



Synthesis of Sol-Gel Silicas functionalized with Schiff Base Ligands

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Abstract—Schiff bases containing azomethine linkage in their structure are good ligands and show great metal binding ability. In last few years sol-gel method is found very attractive for synthesis of gels due to its low cost, low operating temperature and ease of synthesis. This work presents the synthesis of Schiff base functionalized gels through sol-gel method and their use in extraction of metal ions from aqueous medium at room temperature and appropriate pH. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses of both blank and functionalized gels are presented. The analyses data show successful incorporation of the Schiff base in sol-gel matrix. Metal removal data show high efficiency of Schiff base functionalized gels.

Index Terms—Schiff base functionalized silicas, Sol-gel method, Extraction of metal ions.

I. INTRODUCTION

THE organic compounds consisting of azomethine linkage ($-\text{HC}=\text{N}-$) in their structure are called Schiff bases. Hugo Schiff the pioneer synthesized such compounds by the reaction of aromatic amine with aldehyde or ketone [1]. In a Schiff base nitrogen atom is connected to an aryl or alkyl group but not with hydrogen.

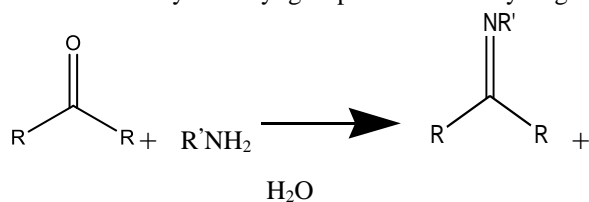


Fig. 1. Formation of Schiff base.

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It is a condensation reaction in which amine, acting as a nucleophile attacks at the electrophilic carbonyl carbon forming Schiff base in which (C=O) of carbonyl group is replaced by (C=N) of imine or Schiff base. A variety of compounds having amino group can be employed for the preparation of Schiff bases as shown in Fig.1 [2-3]. Product (Schiff base) both are very low [4]. pH of the reaction mixture is to be maintained due to high basicity of aliphatic amines. Imines formed from aromatic amines are called Anils. Just like aliphatic amines, aliphatic carbonyls are also not preferred for Schiff bases synthesis as aliphatic carbonyl compounds are less stable [5-7]. Usually aldehyde is the carbonyls of choice due to their better reactivity as compare to ketones. If carbon or nitrogen of (C=N) is attached with aromatic ring, it increases the stability of the Schiff base due to conjugation [8]. Preparation of Schiff base is a reversible reaction. Therefore, the reaction can be used for the protection of amines. It takes place under basic or acidic conditions or simply by refluxing the reactants in a suitable solvent. The equilibrium can be shifted towards forward direction by dehydration with a desiccant such as TiCl_4 [9] or by azeotropic distillation [10-11]. As Schiff bases form crystals they usually show sharp melting points. They are good as ligands and form complexes with metals. Transition metal complexes form a large group in Chemistry [12].

Mechanism of Schiff base formation shows that it is nucleophilic addition reaction due to which an unstable addition product known as carbinolamine is formed. Elimination of water from carbinolamine results in the formation of Schiff base. Its elimination takes place under mild acidic conditions. This step is rate determining step in the synthesis. Therefore the reaction is often done under mild acidic conditions. Harsh acidic conditions can protonate amine diminishing their nucleophilicity and resulting backward reaction. Hydrolysis of Schiff base can be done by water under acidic or basic conditions.

Schiff bases are versatile organic ligands [13-17]. Their biomedical [18] and catalytic [19-21], analytical and other applications are well documented in literature. Previously

Schiff bases have been utilized in estimation [22-23] and separation of metals [24] and estimation of oxo groups [25- 26]. They are well known for their biological activities [27]. Azomethine linkage in the structure of Schiff base is thought to be responsible for their bioactivities [28] against cancer [29], bacterial infections [30-31], AIDS [32-33], fungal infections [34-35], viral infections [36, 37], mosquito larvae [3], flamatory [39] and cancer. Entrapment of bioactive materials in a suitable matrix as support and their transport to the infected parts is an emerging field of research.

