Extraction of Metal Ions Using Chemically Modified Silica Gel Covalently Bonded with 4,4'-Diaminodiphenylether and 4,4'-Diaminodiphenylsulfone-salicylaldehyde Schiff Bases

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Two new chelating materials (Si-DDE-*o*-HB, and Si-DDS-*o*-HB) were synthesized by modifying the activated silica gel phase with Schiff bases of 4,4'-diaminodiphenylether (DDE)/4,4'-diaminodiphenylsulfone (DDS) and *o*-hydroxybenzaldehyde (*o*-HB). The synthesized materials were characterized by FTIR and BET surface area measurement techniques. The extraction of metal ions such as Zn²⁺, Mn²⁺ and Cr³⁺ by the chelating material Si-DDE-*o*-HB was found to be higher than that by Si-DDS-*o*-HB. The order of metal sorption was found to be Zn²⁺ > Mn²⁺ > Cr³⁺. The correlation coefficients for Freundlich and Langmuir adsorption isotherms were compared for the sorption of Zn²⁺ onto the chelating material. The loading and elution of the metal ion solution was examined at optimum pH 7.5 and 0.5 cm³ min⁻¹ flow rate of the solution using a column technique. The preconcentration factor for the elution of Zn²⁺ using dilute HNO₃ was found to be 66.2 with a breakthrough volume of 15 cm³. The data obtained for the preconcentration of Zn²⁺ by the column technique suggested that the material Si-DDE-*o*-HB can find industrial applications.

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Introduction

Silica gel is an amorphous inorganic polymer containing an internal siloxane group (Si-O-Si) with silanol groups (Si-OH) distributed on the surface.^{1,2} It is commonly used as a rigid matrix for ligand immobilization.³ The chemical modification of silica gel surfaces with donor atoms such as N, S, O and P is primarily aimed at improving the adsorption and exchange properties of the silica gel along with incorporation of the particular selective characteristics into the modified silica gel phases towards certain metal ions.⁴ The immobilization of chelating materials containing donor atoms on the silica gel surface can occur *via* chemical bond formation between organic modifiers like amino or chloro modified silica gel phases or through simple physical adsorption processes.⁵ Such a process often incorporates selectivity in synthesized materials.^{6,7} Several new chemically modified silica gels were synthesized, and applied as normal or selective solid phase extractor for many toxic and other metal ions. They were found to be superior to the conventional ion exchange resins in their ability to extract and selectively preconcentrate the heavy metal ions from solutions containing high concentrations of alkali and alkaline earth metal ions.⁸⁻¹⁰ Advantages of the modified solid phase extractors compared with the classical liquid extractor's were reported in many references.^{11,12}

Schiff bases, having multidentate coordination sites, are known to form complexes with transition metal ions readily.^{13,14} The Schiff bases derived from salicylaldehyde (Salens) as

polydentate ligands are known to form stable complexes with transition metal ions.^{15,16}

The present work describes the syntheses of two new chemically modified silica gel covalently bonded with 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulfone-salicylaldehyde Schiff bases. The synthesized chelating materials were used for the preconcentration and separation of Cr³⁺, Zn²⁺, and Mn²⁺ from dilute aqueous solutions. They were compared to determine their metal binding, extraction and selective abilities using batch techniques. The more reactive chelating material, Si-DDE-*o*-HB, was utilized in a column technique for the preconcentration of Zn²⁺ and Cr³⁺. Elution of the sorbed cations in column experimental studies provided an example of using the chelating material in continuous cycle operation and recovery of the metal ions. The analytical precision and accuracy of the result were tested with satisfactory results, and the method was found to be rapid, precise, simple and convenient to use.

Experimental

Apparatus

The specific surface areas of the dry silica and loaded silica were determined by BET method on NOVA 1000, high speed gas sorption analyzer, Quantachrome Corporation, USA. A Shimadzu atomic absorption spectrophotometer (Model AA-680) equipped with a single element hollow cathode lamp and an air-acetylene burner was used for the estimation of metal ions. The instrument parameters were those recommended by the manufacturer. The wave lengths (nm) selected for the analytes were as follows: Mn (279.5 nm), Cr (357.9 nm), and

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Scheme 1 Reaction scheme.

