

Cellulose functionalized with 8-hydroxyquinoline: new method of synthesis and applications as a solid phase extractant in the determination of metal ions by flame atomic absorption spectrometry

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Abstract

8-Hydroxyquinoline has been immobilized on cellulose via a moderate size -NH-CH₂-CH₂-NH-SO₂-C₆H₄-N=N- linker and the resulting macromolecular chelator (and intermediates) characterized by infrared spectrometry, cross-polarization magic angle spinning (CPMAS) ¹³C NMR spectrometry and thermogravimetric analysis (TGA). It has been used for enrichment of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) prior to their determination by flame atomic absorption spectrometry (FAAS), which are quantitatively sorbed (recoveries > 97%) at pH 4.2-6.7, 4.2-7.5, 2.0-3.0, 5.3-6.7, 5.3-6.2, 6.2-9.0 and 4.2-5.3, respectively. The sorption capacity for the seven cations varies from 93.8 to 629.9 (μmol g⁻¹). HCl or HNO₃ (1 mol dm⁻³) may be used to desorb all the cations. The optimum flow rate for sorption and desorption has been found to be 2-4 cm³ min⁻¹. The tolerance limits of electrolytes NaCl, NaBr, NaNO₃, Na₂SO₄, Na₃PO₄ and cations Ca²⁺ and Mg²⁺ (added as chloride and sulphate, respectively) in the sorption of all these metal ions are reported. The preconcentration factor is between 90 and 300. Simultaneous sorption of the cations other than iron(III) is possible if their total concentration does not exceed sorption capacity. The present matrix coupled with FAAS has been used to enrich and determine the seven metal ions in river water samples (R.S.D. < 7.4%) and water samples having a composition similar to certified water sample SLRS-4 (NRC, Canada) with R.S.D. - 2.3%.

Keywords: 8-Hydroxyquinoline; Metal ion; Preconcentration; Flame atomic absorption spectrometer; Chelating cellulose; Enrichment

1. Introduction

Solid phase extraction [1] is a very promising technique for separation and enrichment and consequently its use is also increasing continuously, making it very important for analysts. The technique when applied to metal ions is generally based on

chelating matrices. Therefore, there is a current interest in designing macromolecular chelators having high sorption capacity, selectivity and suitability for on-line applications. 8-Hydroxyquinoline (oxine), a versatile chelating ligand has been immobilized (chemically) on a variety of supports, but not many of them have been studied in detail for their analytical performance (sorption capacity and selectivity, etc.). Silica gel [2-5], cellulose [6-11] and Amberlite XAD-series resins [12,13] are found to be

promising supports for oxine, but its immobilization on cellulose has been reported to give better sorption capacity for metal ions in comparison to other supports. A variety of methods are used to functionalize cellulose with oxine but analytical performance other than the sorption capacity is scantily reported. The linkers used to attach oxine with cellulose influence the sorption capacity. Very short [8] and long [9] linkers (e.g. $\text{O-CH}_2\text{-CH}_2\text{-SO}_2\text{-C}_6\text{H}_4\text{N=N-}$ and $\text{-O-CH}_2\text{-CH(OH)-CH}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-}$, respectively) do not give the best results. Moreover, the presence of too many chelating groups in the linker itself makes the chelating matrix non-specific. Cellulose is also functionalized with oxine via moderate size linkers [14,15], viz. $\text{-O-CH}_2\text{-CH(OH)-CH}_2\text{-SO}_2\text{-C}_6\text{H}_4\text{N=N-}$, $\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{-CH(OH)-CH}_2\text{-SO}_2\text{-C}_6\text{H}_4\text{N=N-}$ and $\text{-O-CH}_2\text{-CH(OH)-CH}_2\text{-NH-C}_6\text{H}_4\text{N=N-}$ which give very good sorption capacity, but the full analytical performance of any of the resulting matrices is scantily reported. It was therefore thought worthwhile to attach oxine with cellulose via linker $\text{-NH-CH}_2\text{-CH}_2\text{-NH-SO}_2\text{-C}_6\text{H}_4\text{N=N-}$ and study the sorption behavior for metal ions. This linker has not been reported so far for immobilizing oxine on cellulose. It gives a matrix of good stability which is found more promising for the enrichment of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) than those based on other linkers. The enrichment procedure based on the new matrix has been applied to determine metal ions in water samples. The results of these investigations are reported in this paper.

