

PREPARATION OF SELECTIVE ION EXCHANGE MATERIALS FOR CHEMICAL ANALYSIS BY SOL-GEL METHOD



DISSERTATION

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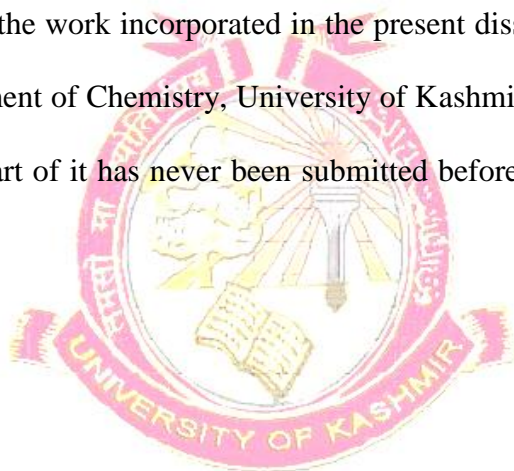
CERTIFICATE FROM SUPERVISOR

This is to certify that the work presented in this dissertation entitled “*PREPARATION OF SELECTIVE ION EXCHANGE MATERIALS FOR CHEMICAL ANALYSIS BY SOL-GEL METHOD*” is original and has been carried out by **Mr. Suhail ul Rehman** under my supervision. This piece of work is suitable for submission for the award of M.Phil Degree in Chemistry. It is further certified that the work has not been submitted in part or full for award of any degree in this or any other University.

(Dr. A. H. Pandith)
Supervisor

DECLARATION

I hereby declare that the work incorporated in the present dissertation was carried out by me in the Department of Chemistry, University of Kashmir, Srinagar, 190006. The entire work or any part of it has never been submitted before for any prize or degree anywhere.



(Suhail ul Rehman)

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Chapter - 1

General Introduction

GENERAL INTRODUCTION:

Analytical chemistry is concerned with the identification of a substance, the elucidation of its structure and quantitative analysis of its composition. It is an interdisciplinary branch of science which deals with various disciplines of chemistry such as inorganic, organic, physical, industrial and biochemistry. It also finds extensive applications in environmental science, agriculture science, clinical chemistry, solid state research and electronics, oceanography, forensic science and space research. The scope of analytical chemistry is very broad and embraces a wide range of manual, chemical and instrumental techniques to be incorporated into the route leading to a completed analysis.

Chemical analysis consists of two parts, the first involving separation and the second pertaining to quantitative determination. A separation procedure can be used for purification, qualitative identification, or quantitative determination. Quantitative determination is carried out either by spectral or optical methods or alternatively by electro analytical techniques. In recent years the field of separation has experienced a rapid growth and not only have underlying principles been extended and more clearly defined, but newer techniques have also been developed. Some of the important separation procedures are listed in Table 1.1.

Out of the various methods of separation, chromatographic methods are the most promising methods of separation. In this analytical technique, a mixture is applied in a narrow initial zone to a stationary porous sorbent, and components are caused to undergo differential migration by the flow of a mobile phase, a liquid or a gas.

Based upon the nature of mobile phase, the technique is classified as “liquid chromatography (LC)” or “gas chromatography (GC)”. In the former a liquid carries the dissolved solutes through the sorbent which can be a column, paper or a thin layer.

In the later an inert gas (carrier gas) carries the gaseous mixtures through the sorption column. Within each of these major divisions, subdivisions may be made based on the nature of the stationary phase. The various chromatographic techniques presently in use are shown in table 1.2.

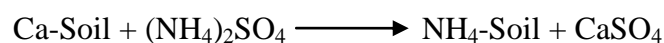
Out of them liquid - solid chromatography can be considered to be a simple and easily operative technique under ordinary laboratory conditions. The solid stationary phase may be an adsorbent (adsorption chromatography) or an ion exchange material (ion exchange chromatography). Ion exchange chromatography is one of the most widely practised analytical techniques.

Ion exchange consists of the interchange of ions of like sign between the two phases, an ion exchange resin - a cross linked polymer network which is the insoluble phase to which an ion is electro statically bound - when contacted with a solution containing ions of the same charges, an exchange can occur in stiochiometric ratios, the extent of which depends on the concentration of the ions in the solution and the affinity of ions for the insoluble phase relative to the solution phase.

Ion exchange is basically a process of nature occurring throughout the ages from even before the dawn of human civilization. The phenomenon of ion exchange is not of a recent origin. The earliest of the references were found in Holy Bible, which says 'Moses' succeeded in preparing drinking water from blackish water by an ion exchange method ¹. Aristotle ² stated that the seawater loses part of its salt content when percolated through certain sands. In 1623, Francis Bacon and Hales described a method for removing salts by filtration and desalination from sea water. In 1790, Lowritz purified sugar beet juice by passing it through charcoal.

In the beginning of 19th century, chemists were quite aware about ion exchange and were busy in new researches. Gazzari (1819) discovered that clay retained dissolved

fertilizer particle. In 1826, Sprengel stated that the humus frees certain acids from soils. Fuchs (1833) pointed out that the lime frees potassium and sodium from some clays. By middle of 19th century sufficient experimental observations and information had been collected but principle of ion exchange had not yet been discovered. Thompson in 1845,³ and Way⁴ in 1850 laid the foundation of ion exchange by Base Exchange in soil. They observed that when soils are treated with ammonium salt, ammonium ions are taken up by the soil and an equivalent amount of calcium and magnesium ions are released. During 1850-55 the agro chemist, Way demonstrated the following mechanism to be one of the ion exchange methods involving the complex silicates present in the soil. As described by Way, the process observed by the Thompson could be formulated:



The ion exchange process is reversible and aluminosilicates (zeolites) are responsible for the exchange in soil, established by Eichorn (1850)⁵. The first synthetic aluminium based ion exchanger was prepared by Harms and Rumpler⁶ in 1903 to purify the beet syrup. According to Lamberg and Wiegner^{7, 8} the materials responsible for the phenomenon were mainly clays, zeolites, gluconites and humic acids. Lamberg also obtained analcite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) by leaching the mineral leucite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) with solution of sodium chloride and found that, this transformation could be reversed by treating analcite with a solution of potassium chloride, thereby exchanging Na^+ again by K^+ .