Sol-gel process was discovered in 1800. Synthesis of organic-inorganic hybrids through sol-gel process has attained much attention. Metal or semimetal alkoxides being the precursor substance of this process undergo two reactions i.e. Hydrolysis and Condensation, which leads to formation of inorganic network within which the organic moiety get entrapped due to low operating temperature. Occurrence of poly condensation reaction at low temperature is the biggest attraction and advantage of this process [40]. These reactions are shown in Fig. 2.

Industrial development is mainly contributing to environment pollution which is affecting the ecosystem as well as human health [41]. Un-loading of these toxic metals from environment is the urgent need of present era. Some of the previous methods for toxic metal removal are oxidation, precipitation, complexation, electrochemical treatment, filtration, distillation, application of selective membranes and sorptonetc [42-44]. Of all, Sorption is superior and more attractive method due to low cost, ecological correctness, higher efficiency and ease of operation. Chelating polymeric materials have been reported for pre-concentration and removal of metals [45-49]. Polymeric resins showed low mechanical and chemical stability, slow kinetics and irreversible adsorption [50]. Unmodified naturally occurring materials [51] and modified naturally occurring materials have also been applied for metal removal.

To overcome the problems of polymeric resins inorganic supports such as silica gel or functionalized silica gel have been applied for metal removal. They have high thermal and mechanical stability, stability to chemicals, negligible swelling, shrinking poisoning and fast sorption kinetics. To avoid some limitations of silica gel modified sol-gel materials have been used as sorbents. Porosity and surface layer composition of sol-gel materials can be tuned for specific application. The sol-gel materials can be physically or chemically functionalized with active chelating ligands for metal removal.

II. EXPERIMENTAL METHODOLOGY

A. General procedure for synthesis of Schiff bases (L1-L4)

10mmol (0.01 M) of 4, 4-oxydianiline was dissolved in methanol to get a clear solution. 20mmol (0.02 M) aldehyde/ketone was also dissolved in the same solvent. Both the solutions were mixed and refluxed. Progress of

reaction was monitored through TLC in appropriate solvent system from time to time. After reaction completion, mixture was evaporated on rotary evaporator followed by the filtration of the product. Solid obtained was weighted, recrystallized and stored in desiccator.

B. Synthesis procedure for L5

To a stirred solution of Salicylaldehyde (10 mmol, 0.01M) in 15 mL ethanol, 10 mmol (0.01M) of sulfanilamide solution in 15 mL ethanol was added slowly. The reaction was refluxed for 120 minutes. Orange precipitates were formed. The product was filtered, recrystallized with Ethanol and weighed.

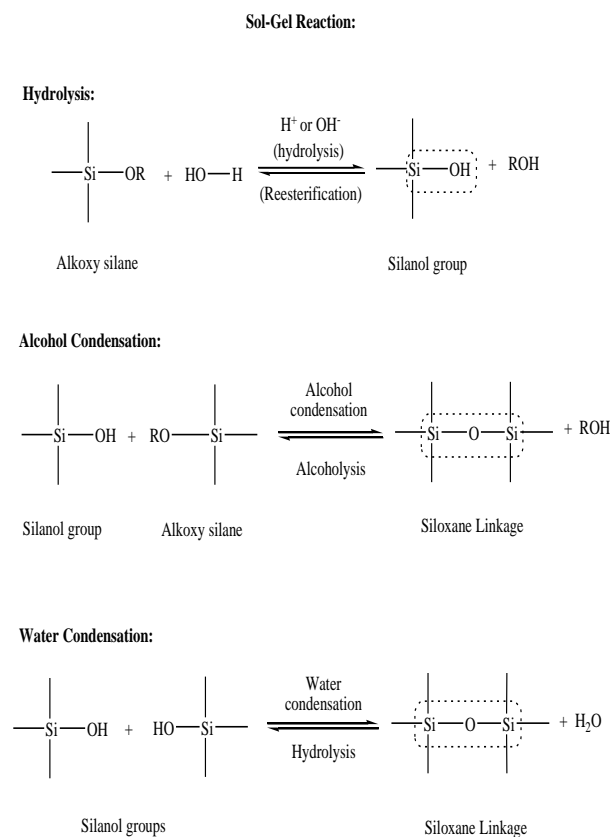


Fig. 2. Sol-gel reaction.