Zn (213.9 nm). The FTIR spectra were recorded in a Perkin Elmer 1800 Model. The pH values of sample solutions were determined by a Systronic digital pH meter Model 335 equipped with a combined glass calomel electrode for pH adjustment.

Reagents

The starting materials such as 3-chloropropyltrimethoxysilane, *o*-hydroxybenzaldehyde (*o*-HB), 4,4'-diaminodiphenylether (DDE), 4,4'-diaminodiphenylsulfone (DDS) were from Merck; they were used without further purification. All other chemicals and solvents (AnalR/GR grade, Merck or BDH, India) were used as received. Silica gel (70–230 mesh) was purchased from SRL, India.

Double distilled deionized water (DDW) was used for the preparation of solutions, wherever required. Standard solutions of AAS grade Cr, Zn and Mn (CDH, India) were used for the preparation of calibration curves in the atomic absorption spectrophotometer. The estimation of metal ions was done according to the reported standard procedure.¹⁷ The buffers used to control the pH of the solution were HCl/KCl, Na₃PO₄/H₃PO₄, and Na₃PO₄/NaOH. Solutions of Cr³⁺, Mn²⁺ and Zn²⁺ were prepared from suitable reagent grade nitrate or chloride salts by dissolving in DDW.

Chemical modification of silica gel

Silica gel (70–230 mesh) was used as the supporting material. Silica gel was refluxed with 6 N HCl for 4 h to remove iron, if present, and was made acid-free by washing several times with DDW and checking the pH of the washing. The conditioned silica, after drying, was sieved by mechanical sieves and the fraction of the mesh size 100–120 was collected. The activated silica, thus obtained, was filtered, washed with ethanol and dried at 90–110°C for 24 h. Approximately 50 g of activated dry silica was immersed in a mixture consisting of 100 cm³ of anhydrous xylene and 10 cm³ of 3-chloropropyltrimethoxysilane to produce 3-chloropropylsilica gel (Si-Cl). The mixture was refluxed under continuous stirring, with careful protection against moisture. Unreacted silanes were extracted with xylene and hexane in a Soxhlet apparatus. After this operation, the silica is subjected to drying under vacuum and then to an end-capping reaction with hexamethyldisilazane in order to deactivate the free silanol groups remaining on the silica surface.¹⁸

Fig. 1 FTIR spectra of silica gel (1), organochloro functionalized silica gel (2), and Si-DDE-*o*-HB (3).

Synthesis of chelating materials Si-DDS-*o*-HB and Si-DDE-*o*-HB

The synthesis procedure is given in Scheme 1. Fifty grams of the above 3-chloropropylsilica gel (Si-Cl) were immersed in 200 cm³ of methanol and reacted with 2.64 g (10 mmol) of 4,4'-diaminodiphenylsulfone (DDS) under reflux condition, in the presence of 0.05 g of CaCO₃ for nearly 5 h. The product (Si-DDS) so formed was filtered, washed thoroughly with methanol and dried *in vacuo* at 60–70°C. In the subsequent step, 40 g of the product Si-DDS was made to react with *o*-hydroxybenzaldehyde (*o*-HB) (5 cm³, 0.6 mmol) to yield the respective Schiff base, which was the desired chelating material Si-DDS-*o*-HB. The color of the chelating material was yellowish brown. The material was filtered off, washed with methanol, and dried *in vacuo* at 60–70°C. Following a similar procedure, the other chelating material Si-DDE-*o*-HB was synthesized. The color of the chelating material was found to be reddish brown.

Analytical studies

The metal ion uptake studies were carried out by both batch and column techniques. The adsorption capacity (Q , mmol g⁻¹), the distribution ratio (D , cm³ g⁻¹), and the selectivity factor (α) were calculated according to the following equations:

$$Q = (C_0 - C_e)V/m$$

$$D = Q/C_e$$

$$\alpha = D_1/D_2$$

Here, C_0 and C_e are the initial concentration and final concentration of metal ions (mmol dm⁻³) at equilibrium,

Scheme 2 Electron shifting in DDS unit.

respectively. V is the volume of the solution in dm^3 , and m is the mass of the chelating materials, D_1 and D_2 refer to the distribution ratios of metal ion 1 and metal ion 2, respectively.