The first application of synthetic zeolite for collection and separation of ammonia from urine was made by Follin and Bell⁹. Gans¹⁰ succeeded in utilizing the synthetic aluminium silicates ion exchangers for industrial purposes like softening of water and also for treating sugar solutions. Due to the limitations in the applications of neutral

and synthetic silicates in various industrial applications and in an attempt to meet the demands of the industries, Adam and Holms¹¹ in 1935 laid the foundation of organic exchangers when they observed that the crushed phonograph records exhibit ion exchange properties. This led to investigators to develop synthetic ion exchange resins. These resins were developed and improved by the former I.G. Farben industries in Germany followed by the manufacturers in U.S.A. and U.K, which proved very effective for separations, recoveries, ionization catalysis etc. Table 1.3 summarizes the stages of development of ion exchangers and sorbents.

TABLE 1.1
METHODS OF SEPERATION

Method	Basis
Precipitation	Differences in solubility
Distillation	Differences in volatility
Sublimation	Differences in vapour pressure
Extraction	Differences in solubility between two phases
Crystallization	Property of solubility usually at lower temperature
Zone refining	Crystallization usually at elevated temperature
Flotation	Differences in density between substance and liquid
Ultra filtration	Size of substance in comparison to filtering device
Dialysis	Osmosis ; flow of a system through a membrane
Electro deposition	Electrolysis at inert electrodes
Adsorption column Chromatography	Distribution of solution between a solid and liquid phase on a column
Partition column Chromatography	Distribution of solution between two liquids on a column
Thin -layer Chromatography	Adsorption or partition on a open thin sheet
Paper Chromatography	Partition on a paper sheet
High pressure liquid Chromatography	Column liquid chromatography under high inlet pressure
Ion exchange Chromatography	Exchange of ions
Molecular Sieves	Size of solute
Gel permeation (filtration)	Size of solute
Gas Chromatography	Distribution of a gaseous solute between a gas and liquid or solid phase
Zone electrophoresis	Separation on a sheet in the presence of an electric field

TABLE 1.2
VARIOUS CHROMATOGRAPHIC TECHNIQUES USED IN
ANALYTICAL CHEMISTRY

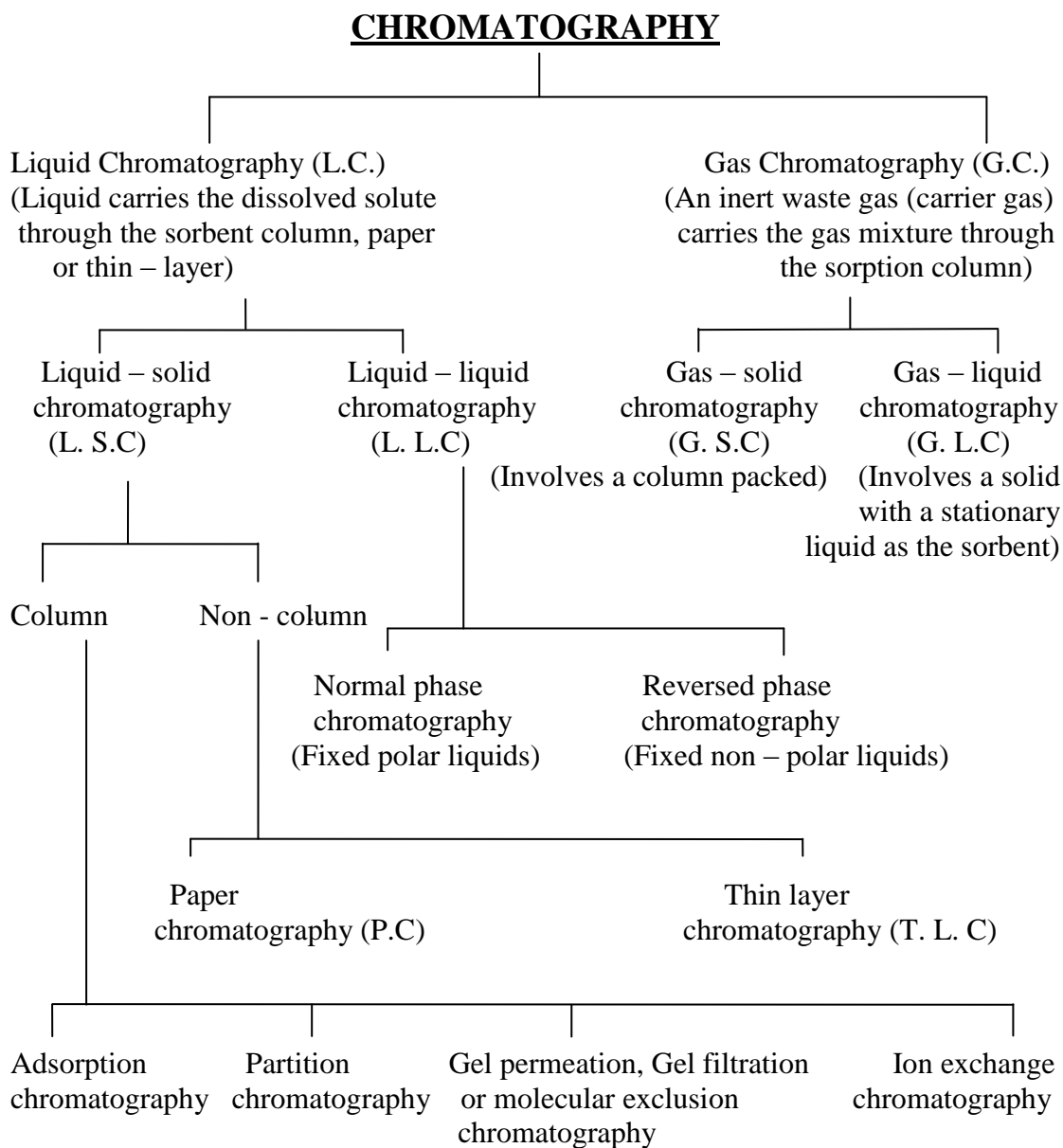


TABLE 1.3
STAGES OF DEVELOPMENT OF ION EXCHANGERS AND
SORBENTS

Period	Development
Up to 1850	First experimental observations and information. The principle of ion exchange has not yet been discovered
1850-1905	Discovery of the principles of ion exchange and the first experiments in the technical utilization of ion exchangers.
1905-1935	Use of inorganic ion exchange sorbents and modified natural organic materials.
1935-1940	Rapid development of organic materials. Inorganic ion-exchange sorbents were almost completely eliminated from all applications.
1940-To date	Continued rapid development of artificial organic inorganic ion exchange sorbents and their practical applications.