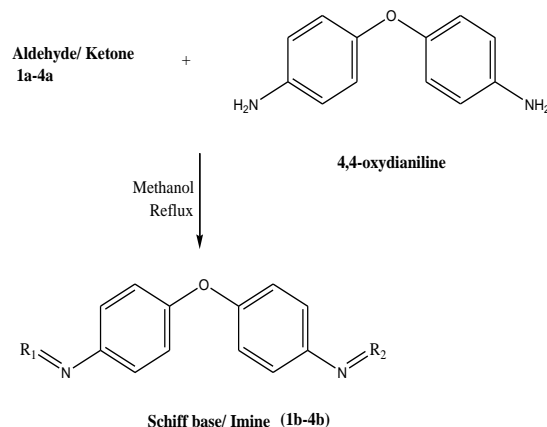


Fig. 3. General reaction for Schiff base (L1-L5).

C. Synthesis of Organically Modified Gel

In a 100 ml container, 20 ml tetraethoxysilane (TEOS), 20 ml distilled water and 40 ml of 0.01M of ligand (L1-L5) solution in ethanol was added, followed by addition of 0.01M ammonium fluoride (NH_4F) solution as catalyst. Shaking of mixture results in immediate gel formation. It allowed the gel to dry for 4-5 days at room temperature.

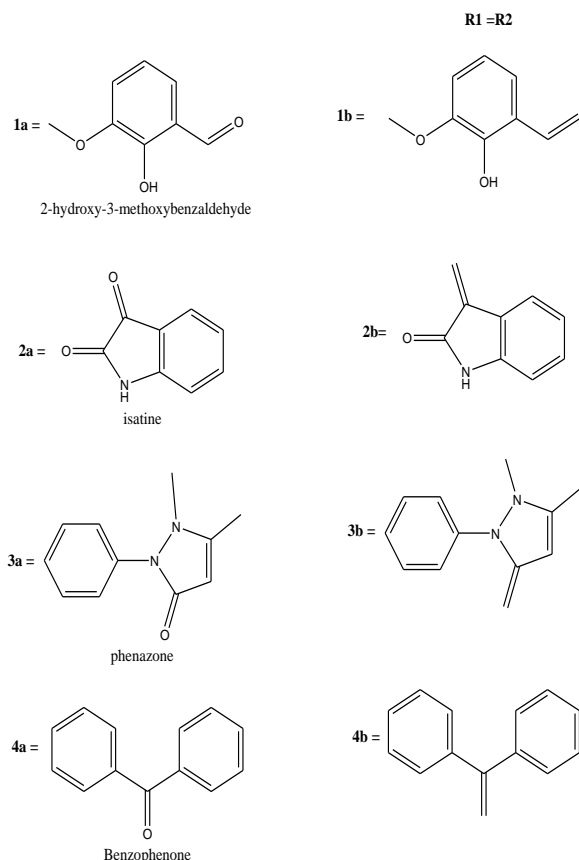


Fig. 4. Aldehydes and Ketones.