Results and Discussion

Characterization by FTIR

Analysis of the FTIR spectra (Fig. 1) of the activated silica gel and the organofunctionalized silica gel shows the presence of Si-O-Si at around 1050 cm^{-1} and a band at $3200\text{--}3400\text{ cm}^{-1}$ corresponding to the silanol group and adsorbed water molecules. Peaks around 1440 , 1410 , and 1356 cm^{-1} are assigned to deformation modes of the $-\text{CH}_2$ -group generated from an organofunctionalized compound. The peak that appeared at about 1560 cm^{-1} was assigned to deformation mode $\delta(\text{NH})$ of $-\text{NH}$ -moiety from organofunctionalized silica gel material. The peak that appeared at 1660 cm^{-1} was assigned to the $\delta(\text{OH})$ of the matrix. The peak that appeared at around 900 and 675 cm^{-1} characterize the presence of the aromatic group in the unit (Si-DDS and Si-DDE). The presence of N-H stretch (H bonded) at 3372 and 3290 cm^{-1} and the C-N stretch at around 1071 cm^{-1} characterizes the presence of amine groups in the chelating material. The peak appeared at 1620 cm^{-1} assigned to C=N in Si-DDE-*o*-HB. These spectral changes confirmed that the organic group is bound to the silica surface.

Surface coverage value in silica gel

The surface area coverage value was obtained by BET surface area measurement technique. The specific surface areas for the activated dry silica (sample density 0.9447 g cm^{-3}), and for the loaded silica surface (Si-DDE-*o*-HB, sample density 0.9725 g cm^{-3}), were examined to obtain the surface area coverage value. The specific surface areas were found to be 486.798 and $41.814\text{ m}^2\text{ g}^{-1}$ for dry silica and loaded silica surface, respectively. Such a large decrease in surface area may be attributed to the blocking of pores by the ligands present at the surface, as a result of which nitrogen can not enter into the pore, resulting in a considerable decrease in the surface area. Embedded ligands also contribute to the decrease of the surface area of the substance.¹⁸

Analytical studies

The effect of contact time upon the sorption of the metal ions from aqueous solution was investigated in batch experiments. The amount of the metal ions sorbed per unit mass of the chelating materials was increased with the increase in contact time period (Fig. 2). The saturation (plateau value) in each curve was obtained within a period of 30 min for Zn^{2+} and Mn^{2+} . However, the sorption of Cr^{3+} required nearly 3 h. For both the chelating materials, the order of sorption of the metal ions was found to be $\text{Zn}^{2+} > \text{Mn}^{2+} > \text{Cr}^{3+}$. Comparing the sorption capacity of the chelating materials, Si-DDS-*o*-HB and Si-DDE-

Fig. 2 Effect of contact time variation. For Si-DDE-*o*-HB: series 1, Zn^{2+} ; 2, Mn^{2+} ; 3, Cr^{3+} . For Si-DDS-*o*-HB, series 4, Zn^{2+} ; 5, Mn^{2+} ; 6, Cr^{3+} . Amount of chelating materials, 500 mg; concentration of the solution, 100 mg dm^{-3} ; pH, neutral; total volume of the solution, 20 cm^3 ; temperature, $28 \pm 2^\circ\text{C}$.