Although inorganic ion exchangers materials were first to be recognized, they lost their utility after the discovery of organic resins. However, revival of the interest in these materials took place in the 20th century, because of their use in the field of nuclear research. At that time there was need of some new materials that were stable at high temperatures and in presence of intense radioactive radiations.

Kraus et al.^{12, 13} at Oak Ridge national laboratory and C.B Amphlett^{14, 15} in United Kingdom did the excellent work on these materials in the initial stages. The work up to 1963 has been summarized by Amphlett¹⁶ in the classical book 'Inorganic Ion exchangers'. The later work up to 1970 has been condensed by Pekarek and Vesely¹⁷. Clearfield^{18, 19}, Alberti^{20, 21} and Watton^{22, 23} have also worked on different aspects of synthetic inorganic ion exchangers. In India Qureshi and co-workers have prepared a large number of such inorganic materials and studied their ion exchange behavior during the last 50 years. Other groups that were engaged in the field of research and whose work is of significant interest are Anil K. De at Shantinikaten and Tandon at Rorkee.

One of the important properties of ion exchange resins is that they contain functional groups attached to the backbone of the polymer that can exchange ions with the ions in the solution phase. These exchangeable ions are not limited to the small inorganic anions and cations typical of water treatment (e.g., Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , Cl^-) but can be organic ions of significant molecular weight (e.g., polymers). Ion exchange resins are useful because of the insolubility of the resin phase. After contact with the ion containing solution, the resin can be separated by filtration. They are also adaptable to continuous processes involving columns and chromatographic separations. Their insolubility renders them environmentally compatible. Since the cycle of loading / regeneration / reloading allows them to be

used for many years. Ion exchange resins have been used in water softening, removal of toxic metals from water in the environment, waste water treatment, hydrometallurgy, sensors, chromatography and biomolecular separations. They have also been used as catalysts both in place of homogeneous catalysts such as H_2SO_4 and to immobilize metallic catalysts. Ion exchange technique can remove traces of ion impurities from water / process liquors and give out a product of ultra pure quality in a single efficient and techno-economically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and separation of radioisotopes and find large application in water treatment and pollution control.

Ion exchangers played an important role in water softening and in chemical industry. In the last decade, ion exchangers have been used in the chemical decontamination process for metal ion recovery, regeneration of decontaminants, and removal of the formulation chemicals from the coolants (Velmurugan et al 1991). Ion exchangers are also used in nuclear reprocessing and treatment of radioactive wastes.

Ion exchange materials have found extensive applications in analytical and industrial chemistry in view of their elegant characteristics such as insoluble matrix, stoichiometric exchange, good selectivity, specificity and applicability to column operations (Jayswal and Chudasama, 2007). Interest of inorganic exchangers in the industrial applications has increased rapidly since the mid 1980's. Increased environmental awareness has resulted in stricter regulations for waste releases and more effective treatment methods are required to meet these conditions. The need for efficiency is especially urgent in nuclear industry, which generates large amounts of radioactive effluents in almost all phases of the nuclear cycle, and from reprocessing of the waste for further use of some of the radioactive elements. Ion exchange as a separation process is relatively facile and energy-efficient compared to other common

solution phase separation procedures used in industry (e.g. solvent extraction and precipitation). The challenge in nuclear waste treatment is the efficient separation of the radionuclide's present in trace amounts from complex solutions, which contain high concentrations of interfering inactive components, or extreme acidity or alkalinity. Therefore, the method for effective separation in such conditions must be selective only for the trace ions in question. The major attraction in the use of inorganic ion exchangers in such applications is their good chemical and thermal stability, and the possibility for obtaining very high selectivities and thus, good separation efficiencies.

Ion exchange was originally discovered in naturally occurring materials such as soils, clays and zeolites. These materials found applicability as water softeners but the commercially available ion exchangers were amorphous aluminium silicate gels. In spite of their low cost, their industrial use was often difficult (impurities, bad physical properties for packed bed operations) and they sometimes needed chemical or thermal pre-treatment. This led to the need for alternative ones and led to the development and synthesis of inorganic ion exchange resins in 1930's. However, the beginning of nuclear technology in the 1940's demanded materials with still better thermal (>150°C) stability. The application of an ion exchanger in the treatment of nuclear waste solutions also requires good resistance of the material to ionizing radiation, which is a property the organic resins tend to lack. Therefore, the focus of researchers returned to inorganic ion exchangers.

Therefore, synthetic inorganic ion exchange sorbents have been extensively used in the past two decades. Insoluble oxides, crystalline silicates, salts of polybasic acids, multivalent metals have been keenly studied as they are characterised by greater thermal stability at elevated temperatures and resistance to high radiation fields, and

their selectivity to certain ions, which are the properties that organic resins lack. They also possess high chemical stability and have compatibility with final waste forms. These inorganic ion exchangers are reported to be not very much reproducible in behaviour and the fabrication of these materials for column operations is quite difficult and also possess less mechanical strength. However, these sorbents were mostly amorphous in nature and elucidation of the ion exchange mechanism, and their physical and chemical properties, was very difficult and limited. The discovery of a crystalline phase of zirconium phosphate in 1964 made it possible to explain its observed ion exchange behaviour in structural terms²⁴⁻²⁵. The increased knowledge of the crystalline structures of many inorganic compounds since then allows for more in-depth studies of the correlation between the structure and observed ion exchange properties of a compound. Although originally the intent of the studies involving inorganic ion exchangers such as hydrous oxides, salts of polyvalent acids, and zeolites, was to explore their suitability for the treatment of nuclear waste solutions and purification of water. Traditionally the development of new materials for specific, desired conditions by the 'trial and error' approach has required a great deal of experimental effort and time. With the understanding of the origin of selectivity in inorganic ion exchangers, one could achieve greater control over the properties of the materials through synthetic design, and thus fine-tune the ion exchange properties for highly selective separation applications for almost any desired conditions. However, because the origin of selectivity in these materials is not yet adequately understood, this approach requires that more fundamental research be carried out with most of the crystalline exchangers known today. By slightly altering the composition or the three-dimensional structure of the compound through systematic changes in synthetic

variables and framework cation substitution, exchangers with desirable properties may be developed.

