Synthesis, Characterization and Metal Uptake Study of Cu and Cd on Poly-5, 5'-Methylene-bis-(2-Hydroxy Benzaldehyde) Ethylenediimine.

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Summary: The Schiff base polymer derived from ethylenediamine and 2-hydroxybenzaldehyde with formaldehyde (*o*-HBED-HCHO) formed chelates with Cu (II) and Cd (II) metal ions. The formation of Schiff base, resin and the polychelates were confirmed by C H N analysis, infrared, UV/Vis spectra and thermogravimetric analysis. The intrinsic viscosity of resin was determined by viscometry in THF. The adsorption characteristics of resin towards Cu (II) and Cd (II) metal ions in dilute solutions were measured, which indicated metal loading of Cu (II) 84.0 % and Cd (II) 70 % at room temperature on an optimized pH 6. The effects of pH optimization, flow rate, capacity of % sorption were studied. After these optimization the resin was examined for adsorption of both Cu (II) and Cd (II) metal ions from their aqueous solutions after desorption and determination by atomic absorption spectrometry.

Introduction

Polymeric adsorbents can be synthesized by suspension polymerization and other reactions. Since the hyper cross linked polymeric adsorbents were developed [1, 2], increasing attention has been paid for their unique adsorption properties resulting from its high surface area, high volume of micro pores and broad range of surface functional groups introduced in their synthetic reaction. Scientists have made many efforts on chemical modification of polymeric adsorbents to improve adsorption capacities, by introducing a number of functional groups [3, 4]. The structure of resin has a direct bearing on its stability as a material for preconcentration and separation of metal ions. The number of functional groups anchored to the polymer backbone and their accessibility in taking the metal ions are factors of prime importance. Studies on chelating resins have evoked considerable interest in recent years due to factors such as high recovery, short analysis time, high enrichment factor, low cost and low consumption of organic solvents.

When adsorption occurs in liquid solution, the adsorbate molecule is drawn from the bulk solution to the adsorbent-phase. The net attractive forces involving the solute, solvent and the adsorbent are assumed to be responsible for adsorption [5-7].

A numbers of complexing reagents have been used for the determination of copper (II), nickel (II), palladium (II), cobalt (II) and oxovanadium (IV) [8, 9] and various methods have been reported particularly for copper such as catalytic fluorimetric methods [10-13], fluorescence quenching methods [14-16] and spectrophotometric methods [17-18]. The tetradentate ligand bis (*o*-hydroxybenzaldehyde)ethylenediimine (*o*-HBED) reacts with copper(II), nickel(II), palladium(II), cobalt(II) and oxvanadium-(IV) to form colored complexes which are not sensitive for spectrophotometer determination of metal ions [19]. Samal et al have reported synthesis, characterization and capacity studies for copper (II) of formaldehyde condensed ethylenediamine and 2-hydroxy benzaldehyde (*o*-HBED- HCHO) [20].

The present work examines the polymer (*o*-HBED-HCHO) as adsorbent for Cu(II) and Cd(II) metal ions for preconcentration, followed by desorption and determination using atomic absorption spectrophotometry. Results of adsorption of both metal ions were presented and discussed.

Results and Discussion

Solubility

The freshly prepared resin (10 mg) was suspended over 5 mL of water at room temperature (27 °C), the solubility of resin was completely

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checked after 24 h. Both resins (*O*-HBED-HCHO)Cu(II) and (*o*-HBED-HCHO)Cd(II) were completely insoluble in water. The resin (*o*-HBED-HCHO) was also insoluble in ethanol and methanol solvents, which could be attributed to the increase in molecular weight of the resins due to the cross linking in the network through $-CH_2-$ groups, leading to a rigid structure as in Fig. 1. The resin was only soluble on heating in high polar solvents like THF and DMF.