Fig. 3 Effect of pH of the medium. For Si-DDE-*o*-HB: series 1, Zn^{2+} ; 2, Mn^{2+} ; 3, Cr^{3+} . For Si-DDS-*o*-HB: series 4, Zn^{2+} ; 5, Mn^{2+} ; 6, Cr^{3+} . Amount of materials, 500 mg; concentration of the solution, 100 mg dm^{-3} ; total volume of the solution, 20 cm^3 ; time of contact, 24 h.

o-HB, the chelating material containing the DDE moiety, showed higher preference towards the metal loading capacity. This could be explained on the basis of the fact that, in the presence of a negative resonance effect of $-\text{SO}_2$ -group in the chelating material containing a DDS moiety, the electrons tend to shift in the manner shown in the Scheme 2. This, in turn, decreases the electron density upon the phenolic oxygen atom and consequently the metal coordination capability. However, the metal chelating nature of the chelating materials also depends on the nature of the ligand groups present and their accessibility towards the metal ions. The steric hindrance of the matrix as well as hydrophobic nature of the ligands may also limit the metal complexation process.

Changes in pH of the medium are one of the most important parameters affecting the preconcentration procedure, which is related to the formation of soluble metal complexes and subsequently their stabilities in aqueous solution.¹⁹ A series of metal ions, Cr^{3+} , Mn^{2+} , and Zn^{2+} , were examined in various buffer solutions of pH 1.0 to 8.0 (Fig. 3). In acidic pH (within pH 1–4), the chelating materials showed low metal ion uptake properties due to the protonation of chelating sites in the ligands that inhibit their binding to metal ions.²⁰ With increase in pH of the medium, the metal sorption of the chelating materials increased due to the increase in coordination ability for the formation of phenoxide ion upon phenolic OH-group and due to the increase in basicity of the imine nitrogen atom. The order of metal ion sorption by both the chelating materials was found to be $\text{Zn}^{2+} > \text{Mn}^{2+} > \text{Cr}^{3+}$, indicating that the highest affinity is towards Zn^{2+} extraction, and the lowest is exhibited for Cr^{3+} .

Fig. 4 Verification of Langmuir adsorption isotherm. For chelating material Si-DDE-*o*-HB; metal ion, Zn²⁺; time of contact, 24 h; temperature, 28 ± 2°C.

Fig. 5 Verification of Freundlich adsorption isotherm. For chelating material Si-DDE-*o*-HB; metal ion, Zn²⁺; time of contact, 24 h; temperature, 28 ± 2°C.

We did not attempt to go beyond pH 8.0 due to the observation of precipitation in the medium.

Sorption kinetics

The effect of metal ion concentration on the uptake behavior of the chelating materials was studied in the concentration range 10 to 100 µg cm⁻³. A leveling effect was noticed at higher concentrations because of saturation of available coordination sites.²¹ The sorption isotherms were evaluated for Langmuir equation and Freundlich adsorption equations.^{22,23} The equation is $C_e/Q_e = 1/Q_0 \cdot b + C_e/Q_0$, where C_e is the equilibrium concentration (µg cm⁻³), Q_e is the amount adsorbed at equilibrium, and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/Q_e versus C_e shows that the adsorption obeys the Langmuir adsorption model (Fig. 4). The correlation coefficient for the linear regression fitting the Langmuir plot was found to be 0.9657. Q_0 and b determined from the Langmuir plot were found to be 270.27 µg g⁻¹ of the chelating material and 0.01 µg⁻¹. The equilibrium parameter R_L is defined by $R_L = 1/(1 + bC_0)$, where b is a Langmuir constant, and C_0 is the initial concentration of Zn²⁺. At two different initial concentration of Zn²⁺, i.e., 10 and 100 mg dm⁻³, the R_L values were found to be 0.5 and 0.09, respectively. The values obtained at two different concentrations lie between 0 and 1, which indicated a favorable adsorption of Zn²⁺ onto the chelating material surface (Si-DDE-*o*-HB). Plotting the Freundlich equation: $\log(x/m) = \log k_{ad} + 1/n \log C_e$, where C_e is the equilibrium concentration of the metal ions in µg cm⁻³, m is the weight of the chelating materials, x is the quantity of metal ion sorbed by the chelating material in µg and n is the constant.

Table 1 Determination of separation factor at different pH values of the medium

Chelating material	pH	α , Zn/Mn	α , Zn/Cr
Si-DDE- <i>o</i> -HB	6	6.18	15.19
	7	7.03	30.31
	8	18.92	75.78

Amount of chelating material, 0.5 g; time of contact, 24 h.