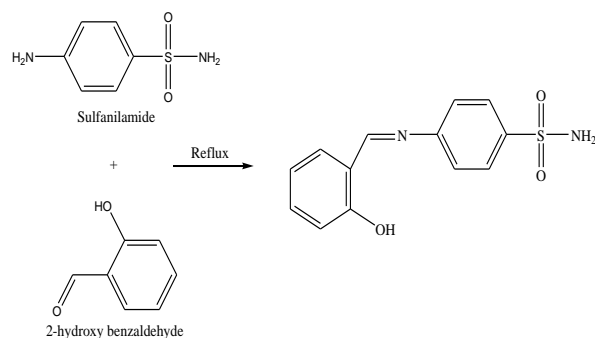


Fig. 5. Synthesis of Schiff base (L5).

Gel got dried and cracks appeared. Later it was placed in an oven at 48°C until weight became constant. After attaining the constant weight gel was crushed into fine powder and soaked in water (washed) in order to remove the undoped reagent. After washing, the gel was again dried (till constant weight by following the same method),

crushed, weighed and stored in desiccator. Fig. 3, 4 and 5 shows synthesis of Schiff base.

D. Removal of Zn^{+2} from aqueous medium using organically modified gels

10 mg/L $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution was prepared in distilled water. 10 ml of the solution was taken in seven different sample vials and pH was maintained at 1-6 respectively in each vial. 30 mg of functionalized gel was added in each vial and was shaken for 30 minutes at room temperature. The results are reported in Fig. 6.

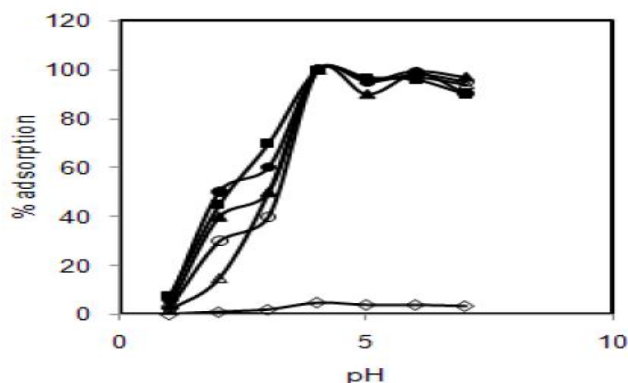


Fig. 6. Removal of metal.

Effect of pH on sorption of Zn (II) by (○) blank gel, (△) L1 Sol Gel, (○) L2 Sol Gel, (▲) L3 Sol Gel, (●) L4 Sol Gel, (■) L5 Sol Gel. Temperature = Room Temperature, Amount of Functionalized gel=30 mg, Shaking time=30 minutes, Zn (II) Concentration=10 mg/L, Volume of suspension=10 mL.

III. RESULTS AND DISCUSSION

A. Schiff base Logands (L1-L5)

Physical properties of the ligands synthesized are reported in Table 1 while the FTIR data of L1-L5 are reported below. Disappearance of C=O stretches of aldehydes and ketones and -NH stretches of primary amines in the FTIR spectrum indicates the Imine formation while physical properties data as shown in Table 1 further confirm the ligand synthesis.

B. 2-((E)-4-(4-((E)-2-hydroxy-3-methoxybenzylideneamino)phenoxy)phenylimino)methyl)-6-methoxyphenol (L1)

Color: Yellow, Yield: 76%, FTIR (ν , cm^{-1}), 1575, 1485 (C=C ring stretch), 3010 (sp^2 C-H stretch), 3450 (-OH stretch), 1200 (C-O stretch), 1620 (C=N stretch)

C. (Z)-3-(4-(4-((Z)-3-oxindolin-2-ylideneamino)phenoxy)phenylimino)indolin-2-one (L2)

Color; Deep yellow, Yield; 65%, FTIR (ν , cm^{-1}), 1590, 1459 (C=C ring stretch), 3051 (sp^2 C-H stretch), 1742 (C=O stretch), 3566 (-NH stretch), 1624 (C=N stretch)

D. (E)-N-4-(4-((E)-2,3-dimethyl-1-phenyl-1,2-dihydropyridylideneamino)phenoxy)benzeneamine (L3)

Color, Pale yellow, Yield, 68%, FTIR (ν , cm^{-1}), 1585, 1460 (C=C ring stretch), 3100 (sp^2 CH stretch), 1200 (C-O stretch), 1624 (C=N stretch)

