CELLULOSE BASED MACROMOLECULAR CHELATORS: DESIGNING AND APPLICATIONS AS METAL EXTRACTANTS

By

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CERTIFICATE

This is to certify that the thesis entitled, **"CELLULOSE BASED MACROMOLECULAR CHELATORS: DESIGNING AND APPLICATIONS AS METAL EXTRACTANTS "** being submitted by **Ms. Vibha Gurnani** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in **Chemistry** is a record of bonafide research work carried out by her. Ms. Vibha Gurnani has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma

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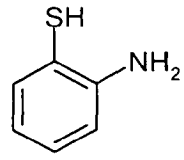
ABSTRACT

8-Hydroxyquinoline (oxine), pyrocatechol, pyrogallol and 2,3-dihydroxypyridine (DHP) have been immobilized through $-NHCH_2CH_2NH-SO_2-C_6H_4-N=N-$ linker on cellulose. DHP has also been immobilized on cellulose via a shorter linker $-O-SO_2-C_6H_4-N=N-$. The matrices were characterized by FT-IR (using model compounds) and ^{13}C CPMAS spectroscopy, TGA and elemental analyses. The IR spectra show a characteristic band for azo group apart from the bands of the ligands immobilized. Similarity between some bands of IR spectra of functionalized cellulose matrices and the corresponding model compounds has authenticated the immobilization of ligands on cellulose. TGA curves indicate the presence of 1.0-3.5 water molecules per repeat unit of the polymer. All the five matrices have been used for enrichment of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Cd(II) and Pb(II).

The optimum pH for quantitative sorption of these metal ions (except Fe) on oxine loaded cellulose is between 4.2 and 7.0. Fe was quantitatively sorbed (recovery 98 %) at a considerable low pH (2-3). The sorption capacity for the seven cations varies from 93.8 to 629.9 $\mu mol\ g^{-1}$. HCl or HNO_3 (1 M) may be used to desorb all the cations. The optimum flow rate for sorption and desorption has been found to be 2-4 $ml\ min^{-1}$. The tolerance limits of NaCl, NaBr, $NaNO_3$, Na_3PO_4, Na_2SO_4, humic acid, EDTA, citric acid, ascorbic acid, sodium tartarate, Ca(II) and Mg(II) in the sorption of all these metal ions (0.25-0.50 $\mu g\ ml^{-1}$) are reported. There is no interference of NaBr, NaCl and $NaNO_3$ up to a concentration of 0.4 M in the sorption of Cu, Zn and Fe. The preconcentration factor is between 90 and 300 and $t_{1/2}$ values are < 5 min except for Ni and Pb.

The sorption on cellulose anchored with pyrocatechol is quantitative for all metal ions except Fe and Cd at around pH ~ 5.0. Desorption was found quantitative

bound at all. Dithiocarboxyaminoethylcarbamoyl cellulose[104] synthesised from aminoethylcarbamoyl cellulose has been applied for preconcentration of Cu(II). The presence of 1M $NaNO_3$ or 1M $Ca(NO_3)_2$ does not interfere with the sorption of Cu(II).



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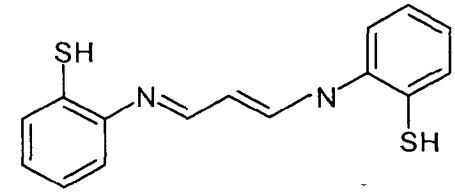

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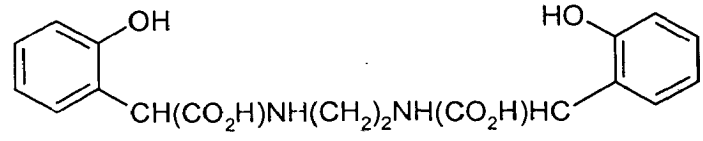
Röeber at al[105] synthesized novel cellulose based chelators by immobilizing 2,2'-ethylenediamine-N,N'-bis[*o*-hydroxybenzeneacetic] (**32**) or 1-(2-thenoyl)-3,3,3-trifluoroacetone (**33**) on cellulose via $-O-CH_2CH_2-SO_2-C_6H_4(OH)-N=N-$. The sorbents had exchange capacity 0.2-0.55 mmol g^{-1}. Cellulose (acrylic acid-cellulose graft copolymer) immobilized with 5-amino-1,10-phenanthroline[106] (**34**) showed strong sorption capacity with respect to Co, Cu and some biologically active molecules. Dialdehyde cellulose thiosemicarbazone, dialdehyde cellulose isonicotinic acid hydrazone, dialdehyde cellulose dioxime and chitosan showed sorption capacity 0.60-3.12 mmol g^{-1} polymer for Cu(II), Hg(II) and Ag(I) which was much higher than that of conventional chelating polymers.[107]