Table 2 Effect of diverse foreign ions

Chelating material	Metal ion	Conc. of metal ion/ mg dm ⁻³	Rec., ^a %	Rec. in the presence of mixture of diverse ion ^b / 20 mg dm ⁻³ each
Si-DDE- <i>o</i> -HB	Zn ²⁺	20	98.4	96.2
	Mn ²⁺	20	98.9	95.1
	Cr ³⁺	20	98.3	95.9
Si-DDS- <i>o</i> -HB	Zn ²⁺	20	98.5	94.1
	Mn ²⁺	20	98.4	95.2
	Cr ³⁺	20	97.3	94.7

Amount of chelating material, 0.5 g; time of contact, 24 h; each reading was an average of three close/concordant values.

a. RSD factor varies between 0.35 – 0.52%.

b. RSD factor varies between 0.32 – 1.16%.

A plot of $\log(x/m)$ versus $\log C_e$ (Fig. 5) is linear and the constants k_{ad} and n are found to be 3.446 and 1.227, respectively. The value, $1 < n < 10$, indicates the favorable sorption of Zn²⁺ onto the chelating material. The correlation coefficient for the isotherm found to be 0.9831, indicating a better fit for the experimental data than the Langmuir plot.

Competitive sorption behavior

Selective extraction or separation of a given metal ion in the presence of other metal ions is controlled mainly by the following factors: (i) the nature of the donating sites in the ligand that are capable of selective bonding to the central metal ion; (ii) the nature of the metal ion to be selectively extracted; and (iii) the hydrogen ion concentration. The chelating material (Si-DDE-*o*-HB) was utilized to study the competitive sorption of Zn²⁺/Mn²⁺, Zn²⁺/Cr³⁺ from dilute aqueous solution at different pH values of the medium. The higher affinity towards Zn²⁺ ions in a competitive environment could be due to the preferentially binding with the positionally active (non-sterically hindered) oxygen atom present in the salicylaldehyde Schiff base ligand. The separation factor α (used as a measure of the chromatographic separation process) is presented by, $\alpha = D_1/D_2$, where D_1 and D_2 are the distribution coefficients of the two metal ions. The separation factors α for separation of Zn²⁺-containing binary mixtures at pH values of 6.0, 7.0 and 8.0 are shown in Table 1.

Effect of diverse foreign ions

The analytical preconcentration procedure for trace heavy metal ions can be strongly influenced due to matrix constituents: e.g., alkali and alkaline earth elements. Therefore, the effect of matrix constituents was examined in the presence of sulfate, nitrate, chloride, NH₄⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺, which are common ionic species in natural water. A high concentration of studied species was chosen to magnify their interference effect. The results (Table 2) indicated that the

Table 3 Effect of flow rate in column operation study

Chelating material	pH	Metal ion/ 20 mg dm ⁻³	Flow rate/ cm ³ min ⁻¹	Sorption, %
Si-DDE- <i>o</i> -HB	7.5	Zn ²⁺	0.5	80.4
			1.0	65.3
			1.5	50.2
			2.0	24.3
Si-DDS- <i>o</i> -HB	7.5	Zn ²⁺	0.5	54.0
			1.0	30.2
			1.5	10.1
			2.0	BQL ^a

a. BQL: below quantitative limit.

matrix ions had little effect on the uptake capacity of the metal ions. The effects of anions like citrate and oxalate were also examined in case of Si-DDE-*o*-HB to discover the effect of organic species upon the recovery of Zn²⁺ only (20 mg dm⁻³). It was found that the presence of citrate and oxalate reduces the metal recovery by 82% and 85%, respectively. The effects of some other organic species are currently under investigation.

