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Inclusion Complex Based Solid Phase Extraction of Cu (II) with B-Cyclodextrin Polymer.

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ABSTRACT

β -Cyclodextrin polymer modified with 1-(2-pyridylazo)-2-naphthol(PAN) is used for the preconcentration of Cu(II) at pH 8.5. The polymer is synthesized and characterized using FT-IR. The factors affecting the recovery of Cu(II) such as pH, adsorbent dose, contact time, sample volume, eluent concentration and volume are also optimized in order to achieve higher sensitivity. The recoveries of Cu(II) are found to be $\geq 95\%$ and the relative standard deviation found by analyzing 3 replicates is 2.5. The preconcentration factor is found to be 100. The limit of detection(LOD) determined as (3σ) is found to be 2.43ng/mL. The proposed method is applied to different water samples successfully.

Keywords: Solid phase extraction(SPE); Preconcentration; Inclusion complex; Polymer.

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INTRODUCTION

The problems of our ecosystem are increasing with the advancement of technology. Due to the negative effects of heavy metal ions for human health, heavy metal pollution is one of the important problems for human [1-2]. Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The release of these heavy metal poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [3-4]. Cu(II) is an essential element at trace levels but its extensive use and intake in large quantities can be toxic [5-6]. Consequently it is of paramount importance and significant to enrich and determine Cu(II) in various environmental samples. Different techniques are used for the separation and preconcentration of metals in the solution. These include liquid-liquid extraction [7], precipitation [8], cloud point extraction [9], solid-liquid extraction [10] and solid phase extraction [11]. Disadvantages such as significant chemical additives, solvent losses, complex and expensive equipments, large secondary wastes, prefiltration problems, expert handling and time consuming procedures, limit the application of most of these techniques. Solid phase extraction, however, solves this problem as it offers several advantages such as high preconcentration factors, short extraction times, low cost, absence of emulsion, ease of use and its ability to be applied using a continuous flow system [12]. Several SPE sorbents as activated carbons [13], silica nanoparticles [14], agricultural adsorbents [15], activated alumina [16], amberlite XAD resin [17], zeolites [18], multi walled carbon nanotubes [19] and modified silica gel [20] etc. have been employed to preconcentrate metal ions at trace level. Supramolecular chemistry with β -Cyclodextrin has been a very active research field in the past few years [21-22]. β -Cyclodextrin (β -CD) can form the Supramolecular complexes with several organic compounds by incorporating them into their hydrophobic cavities. β -Cyclodextrin linked via cross linker is known as β -Cyclodextrin polymer. β -Cyclodextrin polymer has been used as SPE sorbents for preconcentrating several analytes [23-25]. Tridentate *N*-heterocyclic azo ligand containing N atom, 1-(2-pyridylazo)-2-naphthol (PAN) has shown excellent complexing ability for heavy transition metal ions. Analytical applications of this ligand in spectrophotometric determination of the metals are well established [26, 27]. It was therefore, thought worthwhile to prepare a chelating resin of better sorption capacity by including PAN in β -CDBP through physical modification. The resulting chelating polymer was used for the preconcentration of Cu(II) from various real matrices prior to their determination by UV-Vis spectrophotometry. There has not been any report of the use PAN modified β -Cyclodextrin Butanediol Diglycidyl Ether Polymer (β -CDBP) for the preconcentration of Cu(II) till date. It was therefore, thought worthwhile to prepare a chelating resin by immobilizing PAN on β -CDBP and characterize it in a systematic manner for its use in the preconcentration of Cu(II) and its determination by UV-Vis spectrophotometry.

EXPERIMENTAL

Apparatus

A Shimadzu UV-1800 spectrophotometer (Shimadzu Ltd., Japan) equipped with the matched 10-mm quartz cells was used to measure absorbance. All pH measurements were performed using Digital century pH-meter CP 901 with a combined glass electrode. A

thermostatic shaking water bath (Perfit India Ltd.) was used to carry out all the inclusive procedures.

Reagents

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Cu(II) solution was prepared by dissolving 0.249gm. of copper sulphate pentahydrate [CuSO₄.5H₂O] in 100 mL of distilled water to give standard stock solution. 4×10^{-6} M solution of the PAN reagent was prepared by dissolving an appropriate amount of PAN (Fluka Chemical Company) in N,N-dimethylformamide solvent. 1,4-Butanediol diglycidyl ether was obtained from sigma Aldrich chemical company (U.S.A.). β -Cyclodextrin was obtained from SD fine chemical India private limited (Mumbai). Buffer solution used were hydrochloric acid/sodium acetate for pH 2.0-3.5, sodium acetate/acetic acid for pH 4.0-6.5, ammonia/ammonium chloride for pH 8-11. Glass wares were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water.