2. Experimental

2.1. Instruments

The cross-polarization magic angle spinning (CPMAS) ^{13}C NMR spectrum was recorded at 75.3 MHz on a Bruker (Fallanden, Switzerland) 300 spectrometer. The CPMAS parameters used for this purpose are: number of scans 10,509, short width range 39,920.160 Hz and acquisition time 0.0128756 s. A flame atomic absorption spectrometer of the Electronic Corporation of India Limited (Hyderabad, India), model 4139, equipped with air-acetylene flame (air and acetylene flow rates: 10 and $2\text{ dm}^3\text{ min}^{-1}$,

respectively) was used for atomic absorption spectrometric measurements. The wavelengths used for monitoring Cu, Zn, Fe, Ni, Co, Cd and Pb are 324.8, 213.9, 248.3, 232.0, 240.0, 228.8 and 212.0 nm, respectively. A Nicolet (Madison, USA) FT-IR spectrometer, model Protégé 460, was used to record IR spectra (in KBr) in the range $400\text{-}4000\text{ cm}^{-1}$. The pH was measured with an Elico (Hyderabad) pH meter (model LI-120 digital). Thermogravimetric analyses were carried out on a Dupont (Wilmington, DE) 2100 thermal analyzer. A Perkin-Elmer (Rotkreuz, Switzerland) elemental analyzer, model 240 C, was used for elemental analyses. The flow of solution through the column was controlled using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK). The metal ion sorption and desorption studies on the chelating matrix were generally carried out using Pharmacia (Bromma, Sweden) columns (1 cm in diameter and 10 cm in length) equipped with adjustable frits. A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi) with a speed of $200\text{ strokes min}^{-1}$ was used for batch equilibration.

2.2. Reagents and solutions

Microcrystalline cellulose, N,N-dimethylformamide, ethylene diamine, thionyl chloride and 8-hydroxyquinoline were obtained from E. Merck (Mumbai, India). 4-Acetamidobenzenesulphonyl chloride (ABSC) was procured from Acros Organics, NJ. The metal salts and other chemicals used were of analytical reagent grade. The stock solutions of metal ions (1000 mg cm^{-3}) were prepared by dissolving copper(II) sulphate pentahydrate, zinc(II) sulphate heptahydrate, ammonium iron(II) sulphate hexahydrate (followed by aerial oxidation), nickel(II) sulphate hexahydrate, cobalt(II) chloride hexahydrate, cadmium(II) acetate and lead(II) acetate in an appropriate amount of deionized water acidified with 5 cm^3 of the corresponding concentrated acid. HCl, acetate-acetic acid, phosphate and $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer [16] were used to adjust the pH of the solutions, wherever suitable. The water samples from the Ganges river (Rishikesh, India), Shipra river (Ujjain, India) and taps of the New Delhi water supply were collected, acidified with 2% HNO_3 , filtered and stored in glass bottles. The glassware was washed with chromic acid,

soaked in 5% HNO₃ overnight, and cleaned with doubly distilled water before use.

2.3. Synthesis and characterization of oxine-modified cellulose

Chlorodeoxycellulose was synthesized from cellulose by chlorinating cellulose with thionyl chloride according to the method reported by Polyakov and Rogovin [17]. The temperature of the reaction was restricted to 60 °C as at higher temperature degradation of cellulose occurred. Chlorination by this method takes place exclusively at the primary alcohol group of glucose residues of cellulose, as suggested by Horton et al. [18]. Ethylene diamine cellulose (Cell-NHCH₂CH₂NH₂) was prepared from chlorodeoxycellulose by the method reported by Tashiro and Shimura [19]. It was converted to oxine-loaded cellulose (3) by the procedures given below.

2.3.1. Synthesis of Cell-NHCH₂CH₂NHSO₂C₆H₄NHCOCH₃ (1)

1 was synthesised via the SchottenBauman reaction of ethylene diamine cellulose with 4-acetamidobenzenesulphonyl chloride. Cell-NHCH₂CH₂NH₂ (5 g) was added to a mixture of tetrahydrofuran (150 cm³) and distilled water (200 cm³) and stirred at room temperature for a few min to give a slurry. Aqueous NaOH (2.5 mol dm⁻³) was added dropwise to raise the pH of the slurry to 11.5. ABSC (15.8 g) was divided into three equal portions. One portion was added as a solid to the slurry with rapid stirring and the decrease in pH monitored. When the pH became steady (~7.2), THF (30 cm³) and aqueous NaOH (2.5 mol dm⁻³) were added till the pH became 11 again. The procedure was repeated with another portion of ABSC. After addition of the third portion of ABSC, the pH again gradually dropped to 4-5. Aqueous NaOH was added in small aliquots until pH 7.2 was attained. The mixture was stirred for 4 h and filtered. The resulting solid (1) was washed with water and acetone and dried in vacuo.

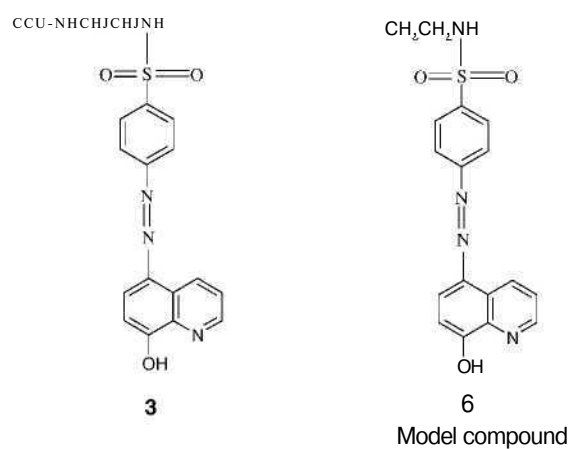
1 was authenticated by its ¹³C CPMAS NMR spectrum which has signals due to the six carbon atoms of the glucose unit at δ: 106.8, 90.4, 76.3, 73.4 and 66.9 ppm. Additional signals consistent with the solution ¹³C{¹H} NMR spectrum of 4-CH₃CONHC₆H₄SO₂ group are observed at δ: 174.4, 145.6, 135.8, 131.8 and 122 ppm in the

¹³C CPMAS spectrum of 1. They may be assigned to the italicized carbon atoms of CO, ArC-SO₂, ArC-NHCOCH₃, Ar-C *ortho* and *meta* to -SO₂-group, respectively. Moreover, the signal appearing at 26 ppm may be assigned to the methyl carbon of the acetamido group.