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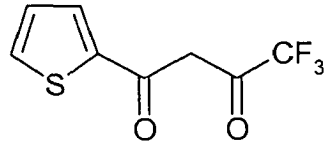

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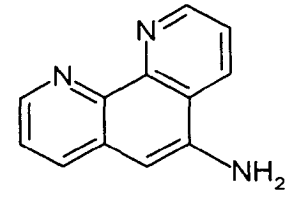

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Properties of hydroxamized cellulose sorbent in comparison to carboxycellulose were studied by Kotsuji et al.[108] with particular emphasis on its application to the extraction of Fe(III). The optimum pH for extraction of Fe(III) on the sorbent was 3.0. The interference of NaCl, $CaCl_2$ and $NiCl_2$ was negligible. The separation of Fe(III) from sea water was quantitative (95 %) and selective. Cellulose functionalized with *p*-benzylazo-2-naphthol[109] group has been used for the separation of Be(II) from Ca(II) and Mg(II). Under optimum conditions, Be was more than 95 % separated from Ca(II) and Mg(II).

Hydrazinodeoxycellulose[110] synthesised by the reaction of chlorodeoxycellulose with hydrazine hydrate was found selective for sorption of mercury and copper with an exchange capacity of 1.60 and 0.42 mmol g^{-1}, respectively for the two. Similarly, cellulose derivatives prepared by the reaction of chlorodeoxycellulose with ethylenediamine, thiourea, thiosemicarbazide and thioacetamide removed mercuric ions to an extent greater than 99 % from a 10 ppm aqueous solution of mercuric chloride.[42]

Nakamura et al.[50] investigated the sorption behaviour of aminoalkyl celluloses (AmACs) prepared from chlorodeoxycellulose and aliphatic diamines $H_2N(CH_2)mNH_2$ (m = 2, 4, 6, 8). Metal ions are sorbed rapidly on AmACs from weakly acidic solutions. The ability of AmACs to sorb metal ions decreases as m increases in diamine moieties, with AmAc from ethylenediamine (m = 2) being the most effective. The sorption of metal ions occurs in the order of $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$, with Cu^{2+} ions being selectively sorbed from solutions containing two different ions. Navarro et al.[37] synthesized a sorbent for heavy metals by introducing polyethyleneimine (PEI) onto porous cellulose carriers via $-O-CH_2-CH(OH)-CH_2-$

linker. Elemental analysis of the adsorbent revealed extensive crosslinking of PEI with the modified matrix. The sorbent had a capacity and a Hg-ligand stability constant of approximately 288.0 mg g^{-1} and 12.9 l mg^{-1}, respectively. Diffusion coefficient of Hg (calculated from adsorption rate experiments) in the carrier was found to be approximately equal to 7.3 x 10^{-14} m^2s^{-1}.

Imai et al.[39] synthesized four dithiocarbamatecelluloses by treating tosylcellulose separately with aniline, benzylamine, n-butylamine and piperazine followed by further reaction with carbon disulfide. Piperazine dithiocarbamate cellulose, which had the highest degree of substitution showed good sorption characteristics with relatively large capacities for Ag^+, Cr^{6+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Se^{4+} ranging from 6.9 to 370 mg g^{-1} of resin.

$HS\text{-}CH(COOH)\text{-}CH_2\text{-}COOH$ $HS\text{-}CH_2\text{-}CH_2\text{-}COOH$ $HS\text{-}CH_2\text{-}CH_2\text{-}NH_2$

$HS\text{-}CH_2\text{-}CH(OH)\text{-}CH_2OH$ $HS\text{-}CH_2\text{-}CH(COOH)\text{-}NH_2$

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Aoki et al.[111] synthesized 6-deoxy-6-mercaptocellulose and its S-substituted derivatives by reacting 6-bromo-6-deoxycellulose with thiourea and thiols (**35**). Thiols used in the study were 2-mercaptobutanedioic, cysteine, α-thioglycerol, 3-mercaptopropionic acid and 2-aminoethanethiol. The prepared derivatives were evaluated for the sorption of Ag(I), Hg(II), Fe(III), Cu(II), Pb(II), Cd(II), Co(II) and Ni(II). Ag(I) was sorbed most strongly by all these cellulose derivatives compared to other metal ions with the sorption capacity ranging between 1.78 and 3.25 meq g^{-1}.