Synthesis of the β -Cyclodextrin polymer (β -CDP)

β -CDP was synthesized by known method [26]. A brief procedure for the synthesis is mentioned here. 20gm of β -CD was dissolved in 50mL of 20% NaOH. To this was added 20mL of 1,4-butanediol diglycidyl ether drop wise. The polymer was formed in 1.5h and dried at 90⁰C. The polymer was ground and sieved first into different mesh fractions. The 80-100 mesh fraction was washed with double distilled water 5-6 times. Then, the polymer was dried again at 90⁰C and kept at room temperature (25⁰C) in a dessicator.

Inclusion of the PAN in the β -CDP cavity to form β -CDP-PAN modified polymer

5.0gm of the synthesized polymer, β -CDP mesh size was taken in a 250 mL Stoppard conical flask. To this was added 10mL of 9.5 pH buffer solution and polymer was allowed to swell for 15 minutes. A fixed volume of 4×10^{-6} M solution of the PAN was added to the treated polymer and made 50mL with distilled water. It was shaken for two hours. The colored polymer so obtained was washed with distilled water and dried at 100⁰C. The modified polymer was stored in a dessicator at room temperature for future use.

Characterization of β -CDP

β -CyD was dried at 90⁰C for 10h. The IR spectra for β -CyD and β -CyD polymer were recorded with an FT-IR spectrophotometer (Perkin Elmer, Boston USA) instrument as KBr pellets in the range 4000-400 cm⁻¹ region. The characteristic peaks for β -CyD, 3600- 3000 ϑ (OH), 2900 ϑ (CH); while for β -CyD polymer a sharp band at 3400 ϑ (OH) is obtained which indicates free OH group as shown in the structure above. A prominent band at 1120 ϑ (COC) ether linkage which is present in the linker and its absence in β -CyD spectra clearly indicates the polymerization process.

Batch extraction procedure

At room temperature i.e., 30°C β -CDP-PAN (0.4gm) and 10.0 mL of buffer solution (pH 8.5) were added to a 100-mL Stoppard conical flask. The mixture was allowed to stand for approximately 15 min so that β -CDP-PAN could be swollen sufficiently. 150 ng/mL of Maneb were added and made up to 100 mL with double distilled water. After the mixture was shaken in the thermostatic shaking water bath for 40 min, 5.0 mL of the supernatant solution was transferred into a 10mL volumetric flask and the absorbance was measured using standard spectrophotometric method [27]. Cu(II) retained on β -CDP-PAN polymer was eluted using 4.0 mL of 2M HCl.

Sample Collection and Conditioning

Water samples were collected from the different parts of Patiala City. The water samples were immediately filtered through cellulose membrane filter (0.45 nm pore size), and stored in precleaned polyethylene bottles. After then, pH of the sample was adjusted to 8.5 and the preconcentration procedure as described above was applied.

RESULTS AND DISCUSSION

Effect of pH

An excess of Cu(II) 150 ng/mL were spiked to a 100 mL of the sample solution containing 0.4 g of resin and shaken for 40 min. The pH of this solution was adjusted in the range of 3.5 to 10.5 using different buffer system and then the preconcentration procedure as described was applied. As it can be seen in (Fig. 1). Quantitative uptake ($\geq 95\%$) was obtained at pH 7.5-10.5 ± 0.01 . Therefore, pH 8.5 is selected for further studies.

Effect of the amount of adsorbent (Bed Height)

In order to optimize the smallest amount of extractant 0.1, 0.2, 0.3, 0.4, 0.5, 0.6gm of the resin were added to the 100 mL of the sample solution containing 150 ng/mL of Cu(II) and preconcentrated by the general procedure. The quantitative recoveries were obtained for and above 0.4gm of resin (Fig. 2). Therefore, 0.4gm of the resin has been used for subsequent experiments.

Kinetics of sorption

Shaking time is an important factor in determining the possibility of application of the β -CDBP-PAN polymer for the uptake of Cu(II). For studying the effect of shaking time on the % uptake, a 0.4 g amount of resin was stirred with 100 mL of solution containing 150 ng/mL of Cu(II) for different shaking time (ranging from 10 to 50 minutes) with an interval of 10 minutes at optimum pH. The results of % uptake of Cu(II) vs. the shaking time show that the percentage uptake reached maximum (above 95%) at 40 min (Fig. 3). Therefore, the shaking time of 40 min. was selected as the adsorption equilibrium time.