The organic resins have qualities of uniformity, chemical stability,²⁶⁻²⁸ whereas, the selectivity towards particular metal ion by inorganic ion exchangers²⁹⁻³⁴ is one of the important factors for their development and are having extensive applications in separation science specially of heavy metals³⁵⁻³⁹.

The limitations with the existing organic ion exchangers is that the mechanical strength and removal capacity tends to decrease at high temperatures and degradation of ion exchange properties under high radiation conditions, whereas problem with inorganic ion exchangers is their low mechanical and chemical strength and difficulty in obtaining granulated materials with suitable mechanical properties for use in column operations as compared to organic ion exchangers. To overcome these limitations, hybrid ion exchangers have been introduced which conjugate mechanical properties of organic counterpart with intrinsic properties of inorganic compound. Therefore, the incorporation of a polymer material into an inorganic ion exchanger provided a class of hybrid ion exchangers with good ion exchange capacity, high stability, reproducibility, and selectivity for heavy metals⁴⁰.

Organic - inorganic hybrid materials have been an important enterprise for people from very diverse origins such as academic, research and industrial sectors. The intrinsic multifunctional character of these materials makes them potentially useful in multiple fields. Illustrative examples of this versatility are their high added value applications such as coatings for corrosion, protection and abrasion resistance, artificial membranes for ultra and nanofiltration, per evaporation and gas separation, catalysts, adsorbents of toxic compounds, materials with specific optical, electrical and or magnetic properties for telecommunications and so forth. The growing interest

of this subject matter has been reflected in two symposia organised recently by the Materials Research Society in 1998 and 1999^{41, 42}. However, the analytical studies on these hybrid ion exchange materials were initiated by Qureshi⁴³ and exhaustive research in this area was carried out by the research group of K.G. Varshney, they mainly concentrated on the amorphous materials. It was based on their observation that in general the gel type materials form good granules or pellets suitable for column operations and thus column chromatographic separations are easily achieved with these materials as compared to the crystalline ones⁴⁴⁻⁴⁶.

Many investigators have introduced organic inorganic hybrid ion exchangers consisting of inorganic ion exchanger and organic binding matrices^{31,47-50}. Most of the organic/inorganic hybrid materials are nanocomposite materials in which the inorganic part and the organic entities interact at molecular level in the nanoscopic domain. The most obvious advantage of organic and inorganic components is that they can favourably combine the often dissimilar properties of organic and inorganic components in one material. These materials have combined the mechanical properties of the organic polymers with the intrinsic properties of the inorganic compound, creating a new class of hybrid organic inorganic materials with improvement in mechanical properties, chemical inertness, high temperature and radiation stability, reproducibility, and high selectivity for harmful ions. Among many possible applications, use of these hybrid materials as ion exchangers has attracted much attention in last few years^{31, 49-64}. Hybrid inorganic ion exchangers are selective to heavy metals and are useful for removal of toxic elements like arsenic, lead etc. from industrial effluents⁶⁵. These hybrid materials contain polymeric species, such as polyacrylonitrile, polystyrene, polyacrylamide, n-butyl acetate, polyaniline, triethylammonium, polymethylacrylate, pectin etc. in their structure. This type of ion

exchanger refers to a composite group of inorganic ion exchangers, which are modified by some binding polymeric materials for the preparation of large size particles with granular strength⁶⁶. Inorganic ion exchange materials were encapsulated through immobilization with porous polymeric materials, such as alginate, agar, polyacrylamide, carrageenan, cellulose acetate and polyvinyl alcohol^{67, 68}. The porous structure of polymers allows metal ions to diffuse into the internal pores and exchange with the internal ion exchanger. Recently, biopolymers have generated a large attention due to their cheap cost and easiness of their preparation techniques which does not involve chemical initiation as the synthetic polymers. Alginate, agar, and carrageenan are known as the major binding biopolymers. On the other hand they are also used to bind metals strongly. Many investigations have been carried out about the application of alginic acid to the aqueous phase separation of heavy metals, and the possibility of alginic acid for the adsorbent material has been suggested^{69, 70}.

The sol-gel process, involves the manufacture of inorganic or inorganic - organic matrices through the formation of a colloidal suspension (sol) and gelation of the sol to form a wet gel, which after drying forms the “dry gel state” (xerogel). The sol-gel approach to material synthesis is based on the preparation of hydrolysable molecular precursors, mostly metal or semi-metal alkoxides e.g. $(\text{Si}(\text{OR})_4)$ due to their high reactivity. Hydrolysis and polycondensation reactions lead to the formation of oxopolymers or metal oxides. The mild conditions used in the sol-gel process allow the introduction of organic molecules inside an inorganic network^{71, 72}. These fundamental chemical processes are influenced by several parameters which, once they are understood for a particular chemical system, allow the control of the homogeneity (or controlled heterogeneity) of the nano and micro-structure of the derived material. Design of sol-gel materials, therefore, is possible, by variation of the

chemical composition of the molecular building blocks and by variation of the nano and micro-structure. Both influence the properties of the final material to a very high degree.

The sol gel process, first reported some 150 years ago, is gaining renewed interest,⁷³⁻⁷⁶ because it provides a convenient way to incorporate heat sensitive materials, including organic molecules and active proteins, in porous ceramic matrices. The discovery of the exceptional tendency of organosilicon compounds to form siloxane polymers containing organic side groups (silicones) caused an explosion of activity in the 1930's that established a chemical and physical basis for understanding the processes of hydrolysis and condensation. The +4 oxidation state of silicon ($z = 4$) is the only important oxidation state in the chemistry of silicon in naturally occurring systems and the coordination number of silicon, (N), is most often 4. Compared to aluminium and the transition metals, silicon is generally less electropositive. This renders silicon comparatively less susceptible to nucleophilic attack. Si-C bonds are thus hydrolytically stable and allow an easy anchoring of functional organic groups. Also, coordination expansion does not spontaneously occur in silicon alkoxides on reacting with nucleophilic reagents. These factors make the kinetics of hydrolysis and condensation considerably slower than that observed for alumina or transition metal alkoxide systems. Consequently, hydrolysis and condensation reactions in silicon-based alkoxide systems are usually facilitated by acid or base catalysis. For common silicon alkoxides, the hydrolysis rate is high under an acidic environment relative to that of condensation. Acid catalysis, therefore, promotes the development of more linear or polymer-like molecules in the initial stages of the reaction. On the other hand, base catalysis results in a higher condensation rate. Thus, this environment tends to produce more of a dense cluster

growth leading to silica with dense, colloidal particulate structures. The main advantages of sol-gel prepared silica are compositional homogeneity and low processing temperatures. Normally the alkoxide is dissolved in alcohol and hydrolyzed by the addition of water under acidic, neutral or basic conditions. The relative simplicity of sol gel technology is also at least partially responsible for its rapid proliferation.