Cellulose sorbents with anion exchange groups have been found to be useful for the preconcentration of anionic metal complexes. Cellex T(triethylamino cellulose) offers an attractive efficiency for enrichment of Au(III) as anionic

chlorocomplexes.[112] Pyrzynska[113] has preconcentrated and separated inorganic selenium (Se(IV) and Se(VI)) on Cellex T and Cellex QAE (diethylhydroxypropylamine cellulose). The sorption of Se(IV) was almost complete over a wide pH range and it can be preconcentrated effectively at the natural pH of environmental water i.e. without any pH adjustment. Se(IV) and Se(VI) sorbed on the resin were eluted with 10 ml of 0.01 mol l^{-1} and 7 ml of 4 mol l^{-1} HNO_3, respectively and determined by electrothermal atomization atomic absorption spectrometry. The detection limit for Se(IV) is 2.1 g l^{-1} and for Se(VI) 2.4 μg l^{-1}. Cellex CM[114] (with carboxymethyl groups) has been used successfully for the preconcentration and determination of nickel in natural water samples. The breakthrough capacities for nickel are 16.2 mg g^{-1} for the hydrogen form and 17.8 mg g^{-1} for the sodium form of Cellex CM.

Phosphate cellulose sorbents such as Cellex P with $O\text{-}PO(OH)_2$ functional groups act as weak acid exchangers and exhibit satisfactory sorption kinetics. Brajter et al.[115] separated the following mixtures by means of Cellex P using glycine as a complexing agent: Cu(II)-Ni(II)-Pb(II), Cu(II)-Co(II)-Pb(II) and Cu(II)-Ni(II)-Cr(III). The method has been applied to the determination of Pb, Mn and Fe in copper alloys. Bi^{3+} has been separated from large excesses of Pb, Cd, Cu, Co, Ni, Fe, Mn and Zn by means of Cellex P using tetrene as a complexing agent.[116] The method has been applied to the determination of Bi in metallic lead. Cellex P has also been used for the preconcentration of Cu(II), Ni(II), Mn(II), Cd(II), Zn(II) and Pb(II) from water in the pH range 5-8.[117]

2.1.1 On-Line Preconcentration

A highly effective enrichment of trace analyte with a simplified analytical procedure can be achieved in a flow-injection (FI) sample processing systems, where

preconcentration is performed on-line prior to the detection. There has been a growing interest in the use of FI technique in atomic spectrometry. An increase in the enrichment ratio is favoured by the miniaturization of the whole set up for transport of solutions, including a substantial decrease of bed volume, which allows the use of much smaller eluent volumes.

Among the sorbents applied for preconcentration of metal ions in FI systems, cellulose sorbents are very suitable for such application owing to reasonably fast sorption and desorption properties. Several on-line preconcentration and matrix/analyte separation systems utilizing cellulose sorbents have been developed for GFAAS,[65,118] FAAS,[112,119, 120] ICP-AES[64] and ICP-mass spectrometric detection.[121] Nagmush et al.[120] obtained the best dynamic characteristics of retention for lead with cellulose sorbents functionalized with phosphonic acid and carboxymethyl groups, indicating a fast elution process of retained lead. The detection limit for the determination of lead was estimated as 0.17 $\mu g\ l^{-1}$ for preconcentration from a 50 ml sample at a flow rate of 7 ml min^{-1}. In another study, Pyrzyñska et al.[122] obtained similar results for preconcentration of Cd. The detection limit was 0.7 $\mu g\ l^{-1}$ and precision (at 10 $\mu g\ l^{-1}$) was 5.6 % with an enrichment factor of 260. Recently, Lásztity et al.[123] have reported the preconcentration of platinum after reduction by iodide or sulphite ion using oxime, sulphoxine and DEN cellulose loaded microcolumns by means of FI-GFAAS method. The detection limits were 0.21, 0.18 and 0.30 $g\ l^{-1}$, respectively at 20 fold enrichment. The method was applied for the determination of platinum in salmeterol xinafoate and Ca-folinate pharmaceutical compounds.[123]