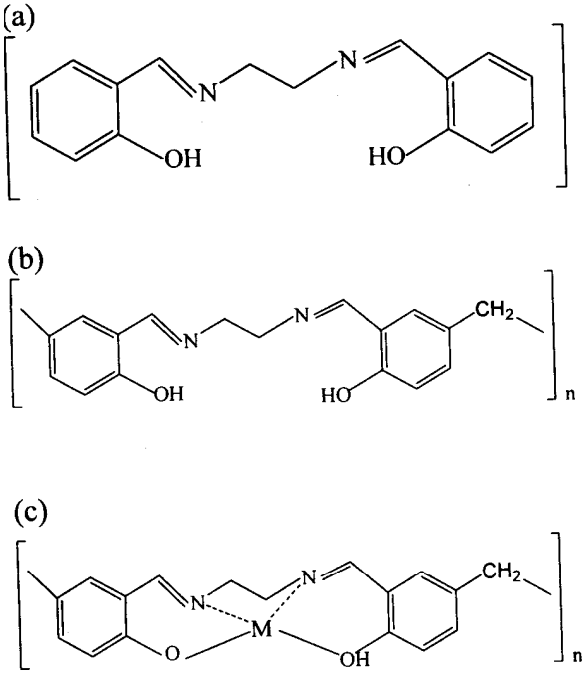

Fig. 1: Structure of (a) bis (2-hydroxy benzaldehyde) ethylenediimine (b) Poly 5,5,'methylene bis (2-hydroxy benzaldehyde) ethylenediimine (c) metal chelats.

Characterization

Spectral Studies

The FTIR spectra of resin (*o*-HBED-HCHO) and their metal chelates are shown in Fig. 2. The spectra of the resin (*o*-HBED-HCHO) indicating that the C=N stretch appears at 1649.5 cm^{-1}, the phenolic *O*-H registers at 1226 cm^{-1} and C=C absorption are at 1574, 1527 and 1443 cm^{-1}. Most of the peaks in the finger print region are sharp and well resolved. The aliphatic C-H stretch for methylene generated on formaldehyde condensation is registered at 2906.5

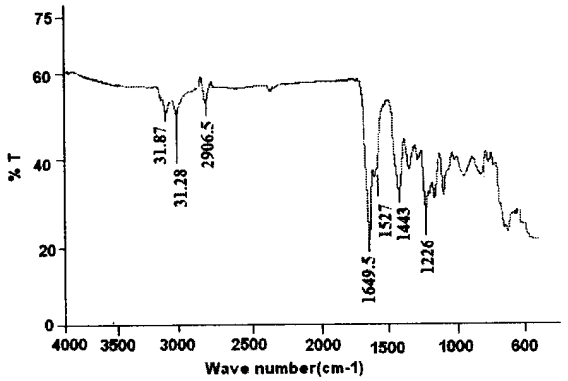

Fig. 2: F T. I.R Spectra of Poly 5, 5'- methylene bis (2- hydroxy benzaldehyde) ethylenediimine (*o*-HBED-HCHO).

cm^{-1} as a weak band. The results agreed with reported values [20].

The measurements of UV/VIS spectra were carried out in THF. The polymeric resin (*o*-HBED-HCHO) indicates two absorption bands at 253.6 nm and 294 nm (Fig. 3a) due to υC=Ç transition in the benzoid rings and υC=N conjugated amino groups respectively. The metal chelates (*o*-HBED-HCHO)Cu(II) indicate three bands (Fig. 3b) and the observation of a new band compared to resin may be attributed to metal- chelates bonding.

The Fig. 4 shows the thermogram of resin. The degradation of polymeric resin occurred in main two stages. In first stage, loss in weight started at 267 °C then in second step loss of 45 % by 340 °C followed by up to 400 °C. Thereafter a slow loss in weight continued upto 700 °C.

The viscosity measurements of resin and metal chelates were recorded within 283 - 323 K with concentration within 0.02-0.08 g/dL in THF. Intrinsic viscosity (η) is a function of molecular mass and it increased with increase in the molecular mass of polymer. Intrinsic viscosity (η) of the resin was observed within 0.2230-0.2784 dL/g and polychelates of both metal ions indicated within 0.2471-0.311 dL/g and 0.2673-0.3390 dL/g.