Organosilicon precursors of the general formula $(R_{4-x}Si(OR^*)_x)$, where R represents, the desired reagent or functional group and, $x = 1-3$ can be hydrolyzed and condensed, with the silicon alkoxides (i.e., TMOS or TEOS) to produce materials with properties, superior to those prepared from either compound alone⁷⁷⁻⁸². These materials have been coined ORMOSILs (Organically Modified Silicates) by Schmidt and co-workers in the early 1980s⁷⁷. Specific organic modifiers that have been used include CH_3 , C_2H_5 , C_6H_5 , $(CH_2)_nNH_2$, $(CH_2)_nSH$. A large diversity of organosilicon derivatives with various functional groups are commercially available. The most commonly used are the trialkoxide silanes ($X=3$), where the functional group R is bound to the silicon via a non-hydrolysable silicon carbon bond. These precursors are often preferentially cross linked with tetraalkoxide ($X=4$) components to impart suitable network connectivity and stability to the solid, although they can be also used alone⁷⁸⁻⁸². One of the distinct advantages this approach provides is that the chemical properties (refractive index, polarity, surface functionality) of the silicate matrix can be readily tailored through the judicious choice of R. This enables composite materials with the desired hydrophobicity, porosity, flexibility, reactivity, and stability to be readily fabricated⁷⁸⁻⁸².

The sol gel process^{83, 84} provides a useful method to prepare inorganic and organic inorganic hybrid materials for use in chemical analysis⁸⁵⁻⁹⁴. The inherent usefulness

of this approach is largely due to the ease at which sol gel derived materials can be prepared, modified and processed. The mild reaction conditions afford an opportunity to incorporate various molecules such as dyes, proteins, enzymes, organic and organometallic reagents into a glass composite. This can be readily achieved by simply doping the reagent into the sol prior to its gelation as demonstrated by Avnir and co-workers⁹⁵ or alternatively via the use of organo-silicon derivatives⁷⁷⁻⁸² $\text{RSi}(\text{OR}')_3$, where R is the desired reagent. The materials are optically transparent, chemically and mechanically stable, and can be prepared in a variety of sizes and shapes, including thin films, monoliths, fibres and powders. Furthermore the average pore size, pore size distribution, surface area, refractive index and polarity of the resultant matrix can be controlled and tailored by manipulations in the sol-gel processing conditions including the type and concentration of the silane(s). One of the main advantages of the sol-gel process is that it allows careful control of the size and morphology of clusters/particles in the sol or gel during the early processing stages, so that high quality end products (in the form of powders, films or coatings) can be developed to fulfil specific demands. The mild reaction conditions allow the incorporation of organic moieties into inorganic networks. These organic-inorganic hybrid materials are particularly useful because components with different combinations of properties can be blended together. The general properties of materials synthesized by the sol-gel method are high purity, better homogeneity, controlled porosity combined with the ability to form large surface area materials at low temperatures, possibility of preparing multi-component systems with broad ranges of compositions and good dispersion of minor components. Ion exchange sites can be introduced into the inorganic framework as a means to preconcentrate an appropriately charged analyte into a film for detection. Template based approaches

can be utilized to design porous inorganic hosts with improved molecular recognition techniques.

Organic / inorganic hybrid materials prepared by sol gel approach have rapidly become a fascinating new field of research in material science. The explosion of activity in this area in the past decade has made tremendous progress in both the fundamental understanding of sol gel process and the development and the applications of new organic/ inorganic hybrid materials.

The sol gel process which is mainly based on inorganic polymerisation reactions, is a chemical synthesis method initially used for the preparation of inorganic materials such as glasses and ceramics. Its unique low temperature processing characteristics also provide unique opportunities to make pure and well controlled composition organic / inorganic hybrid materials through the incorporation of low molecular weight and oligomeric / polymeric organic molecules with appropriately inorganic moieties at temperatures under which the organics can survive.

For the past decade, organic / inorganic nanocomposites prepared by the sol gel process have attracted a great deal of attention, especially in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, and physics. The preparation, characterisation and applications of organic / inorganic hybrid materials have become a fast expanding area of research in material science. The major driving forces behind the intense activities in this area are the new and different properties of the nanocomposites which the traditional macro scale composites and conventional materials do not have. For example, unlike the traditional composite materials which have macroscale domain size of millimetres and even micrometer scale, most of the organic / inorganic hybrid materials are nanoscopic, with the physical constraint of several nanometres, typically 1-100 nm as the minimum size of the components or

phases. Therefore, they are often still optically transparent materials although microphase separation may exist. Through the combinations of different inorganic and organic components in conjunction with appropriate processing methods, various types of primary and secondary bonding can be developed leading to materials with new properties for electrical, optical, structural or related applications.

The incorporation of organic / oligomeric / polymeric materials into organic / inorganic networks by sol gel process makes it possible to optimize selected properties independently. Specifically, the introduction of organic groups into an inorganic network leads to new structure - property variations, thereby promoting new potential applications for the resulting composite material.

The sol gel process provides a number of distinct advantages for the creation of materials with controlled porosity and morphology. These include good thermal, mechanical and chemical stability, flexible solution chemistry, ease with which materials in various configurations (i.e., films, fibres, monoliths) can be processed and the ability to control material porosity and structure through small changes in the sol gel processing variables (i. e, nature and concentration of the catalyst , ratio of water to silicon alkoxide)⁸⁵⁻⁹⁰.

Inorganic supports particularly silica based matrices offer several advantages over organic polymer supports including physical rigidity and high abrasion resistivity, negligible swelling in both aqueous and organic solutions, chemical inertness, high biodegradational, photochemical and thermal stability, and excellent optical transparency and low intrinsic fluorescence.