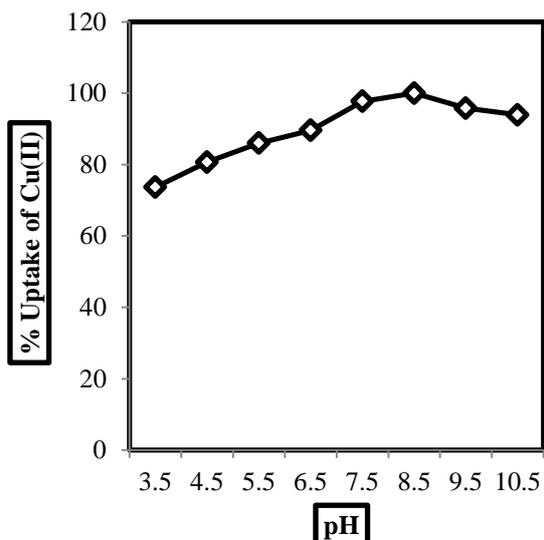


Fig. 1 Effect of pH

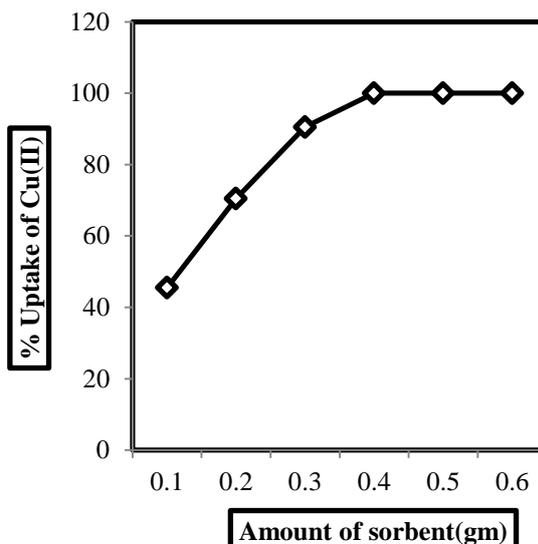


Fig. 2 Effect of adsorbent dose

Effect of the sample volume

In order to explore the possibility of enriching low concentration of analytes from large volume of sample, the effect of sample volume on the retention of Cu(II) was also investigated. 25, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mL. Quantitative uptakes ($\geq 95\%$) were obtained for sample volume of ≤ 400 mL (Fig. 4). Therefore, 100 mL of sample solution was adopted for the preconcentration of analyte from sample solutions. The preconcentration factor is calculated by the ratio of the highest sample volume (400 mL) and the lowest eluent volume (4 mL). Therefore, the preconcentration factor was 100.

Effect of elution conditions on recovery

The effect of eluent concentration on the recovery of eluted solution containing Cu(II) was examined. Different concentrations of HCl ranging from (0.5-4M) were tested in order to strip the Cu(II) from resin. The recovery of all Cu(II) was increased, as the HCl concentration increased up to 2.0M and it decreased above this concentration. Therefore a HCl concentration of 2.0 M was selected for subsequent studies. The results are depicted in Fig. 5. In order to choose proper volume of the eluent, the retained complexes were stripped with different volumes (1–6 mL) of 2.0 M HCl. 4 mL of 2.0 M HCl was chosen for elution of the metal ion complexes for more convenient (Fig. 6).