2.1.2 Chemical Speciation

Chemical speciation may be defined as the analytical procedure developed for the identification and quantitative determination of various species of a given element in a particular material. Numerous analytical speciation procedures have been developed with cellulose based sorbents and AAS detection.[113,119,120,124] The best separation of inorganic selenium species, Se(IV) and Se(VI) was obtained with cellulose sorbent Cellex T[113] in comparison to other anion exchange resins. The effective elution of Se(IV) was achieved using 0.01 M nitric acid, while Se(VI) remains completely in the column. For the elution of selenite retained on the polystyrene matrix anion exchange resins, a more concentrated (0.5 M) solution of nitric acid had to be used. Moreover, under these conditions small amounts of selenate was coeluted together with Se(IV). These results indicate that from the point of view of column separation, the lower affinity of cellulose sorbents than styrene resins, should be regarded as an advantage. Cr(III) (0.1-0.4 μg l^{-1}) and Cr(VI) (0.04-0.1 μg l^{-1})have been separated using IDAEC and diethylamine ethyl cellulose.[124]

2.2 Chelating Matrices Based on Amberlite Series Resins

The commercially available copolymers of Amberlite XAD series are very small gellular microspheres fused into large macrospherical particles with maintained porosity. The remaining network space between the agglomerated microspheres in the particles is continuously porous. Consequently, these copolymers have regions of microporous gel matrix interspersed with macropores. The styrene-divinylbenzene copolymers of the XAD series have been suitably functionalized with chelating ligands and their analytical applications have been explored.[125,126] The review of 1999

with 0.5 M HCl / HNO_3 (for Pb). The elution breakthrough volume has been found between 8 and 20 ml of 0.5 M HCl or HNO_3. The sorption capacity of the matrix for the seven metal ions has been found in the range 85.3-186.2 μmol g^{-1}. The tolerance limits for NaCl, NaBr, NaI, $NaNO_3$, Na_2SO_4, Na_3PO_4, humic acid, EDTA, ascorbic acid, citric acid, sodium tartrate, Ca(II) and Mg(II) in the sorption of all the seven metal ions are determined. Ascorbic acid is tolerable upto 0.8 mmol l^{-1} with Cu and Pb where as sodium tartrate does not interfere up to 0.6 mmol l^{-1} with Pb. The preconcentration factors are between 75 and 300 and $t_{1/2}$ values ≤ 5 min for all the metal ions.

On pyrogallol functionalized cellulose sorption is quantitative (98.0-99.6 %) at pH 5.0-7.0 when flow rate is maintained between 2 and 4 ml min^{-1}. The 0.5 M HCl/HNO_3 instantly elutes all the metal ions (0.25-0.50 μg ml^{-1}). The breakthrough volume for elution is between 8 and 15 ml of 0.5 M HCl/HNO_3. The sorption capacity of the matrix for these cations varies from 92.4 - 202.2 μmol g^{-1}. The preconcentration factor is between 133 and 300. The lowest concentration for quantitative recovery (98.3-99.9 %) varies from 3.3-7.5 ng ml^{-1}. The feasibility of the sorption process was judged from both kinetic and thermodynamic points of view. The negative values of ΔG suggest the sorption process is spontaneous and favaourable thermodynamically. The limits upto which NaCl, NaBr, NaI, $NaNO_3$, Na_2SO_4, Na_3PO_4, Ca(II), Mg(II), humic acid, EDTA, citric acid, ascorbic acid and sodium tartarate can coexist with the seven metal ions during their sorption without adverse effect are reported. The kinetic studies have shown that the loading $t_{1/2}$ of metal ions is less than 2 min except for Ni and Co.

The cellulose having DHP anchored by shorter linker (**1**) shows better sorption capacities (between 69.7 - 431.1 μmol g^{-1}) for the metal ions than those of other

having longer linker (**2**) (51.9-378.1 μmol g^{-1}). The optimum pH ranges for quantitative sorption (recovery ~ 97 –99 %) on both **1** and **2** are between 4.0 and 8.0. The desorption was found quantitative with 0.5 M HCl and 0.5 M HNO_3 (for Pb) from both **1** and **2**. The optimum flow rate of metal ion solutions for quantitative sorption of metal onto a column packed with DHP modified cellulose **1** or **2** is 2-7 ml min^{-1}, whereas for desorption the optimum flow rate for acid solution is 2-4 ml min^{-1}. The $t_{1/2}$ for **1** < 5 min for all the metal ions except Ni and Pb, whereas for **2** it was less than 5 min for Cd apart from Ni and Pb. The tolerance limits for NaCl, NaBr, NaI, $NaNO_3$, Na_2SO_4, Na_3PO_4, humic acid, EDTA, citric acid, sodium tartarate, Ca(II) and Mg(II) in the sorption of all metal ions on both **1** and **2** are reported. The enrichment factor has been found to be between 100 and 300 on both **1** and **2**. The five cellulose based chelating matrices have been applied to enrich metal ion in water (river, tap, synthetic), milk and vitamin samples.

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