2.3.2. Synthesis of

Cell-NHCH₂CH₂NHSO₂C₆H₄NH₃⁺Cr⁻ (2)

1 (2 g) was mixed with HCl (0.75 mol dm⁻³) with stirring. The mixture was refluxed for 20 min, cooled and filtered. The resulting solid 2 was washed with distilled water and dried in vacuo. In this process, degradation of cellulose does not occur.



2.3.3. Synthesis of 3

2 (2 g) was suspended in 1 mol dm⁻³ HCl (100 cm³) at 0 °C and reacted with 10% NaNO₂ solution until the reaction mixture began to give a violet color with starch-iodide paper. The reaction mixture was kept for 1 h at 0 °C. The solid was filtered below 5 °C and treated with 8-hydroxyquinoline (3 g dissolved in 2% aqueous NaOH) at 0 to -5 °C for 6 h. The resulting dark red powder was filtered-off, washed with water and air-dried. Analyses: Found C, 46.00%, H, 5.03%; Calc. for C₂₃H₂₅O₇N₅S(7/2)H₂O: C, 47.80%, H, 5.50%.

The thermogravimetric analysis (TGA) curve for cellulose loaded with oxine (3) was compared with that of pure cellulose. The decomposition of pure cellulose in a nitrogen atmosphere starts at about 320 °C and rapid weight loss occurs at 350-380 °C whereas

oxine-loaded cellulose shows a rapid weight loss at 310-350 °C, a temperature lower than that of pure cellulose. This is consistent with the observations made earlier that organically modified cellulose [20] generally undergoes thermal decomposition at a lower temperature than that of pure cellulose. The total weight loss in TGA at 200 °C suggests the presence of ~3.5 water molecules per repeat unit of the polymer, which is supported by elemental analyses.

2.4. Synthesis of model compounds (4-6)

The model compounds for 1-3, viz. CH₃CH₂NHSO₂C₆H₄NHCOCH₃ (4), CH₃CH₂NHSO₂C₆H₄NH₃⁺C⁻ (5) and CH₃CH₂NHSO₂C₆H₄N₂C₉H₅N-8-OH (6), respectively, were prepared. To synthesize 4 solid ABSC (5g) and 50 cm³ of ethylamine were mixed and heated on a steam bath for 30 min. The mixture was cooled in an ice bath and 6 mol dm⁻³ H₂SO₄ was added in aliquots until acidic. On further cooling the reaction mixture in an ice bath, white needle shaped crystals of 4 appeared. The crystals were filtered-off, washed with cold water (1-4 °C) and air-dried. Compound 4 (2 g) was refluxed in dilute HCl (50 cm³) for 30 min to obtain 5 in solution. The 10 cm³ portion of solution of 5 was cooled to 0 °C and treated with cold 5% NaNO₂ solution until the reaction mixture began to give a violet color with starch-iodide paper. The resulting solution was treated with 8-hydroxyquinoline at 0 °C (0.5 g dissolved in 20 cm³ of 2% NaOH solution). A reddish orange dye 6 was formed which was filtered-off, washed with water and air-dried.

The immobilization of oxine onto cellulose through a linker was supported by comparison of the IR

bands of 3 with those of 1 and model compounds 4 and 6 (Table 1). The assignment of the band around 1570 cm⁻¹ to a -N=N- stretching vibration (Table 1) is on the basis of report by Le Fevre et al. [21]. The IR spectrum of ED cellulose does not differ markedly from that of unmodified cellulose. The two bands present in unmodified cellulose at 1372 and 1163 cm⁻¹ appear modified on formation of 1 due to overlapping with asymmetrical and symmetrical stretching vibrations of the S=O group, respectively. The absence of a band at 1683 cm⁻¹ (ν(CONH)) in the spectrum of 2 is as expected.

2.5. Recommended procedure for preconcentration and determination of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II)

The column and batch methods were standardized for preconcentration and determination of metal ions. The recommended procedures are as follows.