(I) Metal Ion Uptake Studies by Batch Method

(a) Effect of pH

The effect of pH on resin was used as a main determining parameter in achieving the quantitative

adsorption. The effect of pH was varied in the range of 2- 9 for both metal ions, (Fig. 5). Increasing pH beyond the range resulted in precipitation of metal ions as hydroxides. At higher pH, the uptake

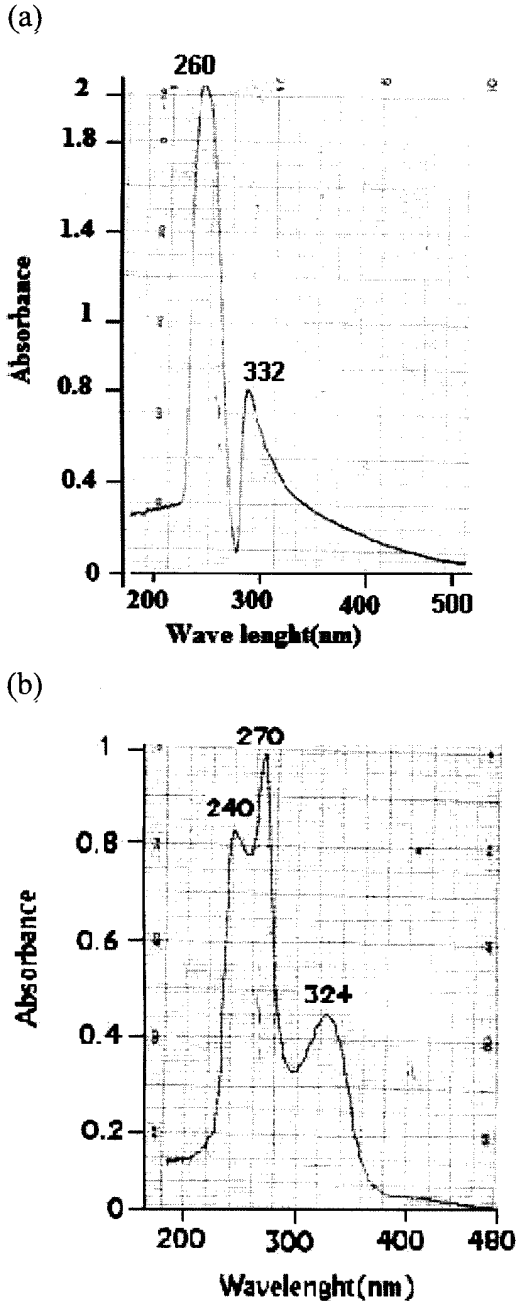

Fig. 3: (a) UV/ Visible absorption spectra of (a) Resin (*o*-HBED-HCHO) and (b) Metal chelates (*o*-HBED-HCHO) Cu (II)).

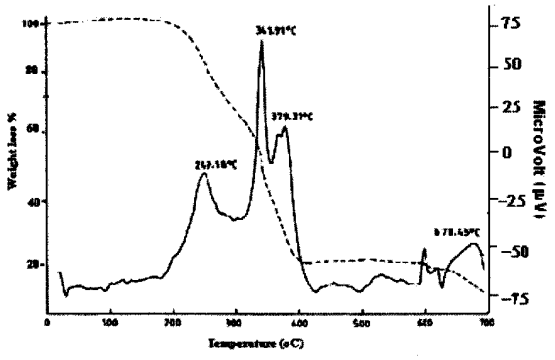

Fig. 4: TG/ DTA Thermograms of Poly 5, 5'-methylene bis (2- hydroxy benzaldehyde) ethylenediimine (*o*-HBED-HCHO).

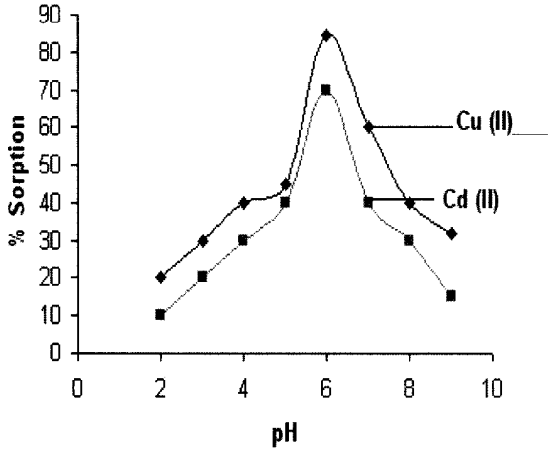

Fig. 5: Effect of contact pH of resin for % adsorption of Cu(II) and Cd(II) in batch method.

behavior of resin enhanced due to increase in basicity of C = N group but at low pH, the C = N group got protonated. Therefore pH 6 was selected an optimized pH for adsorption of both metal ions on resin.

