group 2,-2-dipyridyl ketone as well as aminopropyl group anchored on the silica surface. The loading of nitrogen was found to be 14% mmol/g in dpk-APSG.

### 3.3. Influence of pH on retention of metal ion Cu(II)

The result is depicted in figure 6 as can be seen from the result the quantitative recovery of copper metal ion is obtained at pH range 5-6 for Cu(II). Percentage recovery under optimum condition of pH for metal ion is 91.11- 99.59%.
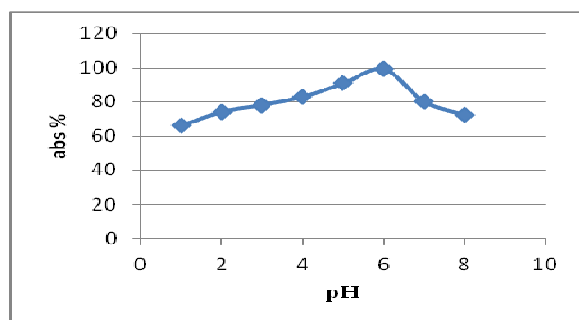
**Figure - 6: Effect of pH on the enrichment of the metal ion.**

### 3.4. Kinetics of metal sorption

The variation of sorption as a function of time for the metal ion is shown in figure 7. Maximum adsorption of metal ion was achieved in less than 30 minutes. It is found that the time required for the adsorption for Cu(II) is 20 minutes.

### 3.5. Effect of flow rate on metal adsorption

The retention for the analyte ion on chelating resin was quantitative for sample flow rate up to 2ml/min. Variation of the elution flow rate in the range of 1-3 mL/min has no effect on the elution efficiency. In consequence, 2mL/min was used as flow rate for sample elution from the chelating resin.

### 3.6. Sorption capacity measurement

The sorption capacity was found out 393 $\mu molg^{-1}$ for Cu(II). The column method was used to determine the sorption capacity.

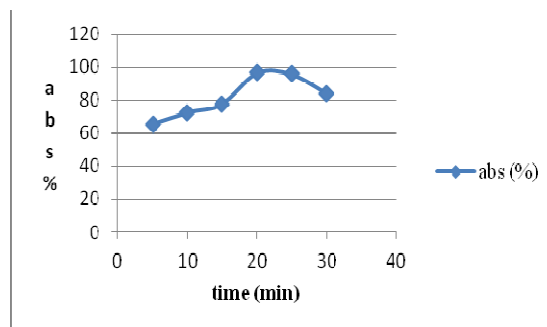**Figure - 7: Effect of time on the enrichment of copper metal ion.**

**Table - 1: Sorption capacity value of analyte metal ion**

| Metal ion examined | Metal sorption capacity ($\mu molg^{-1}$) |
|---|---|
| Cu(II) | 393 |

### 3.7. Recovery of metal ion in presence of interfering electrolytes

The concentration of matrix ions was varied from 0.001 to 0.5 mol $l^{-1}$. Tolerance limit of investigated electrolytes are given in table 3.2. Quantitative recovery was obtained for copper metal ion in the presence of electrolytes under the specified concentrations.

**Table - 2: Tolerance limit of electrolytes**

| Metal ion | Metal conc. $\mu mol/l$ | Electrolytes (mol $l^{-1}$) | | |
|---|---|---|---|---|
| | | NaCl | KCl | Na$_2$SO$_4$ |
| Cu(II) | 0.748 | 0.010 | .050 | 0.001 |

### 3.8. Recovery of copper metal ion in presence of other cations

Decrease in adsorption of metal ion below 90% is regarded as interference by the metal ion added (interfering ion). The used cations Mn(II), Ni(II) and Co(II) are not interference in the adsorption of copper metal ion as shown in the Table 3.

**Table - 3: Recovery of metal ion in presence of cations**

| Recovered Metal ion | Mn(II) | Ni(II) | Co(II) |
|---|---|---|---|
| Cu(II) | 95.1 | 94.3 | 96.3 |

### 3.9. Effect of sample volume on recovery and preconcentration factor for the metal ion

In order to explore the possibility of enriching low concentration of the analyte ion from the large sample volume, the recovery of the

copper metal ion from large sample volume was investigated. The effect of sample volume on the sorption of metal ion was investigated by passing 1000 ml volume through the chelating resin in column. The result is depicted in table 4. Enrichment Factor and Enrichment limit of copper for the chelating resin

### 3.10. Reusability of the chelating resin

The chelating resin dpk-APSG was reused after regeneration with 2M HCl and double distilled water, respectively. The chelating resin was found to be stable up to 5 runs without appreciable loss of sorption capacity.

### 4. CONCLUSION

The synthesis of chelating resin provides a simple, fairly rapid and reliable technique for preconcentration and determination of copper metal ion from the aqueous sample. The elution was easily performed with 2M HCl. The dpk-APSG is quite durable with recycling, without any major change in its quantitative metal recovery nature. The good features of the proposed method showed that it's a convenient and low cost method. This method is more useful for the enrichment of copper metal ion at traces levels.

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