2.5.1. Column method

Oxine-modified cellulose (0.5 g) fully swollen in doubly distilled water for 12 h was packed in a glass column C10/10 (Pharmacia, size 10 cm x 10 mm) by the slurry method [22] using frits. It was thereafter treated with 50 cm³ of 1.5 mol dm⁻³ HCl and washed with doubly distilled water until free from acid. A suitable aliquot of solution containing Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) or Pb(II) in the concentration range 0.0033-1.0 (µg cm⁻³) was passed through this column after adjusting the pH to an optimum value (Table 2) at a flow rate of 2-5 cm³ min⁻¹ controlled with the peristaltic pump. The column was washed with distilled water to remove free metal ions. The

Table 1
IR spectra of 1, 3, 4 and 6

| Band/vibration | Position (cm ⁻¹) in spectra of | | | |
|-------------------------|--|------------|------------------|------------|
| | 1 | 3 | 4 | 6 |
| Phenyl | 1593, 1539, 1496, 1544, 1596 | 1544 | 1596, 1544, 1497 | 1594 |
| ν _{asym} (S=O) | 1374 | 1371 | 1367 | 1386 |
| ν _{sym} (S=O) | 1157 | 1162 | 1158 | 1162 |
| C-S | 749 | 740 | 773 | 784 |
| CONH | 1683 | | 1683 | |
| -N=N- | | 1577 | | 1570 |
| Oxine | | 1502, 1470 | | 1505, 1472 |

Table 2
Optimum experimental conditions for the sorption and desorption of metal ions

| Experimental parameters | Metal ion | | | | | | |
|--|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | Cu(II) | Zn(II) | Fe(III) | Ni(II) | Co(II) | Cd(II) | Pb(II) |
| pH range | 4.2-6.7 | 4.2-7.5 | 2.0-3.0 | 5.3-6.7 | 5.3-6.2 | 6.2-9.0 | 4.2-5.3 |
| HCl concentration for desorption (mol dm ⁻³) | 0.2-1.0 | 0.2-1.0 | 0.6-1.0 | 1.0 | 0.6-1.0 | 0.4-1.0 | 0.6-1.0 ^b |
| Flow rate (cm ³ min ⁻¹) | 2.0-8.0 | 2.0-6.0 | 2.0-5.0 | 2.0 ^a .0 | 2.0 ^a .0 | 2.0-5.0 | 2.0-5.0 |
| Sorption capacity of resin (ixmolg ⁻¹) | 629.92 | 348.71 | 256.23 | 177.68 | 205.72 | 113.66 | 93.76 |
| Average recovery ^a (%) | 99.0 | 99.0 | 98.0 | 98.0 | 97.5 | 98.3 | 99.0 |
| S.D. ^a | 0.0158 | 0.0273 | 0.0387 | 0.0353 | 0.0313 | 0.0482 | 0.0482 |
| R.S.D. (%) | 1.6 | 2.75 | 3.94 | 3.6 | 3.2 | 2.9 | 2.43 |
| Regression equation | $A = 0.072C - 0.004$ | $A = 0.257C + 0.028$ | $A = 0.012C + 0.002$ | $A = 0.023C - 0.006$ | $A = 0.015C - 0.001$ | $A = 0.210C + 0.006$ | $A = 0.019C + 0.001$ |
| R ² | 0.999 | 0.999 | 0.998 | 0.998 | 0.999 | 0.999 | 0.998 |

^aFor five determinations of 10 μg cm⁻³ (2.0 fL g cm⁻³ for Pb).

^bHNO₃ was used for desorption: A is absorbance and C concentration.

bound metal ions were desorbed from the matrix with HCl or HNO₃ (10-25 cm³) of optimum concentration (Table 2) and the eluates were aspirated into the flame of a flame atomic absorption spectrometry (FAAS) instrument, standardized prior to the determination. The concentrated eluates were suitably diluted with doubly distilled water before aspiration.

2.5.2. Batch method

A solution (100 cm³) containing 0.01-20.0 (xg cm⁻³) each of Cu(II), Zn(II), Fe(III), Co(II), Ni(II), Pb(II) or Cd(II) was placed in a glass-stoppered bottle (250 cm³) after adjusting its pH to the optimum value (Table 1). Oxine-modified cellulose (0.25 g) was added to it and the bottle was stoppered and shaken for 30 min. The solid was filtered-off, washed with doubly distilled water, shaken with 1 mol dm⁻³ HCl or HNO₃ (10-25 cm³) for 20 min and again filtered. The filtrate was aspirated into the flame of a pre-standardized FAAS instrument dilution if required.

2.6. Calibration parameters

After setting various parameters at the optimized level (wavelength, slit width, lamp current, etc.) for metal ion determination, the calibration graphs obtained were linear for copper (0.5-8.0 (xg cm⁻³), zinc (0.1-2.0 (xg cm⁻³), iron (0.5-8.0 (xg cm⁻³), nickel (0.5-8.0 (xg cm⁻³), cobalt (0.5-8.0 (xg cm⁻³), cadmium (0.5-2.0 (xg cm⁻³) and lead (1-10.0 (xg cm⁻³) in the range given in parentheses. The linear equations along with the correlation coefficient are given in Table 2.

3. Results and discussion

Optimum conditions for the sorption (pH and flow rate) and desorption (concentration and volume of eluant) for each metal ion were established by the column method by varying one parameter and keeping the rest constant at an optimum level. The sorption and desorption of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) on an oxine-immobilized cellulose column were found to be quantitative with recoveries up to 99%. Simultaneous sorption of

the cations other than iron(III) is possible, if their total concentration does not exceed the sorption capacity.