(b) Effect of Contact Time

The optimized contact time of % adsorption was obtained by plotting percentage of metal uptake against contact time of reaction (Fig. 6), keeping initial metal ion concentration fixed (2000 µg per 10mL). The optimized time was 60 minutes for both metals. The rate of Cu(II) adsorption was higher than

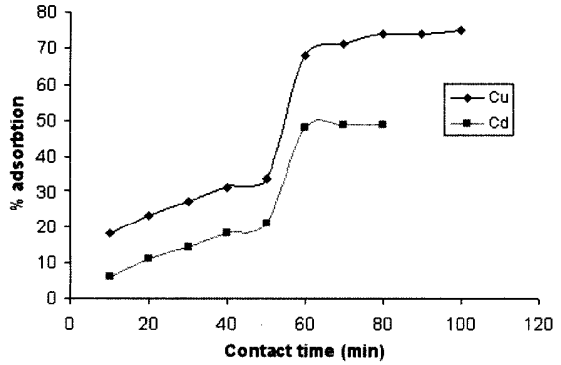

Fig. 6: Effect of contact time on % adsorption of copper and cadmium ions on polymeric resin.

Cd(II) ion may be due to lower activity of resin towards Cd(II).

(c) Effect of Optimum Volume

For the successful attempt of batch method, the pH of resin and amount of metal in solution were kept constant for both metals, while the volumes of metal ion solutions were varied from 10- 60 mL for maximum % sorption. The optimum volumes of 20 and 10 mL were selected for Cu (II) and Cd (II), respectively (Fig. 7).

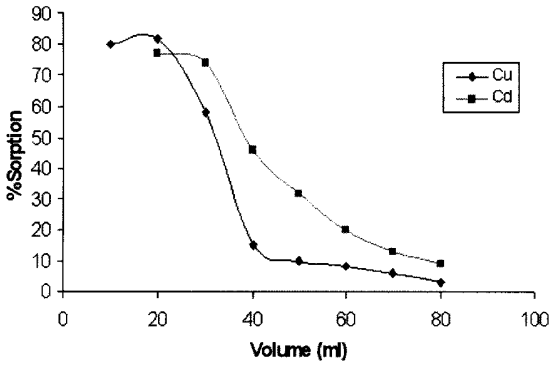

Fig. 7: Effect of volume on % adsorption of copper and cadmium ions on polymeric resin.

(d) Effect of Metal Ion Concentration

The uptake behavior of metal ion concentration on the resin was studied in the range 250-2000 µg per 10mL of the both metal ions. When the concentration of metal ions increased it enhanced the percentage of loading metal ion on the resin (Fig. 8). For both metal ions Cu (II) and Cd (II), the distribution *co*-efficient (Kd), of the resin was computed from Freundlich adsorption isotherm:

$$\text{Log}(x/m) = \log Kd + 1/n\ (\log C)$$

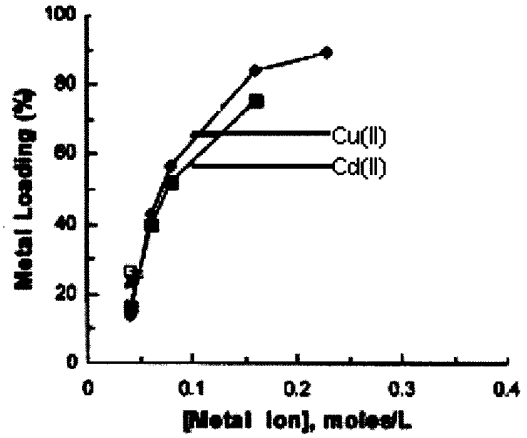

Fig. 8: Evaluation of Freundlich adsorption isotherm for Cu(II) and Cd(II) in batch method.

where C is the initial concentration of metal ion in mmol, m is the weight of the resin in g, x is the quantity of metal ion adsorbed by the resin in mmol and n is a constant.