E. *N*-(diphenylmethylene)-4-(4-(diphenylmethylene-amino) phenoxy) benzamine (L4)

Color, Off-white, Yield, 70%, FTIR (v, cm⁻¹), 1550, 1478 (C=C ring stretch), 3100 (=CH stretch), 1100 (C-O stretch), 1620 (C=N stretch)

F. (E)-4-(2-hydroxybenzylideneamino) benzene sulfonamide (L5)

Color; Yellow, Yield; 78%, FTIR (v, cm⁻¹) 1540, 1453(C=C ring stretch), 3050 (=CH stretch), 3400(-OH stretch), 1320, 1140 (S=O stretch), 3350, 3400 (-NH stretch), 1620 (C=N stretch).

TABLE I
DATA OF SCHIFF BASE LIGANDS

Code	Molecular Formula	M.Mass (g/mole)	M.P (°C)	Colour	Reflux Time (hrs)	% Yie ld
L1	C ₄₈ H ₄₄ N ₄ O ₉	820.88	148-151	yellow	10	76
L2	C ₂₉ H ₂₀ N ₄ O ₃	472.49	146-149	deep yellow	5	65
L3	C ₄₀ H ₂₈ N ₂ O ₃	584.66	188-192	Pale yellow	3	68
L4	C ₃₄ H ₃₂ N ₆ O	540.66	140-142	off-white	3	70
L5	C ₁₃ H ₁₂ N ₂ O ₃ S	276.31	210-211	yellow	1.5	78

G. Organically modified gels (L1-SG to L5-SG)

Analytical data of the synthesized gels are reported in Table II. It shows that color of the blank gel was white while the organically modified gels show color similar to Schiff base ligand that indicates the silica gel is doped by the ligand. The FTIR spectra of all modified gels show a very wide band at 1100 and 470cm⁻¹ for the siloxane linkage (-Si-O-Si-) and a medium intensity band at 3300-3400cm⁻¹ for -Si-OH linkages. The siloxane band hides/masks the other functional groups of the ligands. Fig. 1 shows the FTIR spectra of the ligand (L5), blank gel (SG) and doped gel (L5-SG) as shown in Table III.

TABLE II
ANALYSIS DATA OF BLANK AND MODIFIED GELS

Product Code	Molecular Formula	Molecular Weight (g/mole)	Melting Point (°C)	Colour	% Yield
SG	-	-	Does not melt	White	2.5 g
L1	C ₄₈ H ₄₄ N ₄ O ₉	820.88	148-151	Yellow	76 %
L1SG	-	-	-	Yellow	2.9 g
L2	C ₂₉ H ₂₀ N ₄ O ₃	472.49	146-149	Deep Yellow	65 %
L2SG	-	-	-	Deep Yellow	2.95 g
L3	C ₄₀ H ₂₈ N ₂ O ₃	584.66	188-192	Pale Yellow	68 %
L3SG	-	-	-	Pale Yellow	2.72 g
L4	C ₃₄ H ₃₂ N ₆ O	540.66	140-142	Off-white	70 %
L4SG	-	-	-	Off-white	2.76 g
L5	C ₁₃ H ₁₂ N ₂ O ₃ S	276.31	210-211	Yellow	78 %
L5SG	-	-	-	Yellow	2.74 g

Gel modification with organic ligands is also confirmed through Scanning Electron Microscopy analysis (SEM). Data obtained from SEM studies show that porosity is decreased after modification of the xerogel. It shows the filling of the pores of the xerogel after modification with Schiff base. SEM after metal sorption shows the complete filling of pores and surface of the xerogels as indicated in Fig. 7, 8 and 9. XRD Spectra of the xerogels show amorphous nature of the blank and Schiff based gels.