3.1. Effect of pH on sorption

The pH values for optimum sorption of all the metal ions onto oxine-modified cellulose were standardized. A typical process for optimizing the pH value for Cu is as follows. A set of solutions (volume: 100 cm³) containing 0.25 (xg cm⁻³) Cu was taken. The pH of the solutions was adjusted to different values in the range 2.0-10.0 with 0.1 mol dm⁻³ HCl, acetate, phosphate or NH₃-NH₄Cl buffer and the solutions passed through the column (filled with 0.5 g of oxime-loaded cellulose) at a flow rate of 3 cm³ min⁻¹ controlled by a peristaltic pump. The bound metal ions were eluted from the solid matrix of the column by elution with 10 cm³ of 1 mol dm⁻³ HCl/HNO₃ after washing-off free metal ions with water. The final volume of eluate was made up to 25 cm³ and its concentration was determined by FAAS. The metal ions were not significantly desorbed (<1.5%) by distilled water; therefore chelation contributes predominantly to the retention of metal ions. The optimum pH values for Cu are given in Table 2. For other metal ions the optimum pH values for sorption ascertained in a similar fashion are summarized in Table 2. The recovery was quantitative (up to 99 %) for all the metal ions (concentration < 1.0 xg cm⁻³). The variation of sorption with pH for all the metal ions is shown in Fig. 1. The use of acetate, phosphate and ammonia buffer made to adjust the pH does not affect the sorption behavior. The maximum sorption of the metal ions was found to be in the pH range 4.2-9.0, except for iron for which the considerably lower pH 3 was found to be adequate for quantitative sorption.

3.2. Effect of flow rate for sorption and desorption

The optimum flow rates (controlled with a peristaltic pump) for maximum loading of metal ions onto oxine-modified cellulose are in the range 2-8 cm³ min⁻¹. Similarly for desorption, a flow rate of 2-4 cm³ min⁻¹ was found to be sufficient. A flow rate of >8 cm³ min⁻¹ was found to be

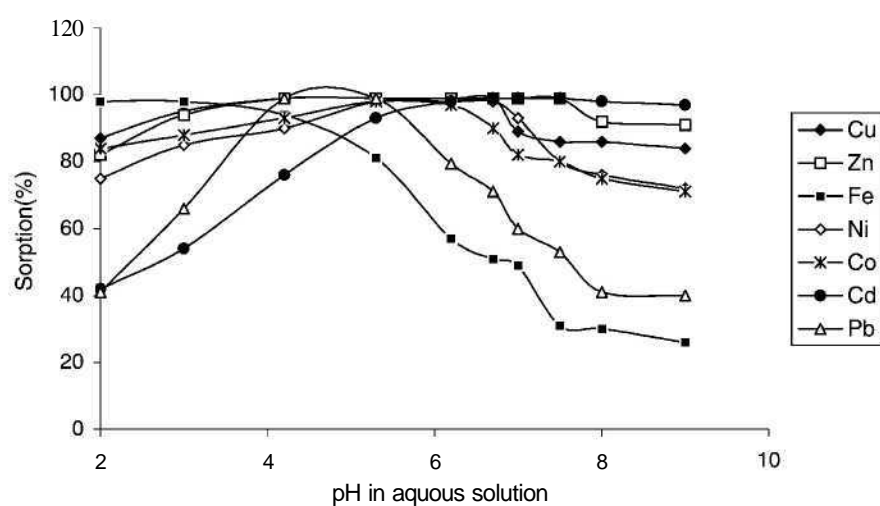


Fig. 1. Effect of pH on the sorption of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II).

insufficient for quantitative enrichment of metal ions onto the solid matrix. A flow rate of $<2\text{cm}^3\text{min}^{-1}$ was not studied to avoid a longer time of analysis.

3.3. Optimum acid concentration and volume of eluent for desorption

The optimum acid concentration for elution was determined by eluting the metal ions from the modified cellulose column with 10-25 cm^3 of HCl/HNO₃ of varying concentrations (0.001-2.0 mol dm^{-3}) keeping the optimum flow rate. It was found that 0.2-1.0 mol dm^{-3} HCl/HNO₃ was sufficient for the quantitative desorption of all the metals except Pb for which only HNO₃ was found to be suitable. With 0.1 mol dm^{-3} HCl, the recovery of Cu(II) and Zn(II) was 75%. For further study, 1 mol dm^{-3} HCl/HNO₃ was used for desorption of all metal ions. The elution with acid also regenerates the chelating matrix, which can be reused. The efficacy of the eluent (1 mol dm^{-3} HCl) was studied by taking different volumes (3-25 cm^3) and applying the recommended column procedure (metal concentration $< 1\text{figcm}^{-3}$). It was found that 8 cm^3 of HCl (1 mol dm^{-3}) was sufficient for quantitative recovery (~99%) of Cu and Zn, 10 cm^3 for Fe and Cd and 20 cm^3 for Ni and Co. For Pb 10 cm^3 of 1M HNO₃ gave 99% recovery.