Silica matrices also have some notable drawbacks including fragility, hydrolysis at high pH, high gelation temperatures, which preclude laboratory shaping of porous silica and limit their analytical applications to commercially available geometric

configurations, large cation exchange capacity, attributable to surface silanol groups and the complicated procedures required for immobilizing organic reagents

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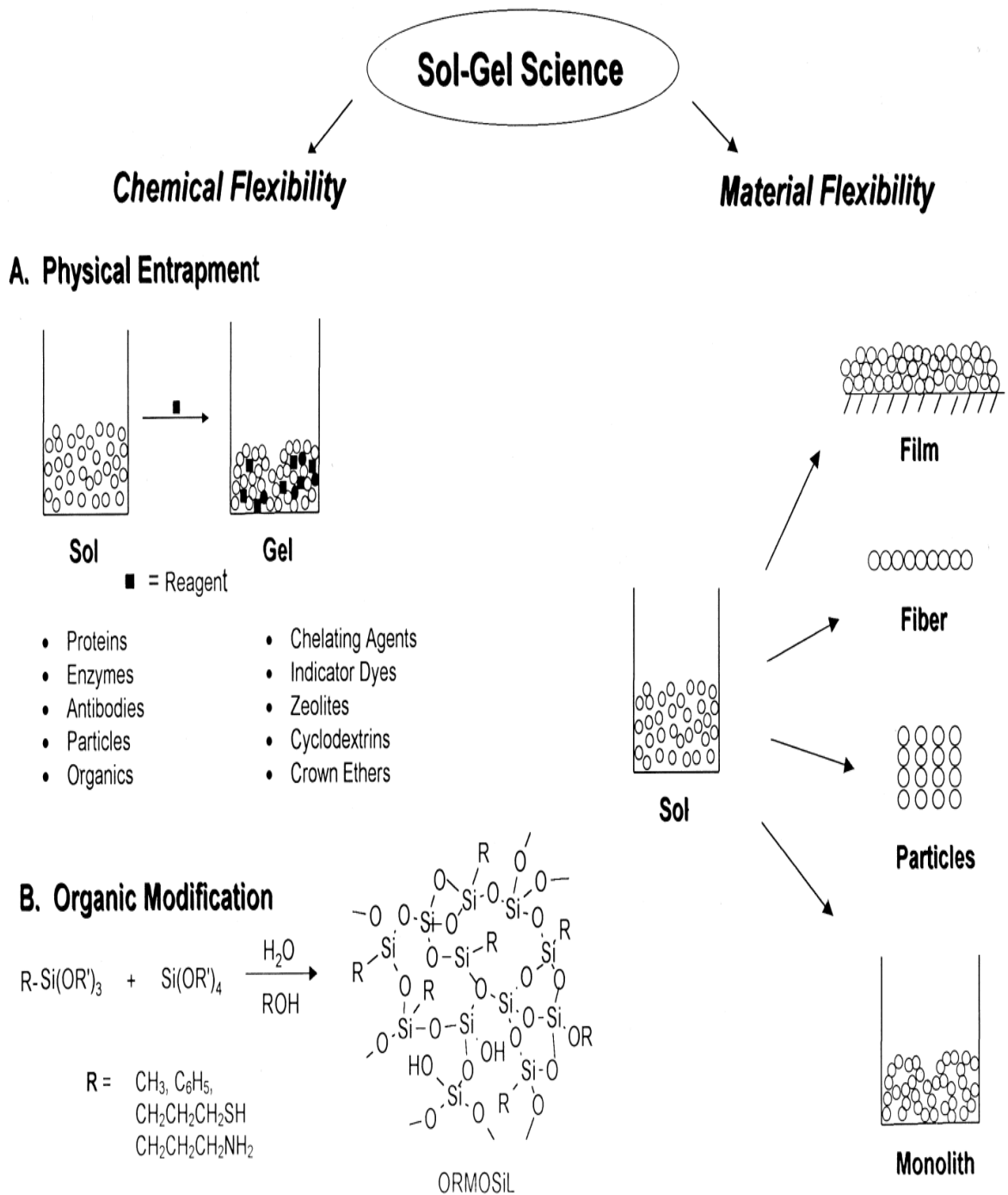


Figure 1.1: The immense flexibility of the sol-gel process.

Sol gel technology provides a convenient tool for the fabrication of inorganic and inorganic - organic hybrid materials via the hydrolysis and condensation of metal alkoxides⁸³. The ease with which these materials can be prepared, modified and processed in conjunction with their high optical quality, photochemical and electrochemical stability and good mechanical and chemical stability has made them an attractive alternative to conventional organic polymers for various optical applications, composite material fabrication and chemical sensor development^{85-88, 96,97}. While these porous solids are routinely used as stable host matrices for advanced applications, they are chemically complex. The detailed synthetic, aging, and drying conditions used in their preparation determine their average chemical and physical properties. These properties also vary dramatically within individual samples on a local scale. Such heterogeneity results from variations in pore size, shape, surface composition and local solvent composition, leading to the formation of a wide range of chemically and physically distinct molecular scale environments⁹⁸. These specially varying attributes control local material and dopant stability, as well as dopant and solvent mass transport. A better understanding of the types of environments found in these materials is, therefore, of both fundamental and technological interest.

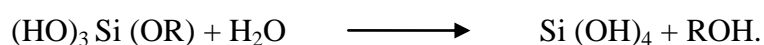
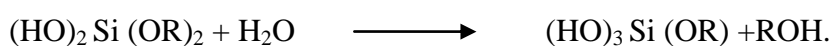
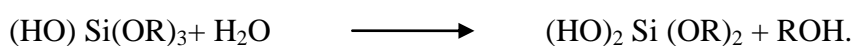
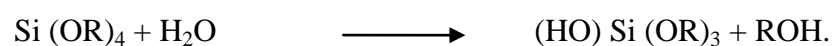
The sol gel process generally starts with alcoholic or other low molecular weight organic solutions of monomeric metal or semimetal alkoxide precursors $M(OR)_n$, where M represents a network forming element such as Si, Ti, Zr, Al, B etc. and R is typically an alkyl group (C_xH_{2x+1}) and water. The most widely used precursors to prepare materials for use in chemical analysis applications have been the silicon alkoxides particularly tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). These reagents can be readily hydrolysed and condensed under relatively mild

conditions. Generally, both the hydrolysis and condensation reactions of organosilicon precursors occur simultaneously.

Once the hydrolysis reaction has been initiated, the thermodynamics of these reactions are governed by the strength of the entering nucleophile, the electrophilicity of the metal, and the partial charge and stability of the leaving group and generate low molecular weight by products such as alcohol and water. These small molecules must be removed from the system, and such removal would lead, to a tetrahedral SiO₂ network if the species were silicon. The removal of these by-products also contributes to the high shrinkage that occurs during the classical sol gel process. For non-silicate metal alkoxides e.g. aluminium alkoxide, generally no catalyst is needed for the hydrolysis and condensation reactions. The reactions are very rapid. In the case of silicon based metal alkoxides, the hydrolysis and condensation reactions typically proceed with either an acid or base as catalyst. Therefore, the structure and morphology of the resulting network strongly depend on the nature of the catalyst and the pH of the reaction.