The equation of the corresponding line for Freundlich adsorption isotherm can be written as:

For *O*-HBED-HCH*O*-Cu (II), $a=0.9622b + 0.6634$, $R^2= 0.9757$

And *O*-HBED-HCH*O*-Cd (II), $c=0.7235d + 0.5091$, $R^2= 0.9867$

where a, c, b, d correspond to log (x /m) and log C, respectively.

The adsorption *co*-efficient (Kd) of Cu (II) and Cd (II) ions on resin were found to be as 2.6601 and 3.791 s^{-1}, respectively. However, the high Kd values show that the saturation time for adsorption of metal ion is attained quickly.

(II) Metal Ion Uptake Study Using Column Technique

After the successful attempt of batch method, effect of pH, contact time, volume and

concentration were optimized, for column sorption keeping above parameters constant but further parameters were optimized for column study.

(a) Effect of Flow Rate

The effect of flow rate on the sorption was studied in the range of 1-6 mL/min at the pH chosen for maximum sorption, (Fig. 9). It was observed that at flow rate more than 2 mL/min for copper and 1mL/min for cadmium decrease in % sorption was indicated. Therefore flow rates of 2 and 1mL/min were selected for adsorption of Cu(II) and Cd(II) metal ions on the resin.

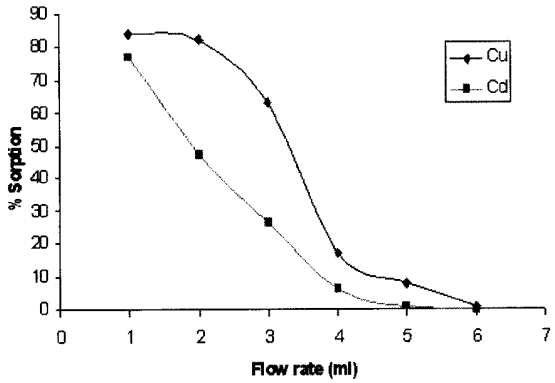

Fig. 9: Effect of Flow rate on % adsorption of Cu(II) and Cd (II) ions on polymeric resin.

(b) Desorption

In order to determine the amount of copper and cadmium eluted from the resin column, 10 mL of 1M HCl was used. Attempt was taken to elute the metal ions from resin by using aqueous hydrochloric acid. At 5- 6 mL of 1 M HCl, the metal ions were desorbed completely from resin column.

Application of Method

The Cu (II) ions were determined from different concentration of copper solutions by passing from resin filled column through peristaltic pump at pH 6. The % adsorption was obtained from eluents by atomic absorption spectrophotometer. Similarly various concentrations of cadmium solutions were taken for the determination of Cd (II) ions by passing through same polymeric resin.

Experimental

Instrument

Determination of Cu (II) and Cd (II) ions were carried out using the Spectra AA.20 (Varian) Atomic absorption spectrophotometer. All solutions were passed through the resin packed column using a peristaltic pump. FTIR-Spectra were recorded on Nicolet Avatar 330 FT-IR with total attenulated reflectance (ATR) accessory. Spectrophotometeric studies were carried out in dimethyl formamide (DMF) and tetrahydrofuran (THF) using double beam Hitachi 220 spectrophotometer (Hitachi (Pvt) Tokyo, Japan). Thermogravimatry (TG) and differential thermal analysis (DTA) were recorded on Thermalgravimetric / Differential thermal Analyzer, Pyris Diamond TG / DTA (Perkin Elmer, Japan) from room temperature to 600 °C with a heating rate 15 °C /min and nitrogen flow rate 50 ml/min. The sample 10 mg was placed in platinum crucible and recorded against α-alumina as reference.