3.4. Sorption capacity

The sorption capacity (maximum amount of metal sorbed per gram of the matrix) for each metal ion was determined by the batch method. A solution (100 cm^3) containing 60(xgcm^{-3}) of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) or Pb(II) was placed in a glass-stoppered bottle (250 cm^3) after adjusting its pH to the optimum value (Table 2). Oxine-modified cellulose (0.05 g) was added to it and the bottle was stoppered and shaken for 12 h. A suitable aliquot of the solution was removed and the capacity determined from the difference between the metal ion concentration in the solution before and after sorption. The solid matrix was filtered-off, washed with distilled water and metal ions loaded on it were desorbed with 100 cm^3 of 1 mol dm^{-3} HCl/HNO₃. After filtering-off the solid matrix the filtrate was diluted suitably (to bring the metal ion concentration in to the working range) and subjected to determination by FAAS. The capacity values (Table 2) determined by the two methods are consistent and in the range of 94-630 fxmolg^{-1} . The capacity of the modified cellulose was found to be almost same for the different batches of oxine-modified cellulose. Also, the capacity of oxine-modified cellulose for Cu(II) is significantly higher than that of ED cellulose (445 fxmolg^{-1}) reported by Nakamura et al. [23].

3.5. Kinetics of metal sorption

The percent sorption of metal ions as a function of time was studied by the batch method. Oxine-immobilized cellulose was shaken (on an electrical shaker) with 100 cm³ of a metal ion solution (concentration = 75 (µg cm⁻³)) for different time intervals (2, 5, 10, 20, 30, 40, 60 min, 1.5, 2, 3 and 4 h). The concentration of metal ions loaded onto the matrix as well as present in the supernatant solution was determined by FAAS after appropriate dilution (in case of desorption from the matrix). The loading half-time (t_{1/2}) needed to reach 50% of the total loading capacity was found to be <2 min for Cu, Zn and Fe and 5 min for Co and Cd. The equilibration time of 10 min was found to be sufficient for saturation of 50% of the matrix with Ni and Pb. The equilibration time of 5 min was sufficient for quantitative sorption of Cu and Zn whereas a 20 min equilibration was enough for >90% saturation of the matrix with Fe. The profile of sorption as a function of time (Fig. 2) on oxine-immobilized cellulose suggests that the surface functional groups are accessible for chelation to the metal ion without much steric hindrance.

3.6. Preconcentration limit and enrichment factor

The enrichment factor was determined by increasing the dilution of metal ion solution while keeping the total amount of loaded metal ion fixed at 10 (µg for Cu, Zn, Fe or Cd and 25 (µg for Co, Ni or Pb and

applying the recommended column procedure. The maximum preconcentration factors achieved, the corresponding lowest concentration (below which recoveries become non-quantitative) and final volume for elution are given in Table 3. The feed volume, i.e. maximum volume of solution passed and the recoveries at the lowest concentration are also reported. The limit of detection (LOD) values (defined as (blank + 3 s) where s is the S.D. of the blank determination) are 0.79, 0.84, 2.51, 1.61, 1.09, 2.59 and 2.44 µg dm⁻³ for Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II), respectively, and the corresponding limit of quantification (blank + 10s) values are 0.92, 0.94, 2.76, 1.78, 1.21, 2.81 and 2.77 µg dm⁻³, respectively.

3.7. Effect of electrolytes and cations

Chelating matrices are commonly used to enrich metal ions from water samples, which are also the target applications of the present matrix. Chloride, nitrate and phosphate ions present in natural water have the capability to complex with many metal ions. Consequently, they may compete for metal ions with the immobilized ligand on the cellulose and reduce the extraction. Thus, the effect of NaCl, NaBr, Na₃PO₄, Na₂SO₄ and NaNO₃ on the sorption of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) onto the functionalized cellulose was studied. The effect of doubly charged cations such as Ca(II) and Mg(II) (added as chloride and sulphate, respectively) was also investigated. A set of solutions containing 25 (µg of a metal

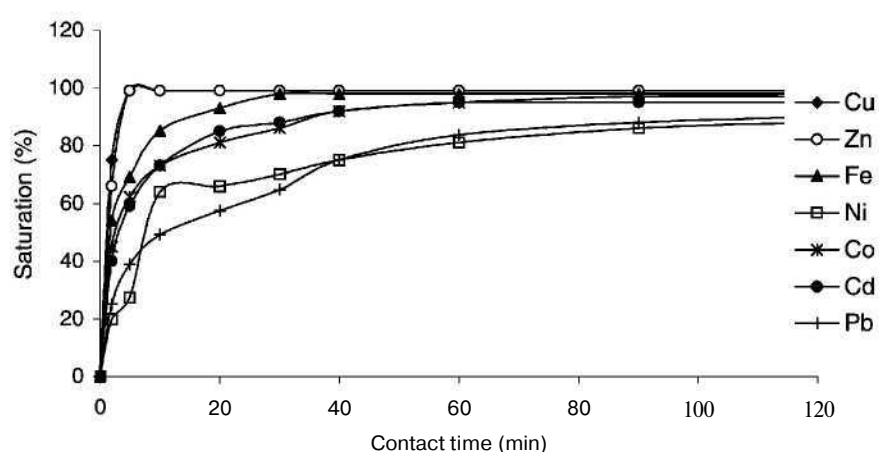


Fig. 2. Kinetics of metal ion sorption on oxine-loaded cellulose.