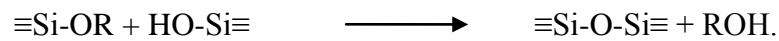
The polycondensation of alkoxy silanes can be summarised in three reactions: - hydrolysis of the ester, silanol- silanol condensation, silanol ester condensation.

Hydrolysis: Hydrolysis of a metal or semi-metal alkoxide to form a hydroxylated product and the corresponding alcohol.

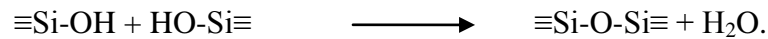


This mechanism is highly dependent on pH and can be catalysed under acidic or basic conditions.

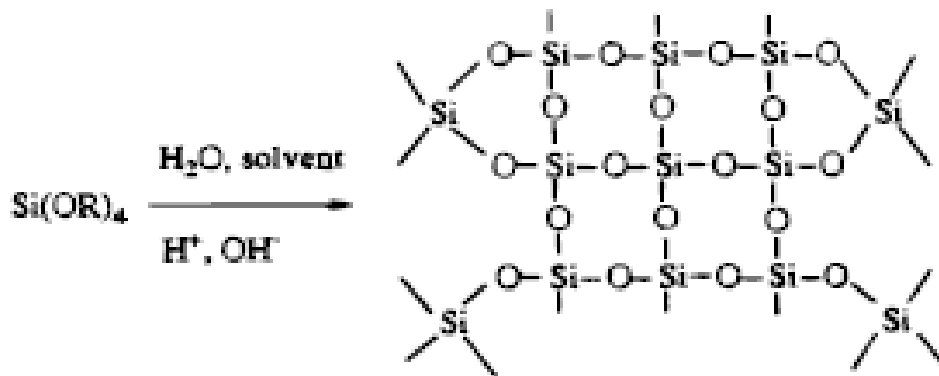
Alcohol Condensation (Alcoxolation): Condensation between an unhydrolyzed alkoxide group and a hydroxyl group or between two hydroxyls eliminates the solvent (water and alcohol) and forms a colloidal mixture called the sol.



Water Condensation (Oxolation) :



Overall Reaction: Polycondensation between these colloidal sols as well as additional networking eventually results in the generation of a porous three dimensional network.



In a typical procedure, TMOS or TEOS is combined with water in a mutual solvent (i.e., methanol or ethanol) and a suitable catalyst (acid, base, or nucleophile) is added. During the sol-gel transformation, the viscosity of the solution gradually increases as the sol (colloidal suspension of very small particles, 1 to 100 nm) becomes interconnected to form a rigid, porous network - the gel. Generally, it is a process concerning transition of a system from liquid 'sol' (the colloidal suspension of

particles) into solid 'gel'. Gelation can take place on the time scale of seconds to minutes to days to months (or longer) depending on the sol-gel processing conditions. After drying, a xerogel is formed. Xerogels and aerogels are useful in the preparation of dense ceramics, but they are also interesting in themselves because their high porosity and surface area make them useful as catalytic substrates, filters and so on. Most gels are amorphous (i.e. non-crystalline), even after drying, but may be crystallized when heated at high temperatures or calcined. It is found that the dried gel contains many labile sites that offer opportunities for new chemical reactions. A large amount of shrinkage accompanies drying, often with cracking unless the monolithic materials are dried slowly or drying control additives are added to the sol^{83,84}.

The gel point is defined as the point at which the entire solid mass becomes interconnected. At the initial stages of polymerization, the silanol functional groups at the surface of the growing particles are partly deprotonated and their negative charge provides a repulsion barrier that stabilizes the sol. Later, solvent evaporation and water consumption by alkoxy silane hydrolysis concentrate the solution and destabilizes the suspension.

During the drying phase, stress is created which causes cracks in large monoliths and is responsible for fractures in dry monolithic sensors upon immersion in water. However, addition of surface active drying control chemical additives such as Triton-X and formamide to the sol gel precursors prevent fractures and these compounds are easily rinsed out and do not interfere with the subsequent high temperature densification.

The incorporation of cationic surfactants such as cetylpyridinium bromide prevents fractures of monoliths during gelation and on repeated wet - dry cycles.

The chemical reactions that occur during the formation of sol gel and xerogel strongly influence the composition and properties of the final product. In general, the sol-gel process offers significant control over specific surface area, porosity, pore volume and pore size distribution of the material.

Both hydrolysis and condensation reactions of organosilicon precursors occur by nucleophilic substitution (SN) mechanisms which involve three steps: nucleophilic addition (AN), proton transfer within the transition states, and removal of the protonated species as either alcohol or water. For non-silicate metal alkoxides, generally no catalyst is needed for hydrolysis and condensation because they are very reactive. In the case of silicon based metal alkoxides, the hydrolysis and condensation reactions typically proceed with either an acid or base as catalyst. Therefore, the structure and morphology of the resulting network strongly depend on the nature of the catalyst, in particular, the pH of the reaction. In the case of the common silicon alkoxides, since the hydrolysis rate is high under an acidic environment relative to that of condensation, acid catalysis promotes the development of more linear or polymer-like molecules in the initial stages. For a pure metal alkoxide system, this will result in the formation of high-density, low fractal dimension structures. On the other hand, base catalysis results in a higher condensation rate. Therefore, this environment tends to produce more of a dense-cluster growth leading to dense, colloidal particulate structures⁹⁹⁻¹⁰². In addition to the pH of the reaction, the size of the alkoxy group can also influence the hydrolysis and condensation reactions through a steric or leaving group stability effect. For example, species such as tetramethoxysilane (TMOS) tends to be more reactive than tetraethoxysilane (TEOS). Among numerous applications, the sol gel approach is being used extensively in the development of new materials for catalysis,^{103, 104} chemical sensors,^{89, 90} membranes,

¹⁰⁵ optical gain media, ¹⁰⁶ photochromic and nonlinear applications, ¹⁰⁷⁻¹⁰⁹ and solid-state electrochemical devices ^{110, 111}. For example, sol gel technology has been used to prepare both pure inorganic and organic-inorganic hybrid supports of catalytically active transition metal complexes, dispersed metal particles, and biocatalysts ^{103, 104}. Silica gel-entrapped proteins and enzymes have been employed in numerous biological sensing applications ^{85, 94}. Whereas the organic and organometallic doped materials have been utilized as sensors for metals, ions, pH, and gasses ⁸⁶⁻⁹³. The organically modified materials have been used recently to fabricate leak-free chemical sensors and materials for nonlinear optical applications ^{80, 82, 92}.