Reagent and Materials

All chemicals were of analytical grade which included *o*-hydroxylbenzaldehyde, ethylene-diamine, sulfate salts of copper and cadmium, formaldehyde and organic solvents. The buffers used to control the pH of the solution were acetic acid-sodium acetate (Ph 3 -6) and ammonium hydroxide–ammonium chloride (pH 8 -10)

(i) Preparation of Schiff Base: Bis(2- hydroxyl benzaldehyde) Ethylenediimine

The Schiff base (*o*-HBED) and its resin (*o*-HBED-HCHO) were synthesized by reported method [20], as follows:

The Schiff base monomer was synthesized by reacting (0.01 M) of ethylenediamine, dissolved in 10 mL MeOH, with (0.02 M) of (2- hydroxyl benzaldehyde) in the presence of 0.5 g of anhydrous sodium acetate. After one hour of refluxing at 70 °C, precipitations were filtered and recrystallized from ethanol. The Schiff base (*o*-HBED) was isolated as a light yellow crystalline with molecular formula $(C_{16}H_{16}N_2O_2)n$ and calculated % C, H and N as 71.6%, 5.97% and 10.44% and observed % of these elements to be 72%, 5.13% and 10.2% respectively.

(ii) Preparation of Poly 5, 5' methylene Bis(2-hydroxy benzaldehyde) Ethylenediimine (Resin)

One gram of Schiff base was suspended in 25 mL distilled water and dissolved with addition of minimum about 10-12 drops of 2 M NaOH; the mixture was warmed to 50- 60 °C for 5 min and formaldehyde (37 %, v/v) was added to a final molar ratio of 1:2 with respect to Schiff base. The mixture was then refluxed on oil bath at 120-130 °C for 2 h. The insoluble resin was filtered, washed with distilled water followed by petroleum ether and finally dried at 70°C.

Metal Uptake Studies

The metal ion uptake behavior of the resin was determined following both batch and column techniques briefly given as under:

Batch Method

0.2 g of the resin portions were treated with aqueous solution (10 mL) of 0.05 M Cu(II) and Cd(II) metal ions. The pH of solution was adjusted using suitable buffers; suspensions were agitated for a set time period placed on a hot plate equipped with magnetic stirrer. The loaded resin portions were filtered off and washed thoroughly with demineralized water. The filtrate and washing were collected and analyzed by flame atomic absorption spectrophotometer, using air acetylene flame.

Column Method

Five hundred milligrams of synthesized resin (*o*-HBED-HCHO) was slurried in water and then poured into a pyrex glass column of 10 inches with a diameter (50 mm). A little plug of quartz wool was placed at both ends of the column so as to avoid the loss of resin (adsorbents). The column was connected through peristatic pump. The metal ions solution was passed through peristaltic pump to the column filled with resins. The eluent was analyzed for metal concentration by atomic absorption spectrophotometer.

From the data, the percentage of metal ions loading on the resin and finally the distribution co-efficient (kd) values were calculated from the following relations.

Metal uptake (%) = Ci- Cf / Ci x 100

Ci = Initial concentration of metal ions in solution (μg)

Cf = Final concentration of metal ions in solution in filtrate and washing (μg).

$$Kd = \frac{\text{mmol metal ion on resin}}{\text{mmol metal ion in the solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of resin (g)}}$$

Procedure for Samples Preparations

Following procedures were applied for the determination of % sorption with copper and cadmium ions from their aqueous solutions of different solutions, respectively:

Procedure for the Use of Samples on Column

10 mL of individual metal solution was passed from the column filled with 0.5 g resin (*o*-HBED-HCHO) through peristaltic pump. The pH of the metal solutions was adjusted with 2 mL of optimized buffer pH 6 solutions. The eluent was analyzed for metal concentration by atomic absorption spectrophotometer. The analyte was desorbed with 1M HCl at optimized flow rate (1-2 mL) and then the eluent was also analyzed by AAS.

The total amount of metal ions was calculated with the addition of both results of eluents by atomic absorption spectrometry. Therefore % adsorption of Cu (II) and Cd (II) ions were determined by atomic absorption spectrophotometer.

Conclusion

The Schiff base polymer 5, 5, - methylene bis(2-hydroxybenzaldehyde)ethylenediimine is used for adsorption of Cu(II) and Cd(II) from aqueous solution at pH 6. Batch and column methods were examined for Cu(II) and Cd(II) ions and % adsorptions were observed with 84.0 % and 70 % respectively. The desorption with hydrochloric acid (1 M) was quantitative with 5- 6 ml solution. The monitoring was made by air- acetylene flame atomic absorption. The method was applied for the determination of Cu (II) and Cd (II) metal ions.

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