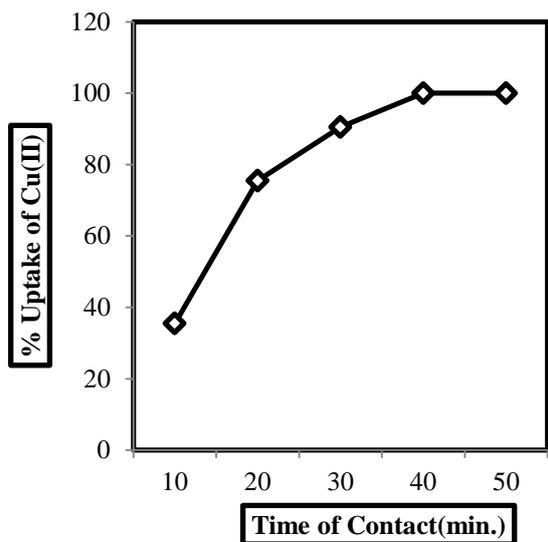


Fig. 3 Effect of the contact time

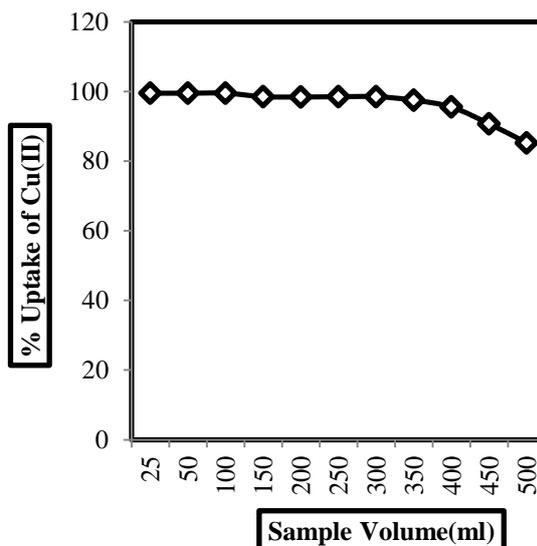


Fig. 4 Effect of sample volume

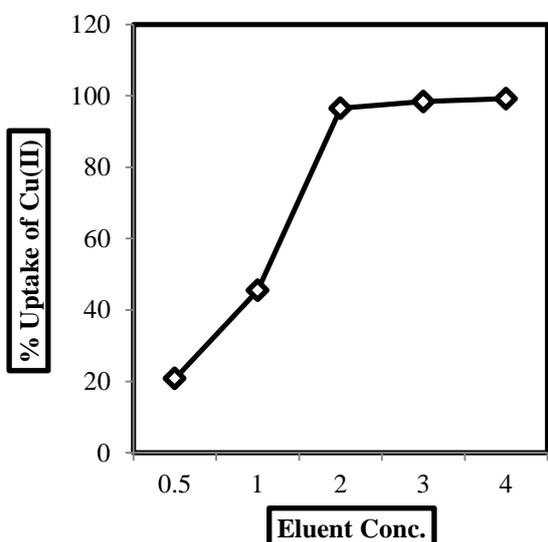


Fig. 5 Effect of eluent conc.

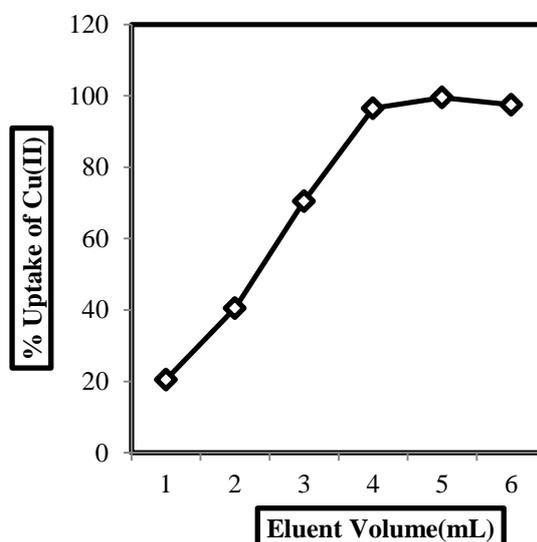


Fig. 6 Effect of eluent volume

Effect of interfering ions

Table 1: Tolerance limit of foreign ions in the determination of Cu(II)

Ion	Tolerance Limit [W _{foreignion} /W _{Cu(II)}]
NO ₃ ⁻ , SO ₄ ⁻ , HPO ₄ ²⁻ , SCN ⁻ , NO ₂ ⁻ , PO ₄ ³⁻ , ClO ₃ ⁻ , IO ₃ ⁻ , Cl ⁻ , I ⁻ , Br ⁻ , CH ₃ COO ⁻ , C ₂ O ₄ ²⁻	>1000
Na(I), K(I), Mg(II), Ba(II), Al(III), Rb(I), Cs(I), Ag(I)	1000
Sb(III), Ca(II), Zr(IV), Ti(IV)	500
Th(IV), Sn(II), As(III)	100
Fe(III), Ni(II)	10
Zn(II), Pb(II), Fe(II), Mn(II), Hg(II), Cd(II)	1
EDTA, CN ⁻ , F ⁻ , S ₂ O ₃ ²⁻	1

The effect of various foreign ions on the % recovery of a solution containing 150ng/mL of Cu(II) was studied. The results are summarized in Table. 1.

Application to water samples

The developed method has been employed for the preconcentration of Cu(II) in different water samples. For that purpose, the preconcentration procedure as given has been applied. The results are shown in Table 2.

Table 2: Determination of Cu(II) in different water samples

Sample	Spiked (ng/mL)	Found (ng/mL)	% Relative Error	% Recovery \pm RSD(%)
Tap Water	0.0	N.D.	-----	-----
	45.0	43.5	3.3	96.7 \pm 1.6
	35.0	33.6	4.0	96.0 \pm 2.4
Rose Water	0.0	N.D.	-----	-----
	60.0	58.1	3.7	96.8 \pm 1.5
	65.0	63.7	3.5	96.4 \pm 1.5
Mineral Water	0.0	N.D.	-----	-----
	55.0	53.4	2.9	96.5 \pm 1.5
	40.0	38.5	3.8	96.2 \pm 1.7

N.D. (not detected)

CONCLUSION

The developed SPE procedure allowed the determination of Cu(II) ions to be carried out at ng/mL. Due to preconcentration step, it was possible to obtain low limit of detection for Cu(II). The adsorbent is ecofriendly and a very small amount of it is consumed per analysis making it highly economical. The advantages of the proposed method are simple, time saving, convenient, rapid and low cost. The proposed method was successfully applied for the determination of analytes in different water samples.

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