Table 3
Enrichment factors and enrichment limits of metal ions

| Metal ion | Total volume (cm ³) | Lowest concentration (ngcm ⁻³) | Final volume (cm ³) | Recovery (%) | Preconcentration factor |
|-----------|---------------------------------|--|---------------------------------|--------------|-------------------------|
| Cu | 3000 | 3.3 | 10 | 99.0 | 300 |
| Zn | 2500 | 4.0 | 10 | 99.0 | 250 |
| Fe | 3000 | 3.3 | 10 | 98.0 | 300 |
| Ni | 1800 | 13.8 | 20 | 98.0 | 90 |
| Co | 2000 | 12.5 | 20 | 97.5 | 100 |
| Cd | 2500 | 4.0 | 10 | 98.3 | 250 |
| Pb | 2000 | 12.5 | 10 | 99.0 | 200 |

ion (50 µg in the case of Pb) was taken and spiked with various amounts of electrolytes or cations. The final concentration of each electrolyte or cation was adjusted to between 0.001 and 1.0 mol dm⁻³ for each metal ion. After making up the volume to 100 cm³, each solution of the set was passed through the modified cellulose column and the sorbed metal was eluted with acid of optimum concentration (Table 2). The tolerance limit of electrolytes Ca(II) and Mg(II) are given in Table 4. A 3% lowering in the recovery in comparison with the value observed in the absence of interfering species was used as a criterion of interference. Each reported tolerance/interference is in the preconcentration and not in the determination by AAS, as checked with the help of reagent matched standard solutions. The oxine-immobilized cellulose shows good tolerance towards most of the electrolytes. There is no interference of NaBr, NaCl and NaNO₃ up to a concentration of 0.4 mol dm⁻³ on the sorption of Cu(II), Zn(II) and Fe(III). Ca(II) does not interfere up to 0.3 mol dm⁻³ in the determination of 0.25 µg cm⁻³ Cu(II), Zn(II), Ni(II) or Cd(II). However, Na₃PO₄ is tolerable only at lower concentration

levels (0.001-0.005 mol dm⁻³) and shows interference in the determination of Fe(III) while Mg interferes with the determination of Pb(II) and Cd(II).

3.8. Reusability and stability of the matrix

The reusability of the matrix was tested by using the same matrix bed for sorption-desorption of the seven metal ions for twenty times. The maximum change in the performance (sorption capacity) of the matrix after twenty repeated uses was <3%, indicating that its repeated use is feasible as leaching of the ligand from the matrix or its deterioration with use is insignificant. For preconcentration of metal ions from river or tap water samples also the same column may be used for at least 14-15 times. The sorption capacity of the chelating matrix stored for more than 10 months under ambient conditions has been found to be practically unchanged. The resin cartridge after loading with river water samples can readily be regenerated with 2 mol dm⁻³ HCl/HNO₃. However, the modified cellulose on treatment with HCl/HNO₃ of concentration >2.75 mol dm⁻³ showed signs of degradation.

Table 4
Tolerance limit of electrolytes and cations Ca(II) and Mg(II)

| Electrolytes/cations | Tolerance limits (mol dm ⁻³) with | | | | | | |
|---------------------------------|---|--------|---------|--------|--------|--------|--------|
| | Cu(II) | Zn(II) | Fe(III) | Co(II) | Ni(II) | Cd(II) | Pb(II) |
| NaNO ₃ | 0.50 | 0.50 | 0.50 | 0.0 | 0.0 | 0.06 | 0.04 |
| NaCl | 0.70 | 0.70 | 0.60 | 0.60 | 0.50 | 0.40 | 0.08 |
| NaBr | 0.60 | 0.50 | 0.40 | 0.40 | 0.40 | 0.40 | 0.04 |
| Na ₂ SO ₄ | 0.85 | 0.20 | 0.25 | 0.35 | 0.20 | 0.20 | 0.06 |
| Na ₃ PO ₄ | 0.005 | 0.005 | I | 0.002 | 0.002 | 0.002 | 0.001 |
| Ca(II) | 0.60 | 0.50 | 0.003 | 0.400 | 0.40 | 0.30 | 0.01 |
| Mg(II) | 0.08 | 0.04 | 0.002 | 0.001 | 0.002 | I | I |

I: interferes.