The porosity analysis is reported in Table IV. The interpretation of results was done by getting help from reported literature. The analyses data show successful incorporation of the Schiff base molecules inside the xerogel matrix. Sorption studies further confirm the functionalization of the xerogel. Application of organically modified gel in Zn (II) sorption. The sorption studies were conducted using zinc acetate. Sorption increases with rise in pH as of 1-4, achieves its maximum value at pH 4. Insignificant sorption is examined at pH 1-2. More increase in pH above 4 decreases the sorption to a small degree as shown in Fig. 2. The reduced sorption at low pH value may be due to competition of H₃O⁺ ions with metallic ions for complexation with some active positions of Imines.

TABLE III
FTIR DATA OF BLANK AND SCHIFF BASE MODIFIED GELS (KBr PELLET, v cm⁻¹)

Name	(C=N)	(Si-OH)	(Si-O-Si)
SG	-	3300-3000	1100, 470
L1	1620	-	-
L1SG	1620	3300-3000	1107, 471
L2	1624	-	-
L2SG	1624	3400-3000	1100, 470
L3	1624	-	-
L3SG	1624	3300-3000	1101, 470
L4	1620	-	-
L4SG	1620	3300-3100	1102, 469
L5	1620	-	-
L5SG	1620	3100-3400	1100, 470

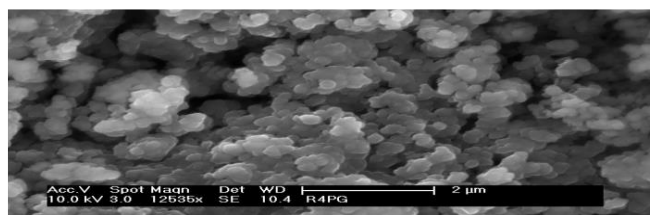


Fig.7. SEM of blank gel (SG).

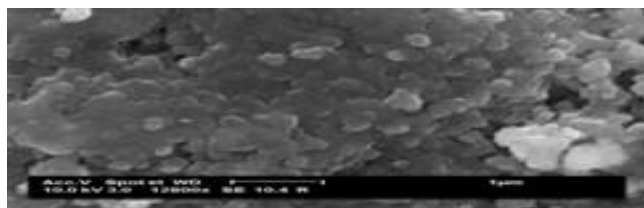


Fig. 8. SEM of organically modified gel (SBSG).

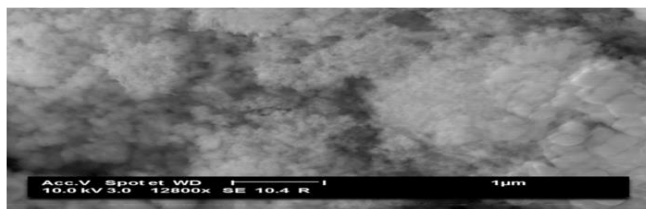


Fig. 9. SEM of modified gel after sorption of metal ions.

TABLE IV
POROSITY DATA OF BLANK AND MODIFIED GELS

Xerogels	Surface Area (m/g) ²	Pore volume (g/cm) ³	Pore diameter (nm)
SG	269	0.73	17.10
L1SG	249	0.53	9.12
L2SG	235	0.54	9.09
L3SG	265	0.60	10.00
L4SG	250	0.56	11.00
L5SG	255	0.49	0.88

functionalized gels. The data shows high efficiency of the functionalized gels as compared with blank gel. The advantage of the work is that it shows high efficiency at room temperature and moderate pH.

IV. CONCLUSION

In the light of above study it is concluded that Schiff bases being good ligands for toxic metals retain metal extraction potential even after doping of silica. Sol-gel method is a good approach for synthesis of organically modified gels. The Schiff base modified gel is more promising for metal extraction than the blank gel. SEM and XRD analysis data show the successful incorporation of the Schiff base ligand into the gel. Present study confirms that Schiff base modified gels are found very promising for extraction of Zinc metal at moderate pH at room temperature as compared to blank gel.

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