Metal ion uptake sorption and desorption studies using column technique

The results of column operation studies are furnished in Table 3. Due to the higher rate of sorption of Zn²⁺ by the chelating material, as observed in batch operation study, Zn²⁺ was chosen for the column operation study. The studies were carried out at a pH value of 7.5. For Si-DDE-*o*-HB, it was observed that, at pH 7.5 and 0.5 cm³ min⁻¹, the flow rate of the solution, the column successfully retained nearly 80% of the Zn²⁺ ions. The flow rate was varied between 0.5 – 2.0 cm³ min⁻¹ and sorption of metal ions found to decrease substantially with increasing flow rate. At higher flow rates, the contact time of metal ions with the column materials was shorter. This may be attributed to the increase in sorption process with increasing residence time of the solute in the column. We did not go below the flow rate of 0.5 cm³ min⁻¹ due to the extended time consumption in analysis.

Desorption of metal ions from the packed column was also attempted with ≥ 1.0 mol dm⁻³ HNO₃ solution. The above Zn²⁺-loaded column was eluted with dilute HNO₃ (20 cm³, > 1.0 mol dm⁻³ concentration); the flow of the eluting agent was controlled (0.5 cm³ min⁻¹) using the stopcock. Nearly 75 – 80% of the loaded metal ions could be successfully eluted from the loaded columns in the first cycle. With second and third elution with HNO₃ solution, almost 100% removal of the loaded cation from the column was possible. Increasing the flow rate of the eluting agent, however, decreases the percentage of elution. The preconcentration factor was found to be 66.2, with breakthrough volume of 15 cm³. Still higher preconcentration factors may be achieved by decreasing the elution volume.

The stability and reusability of the chelating materials was also tested by the following method. The Zn²⁺ was sorbed and desorbed on 1.0 g of the chelating material for three times. After three cycles, the equilibration changes by 3 – 4% only. The sorption capacity of the chelating material which was stored for 2 months under ambient condition has been found to be practically unchanged.

Preconcentration of heavy metal ions from natural tap water sample

Drinking water samples (spiked separately with Zn²⁺, Mn²⁺, Cr³⁺ (0.5 – 1.0 mg dm⁻³), were prepared. Then 500 mg of

Table 4 Analysis of drinking water samples

Chelating material	Metal ion	Metal ion added/ mg dm ⁻³	Metal ion found/ mg dm ⁻³	Recovery, %
Si-DDE- <i>o</i> -HB	Zn ²⁺	0	0.54	—
		0.5	1.01	97.2
		1.0	1.48	96.2
	Mn ²⁺	0	0.34	—
		0.5	0.81	96.3
		1.0	1.30	97.0
	Cr ³⁺	0	0	—
		0.5	0.49	98.0
		1.0	0.98	98.0

chelating material Si-DDE-*o*-HB was added. These mixtures were stirred for 3 h, and then filtered; the unsorbed metal ions were determined by AAS (Table 4). The result showed that in all the cases the recoveries of metal ions was found to be $> 96\%$.

Conclusions

Two new chelating materials (Si-DDE-*o*-HB and Si-DDS-*o*-HB) were synthesized by modifying the activated silica gel phase. The materials were characterized and tested for the preconcentration of metal ions like Zn²⁺, Mn²⁺ and Cr³⁺ in batch and column techniques with variation in parameters in competitive and non-competitive conditions. The saturation values for the uptake of Zn²⁺ and Mn²⁺ by both the chelating materials were obtained in about 30 min, whereas the sorption of Cr³⁺ required nearly 3 h. The sorption capacity of Si-DDE-*o*-HB was found to be higher than that of the Si-DDS-*o*-HB, this could be explained on the basis of negative resonance effect in DDS unit. The order of metal sorption for both the chelating materials was found to be Zn²⁺ $>$ Mn²⁺ $>$ Cr³⁺. Sorption capacities of similar types of silica base immobilized metal chelate Schiff bases were also evaluated extensively by some other authors for metal ions like Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺.²⁴ The reactivity of metal ion sorption was discussed in the light of bulkiness, orientation of immobilized chelate, and participation of azomethene nitrogen and phenolic hydroxyl group oxygen atoms. In the present case, the preconcentration factor for the elution of Zn²⁺ using a column technique was found to be 66.2 with a breakthrough volume of 15 cm³. The column experiment suggested that the material Si-DDE-*o*-HB can find applications for the metal sorption from dilute aqueous solution.

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