Table 5
Determination of metal ions in water samples

| Origin of sample | Method | Metal ion (μgdm^{-3}) | | | | | | | | | | | | | |
|---------------------------|--------|------------------------------------|---------------|--------|---------------|---------|---------------|--------|---------------|--------|---------------|--------|---------------|--------|---------------|
| | | Cu(II) | R.S.D. (%) | Zn(II) | R.S.D. (%) | Fe(III) | R.S.D. (%) | Ni(II) | R.S.D. (%) | Co(II) | R.S.D. (%) | Cd(II) | R.S.D. (%) | Pb(II) | R.S.D. (%) |
| Ganga river, Rishikesh | Direct | 22.75 | 1.5 | 3.75 | 2.6 | 53.75 | 6.2 | 8.26 | 3.0 | 7.12 | 4.8 | 5.61 | 4.6 | 6.75 | 4.7 |
| | SA | 20.56 | 1.2 | 3.22 | 1.8 | 20.56 | 2.76 | 7.99 | 2.7 | 6.34 | 4.1 | 6.78 | 3.3 | 6.23 | 3.6 |
| Shipra river, Ujjain | Direct | 31.25 | 2.1 | 2.75 | 2.4 | 31.25 | 5.3 | 6.23 | 3.9 | 6.99 | 4.6 | 9.22 | 4.5 | 9.25 | 5.4 |
| | SA | 33.32 | 1.6 | 2.46 | 2.3 | 27.87 | 5.4 | 5.86 | 3.7 | 7.23 | 3.9 | 10.12 | 3.8 | 9.76 | 3.9 |
| Tap water, New Delhi | Direct | 48.75 | 3.2 | 17.75 | 4.3 | 355.25 | 7.4 | 10.12 | 7.2 | 10.12 | 7.0 | 2.66 | 6.6 | 19.00 | 7.3 |
| | SA | 46.23 | 2.6 | 18.34 | 3.54 | 378.45 | 6.9 | 13.54 | 5.8 | 10.45 | 6.5 | 2.58 | 5.4 | 17.22 | 4.9 |

Direct: recommended procedure directly applied; SA: standard addition method; R.S.D. for five determinations.

4. Applications of the method

4.1. Determination of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) in river and tap water samples

Cellulose loaded with 8-hydroxyquinoline was used to preconcentrate and determine Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II) ions in water samples collected from the Ganges river (Rishikesh, India), Shipra river (Ujjain, India) and New Delhi water supply taps (preserved by acidifying with 2% HNO₃). The estimation of all the seven metal ions was made with and without (referred as direct determination) standard addition (SA) by passing 1000 cm³ of water sample (spiked with 50-100 µg of each of the seven metal ions in case of the standard addition method) through the column packed with 0.5 g of matrix after adjusting the pH to an optimum value (Table 2) and determining the metal ions as described in the present recommended column procedure. The spiking of 1 dm³ tap water samples was made with 100 µg of each of the seven metal ions. The results are given in Table 5 and reflect the suitability of the resin for water analysis. The concentrations reported in Table 5 as estimated by a standard addition method are the values obtained by subtracting the amount of metal added for spiking from the total metal recovered. The closeness of results of the direct and SA methods indicates the reliability of the present results of metal analyses in water samples.

4.2. Determination of Co in pharmaceutical samples

Solid phase extraction with the oxine-anchored cellulose coupled with FAAS determination was applied to determine cobalt in pharmaceutical samples. Ten tablets (3.28 g) of Polybion (E. Merck, Mumbai, India) were digested in a beaker containing 20 cm³ of concentrated HNO₃ by slowly increasing the temperature of the mixture to 400 K. The mixture was further heated till a solid residue was obtained. It was allowed to cool and dissolved in 25 cm³ of concentrated HNO₃. The solution was gently evaporated on a steam bath until a residue was left again. It was mixed with 50 cm³ of distilled water and concentrated HNO₃ was added dropwise until a clear solution was obtained on gentle

heating. The pH of the solution was adjusted to 5.3 by adding acetate buffer, and the concentration of cobalt was estimated by the recommended column procedure using flame AAS. The average (four determinations) amount of cobalt was found to be 1.95 µg g⁻¹ of tablet with an R.S.D of 2.82%. The reported value of cobalt in the tablet is 1.99 µg g⁻¹.

4.3. Validity and accuracy

To check the validity and accuracy of the present matrix coupled with FAAS for metal ion monitoring the recommended procedure was applied to determine the copper, zinc and iron content in synthetic water samples (1000 cm³) having a composition similar to certified river water samples SLRS-4 (National Research Council, Ottawa, Ont., Canada). The average of three determinations of copper, zinc and iron was found to be 1.76, 0.90 and 105.2 µg dm⁻³ with R.S.D. values 1.4, 1.8 and 2.3%, respectively. Certified values for trace metal ion concentration (µg dm⁻³) are: Al, 54 ± 4; As, 0.68 ± 0.06; Ba, 12.2 ± 0.6; Be, 0.007 ± 0.002; Cd, 0.012 ± 0.002; Cr, 0.33 ± 0.02; Co, 0.033 ± 0.006; Cu, 1.81 ± 0.08; Fe, 103 ± 5; Pb, 0.086 ± 0.007; Mn, 3.37 ± 0.18; Mo, 0.21 ± 0.02; Ni, 0.67 ± 0.08; Sb, 0.68 ± 0.04; Sr, 26.3 ± 3.2; U, 0.050 ± 0.003; V, 0.32 ± 0.03 and Zn, 0.93 ± 0.10, whereas for other metals the values (mg dm⁻³) are: Ca, 6.2 ± 0.2; K, 0.68 ± 0.02; Mg, 1.6 ± 0.1 and Na, 2.4 ± 0.2.

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