Ion exchange and permselective materials are important in many applications, particularly those involved in chemical analysis. These materials can be used to selectively preconcentrate reagents at an electrode surface and/or at an optically transparent substrate for analysis or can be used as permselective coatings to essentially prevent interferences from being detected. The development of permselective and ion-exchange films becomes very important in many bioanalytical applications where it is necessary to exclude numerous interferences from the underlying surface or in analytical applications where detection limits can be extended via preconcentrating the analyte of interest in a thin film. One of the distinct advantages sol-gel-derived materials provide over other commonly used organic polymers is the inherent flexibility associated with material preparation and the processing. For example, the porosity, hydrophobicity, and network connectivity can be manipulated via changes in the sol-gel processing and drying conditions ^{83,84,112}. This flexibility enables materials with ideal response time, permselectivity, and ion-exchange to be fabricated. In addition, sol-gel-derived materials can be made to have good optical transparency, chemical, photochemical, and electrochemical stability,

and are less susceptible to solvent-induced swelling/shrinking that often plague polymer films⁸⁵⁻⁸⁹. To date, most work has focused on the incorporation of (1) quaternary ammonium salts, (2) polyelectrolyte's , or (3) organosilicon reagents that contain acidic or basic functional groups into the sol as a means to introduce specific ion exchange sites within the silica host structure. Sol-gel materials help us detect metal ions in two ways; firstly, the silane groups offer sufficient sensing sites to metal ions as they possess a large surface area, and secondly, due to the presence of entrapped recognition molecules. These features provide extra ordinary sensitivity for metal ion detection. The entrapped ligand in the sol-gel matrix possesses sufficient freedom to reorient for complex formation with target metal ions.

One of the first examples of the use of sol-gel materials in ion-exchange applications was reported by Lev and co-workers in 1992¹¹³. Their study showed that it is possible to trap quaternary ammonium salts (e.g., cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB)) into a solid silica support by physically doping these compounds into a sol prepared from TEOS. The ion exchange properties of these immobilized quaternary ammonium exchangers toward chloride, bromide, sulfate, and nitrate were assessed with the ground glasses using ion chromatography. Dopant leaching was also evaluated using total organic carbon analyzer and ion chromatography. In terms of good ion exchange activity and good trapping, the quaternary amine ion-exchange compounds were found to be best¹¹³.

More recently, Park and co-workers have doped the quaternary ammonium salt tridodecylmethylammonium chloride (an ionophore for chloride) into a inorganic-organic composite prepared from the organosilicon precursor¹¹⁴.

Hsueh and Collinson have shown that organosilicon reagents that contain NH_3^+ , COO^- , or COOEt functionalities can be hydrolyzed and co-condensed with

methyltrimethoxysilane (MTMOS) to form materials that contain anion or cation exchange sites, respectively ¹¹⁵. In this work, the sol was spin cast on the surface of a glassy carbon electrode and the ion-exchange and permselective properties of the resultant thin films evaluated using cyclic voltammetry.

In a more recent work, Wei and Collinson have shown that 3-aminopropyltriethoxysilane (APTEOS) can be hydrolyzed and co-condensed in various ratios with different organosilicon reagents (R-Si (OCH₃)₃ where R = CH₃, CH (CH₃) CH₃, C₆H₅, or OCH₃) to form stable thin films ¹¹⁶. The major objective of this study was to prepare materials with different amounts of ion-exchange sites, different hydrophobicity, and variable porosity to vary the selectivity and specificity of these composite materials ¹¹⁶. These results showed that both the magnitude and the rate of ion-exchange of potassium ferricyanide can be controlled via the amount and type of organosilicon precursor introduced into the sol.

Heinemann, Seliskar, and co-workers have taken a different approach to the incorporation of ion-exchange sites into a silicate matrix ¹¹⁷⁻¹²². In their work, polyelectrolyte's have been chemically doped into the hydrolyzed sol and the resultant composite spin cast on the surface of an electrode or an optically transparent substrate and used to preconcentrate analytes ¹¹⁷⁻¹²².

In other studies, a silicon alkoxide modified with a quaternary ammonium functional group has been incorporated in a silica host and used to sense anions ^{123, 124}. Chau and coworkers have hydrolyzed and co-condensed N-trimethoxy silylpropyl-N, N, N-trimethyl ammonium chloride with TMOS to prepare anion-exchangeable ORMOSIL powders and films ¹²³. The materials thus produced were able to ion-exchange potassium ferricyanide and exhibited selectivity for Cl⁻ over Br⁻ and I⁻.

As far as xerogel powders are concerned, the vital breakthrough in the late 1960's was the demonstration that the process could be used to control the shape and size of solid particles; in particular, high-density spherical particles with narrow controlled size ranges could be achieved. One example of this was demonstrated by Stober and co-workers in 1968 when they synthesized monodispersed spherical particles with uniform sizes (0.05 – 2 μm) by the sol gel method.

Recently, there have been reports of mesoporous materials with various particle shapes such as fibres, spheres, ropes, discoid's, toroid's, hollow tubes, hollow spheres and dodecahedra. The templates that have been used to date are surfactants, organogelators, hydroxy carboxylic acids, as well as porous or fibrous materials such as carbon nanotubes and membranes.

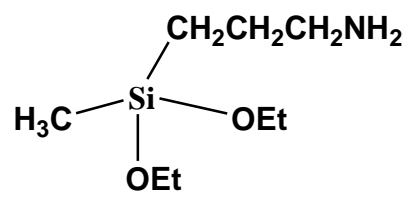
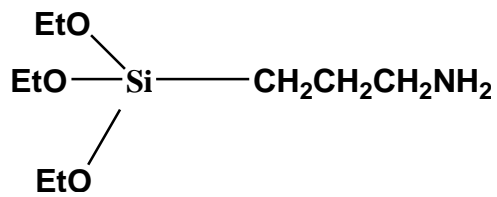
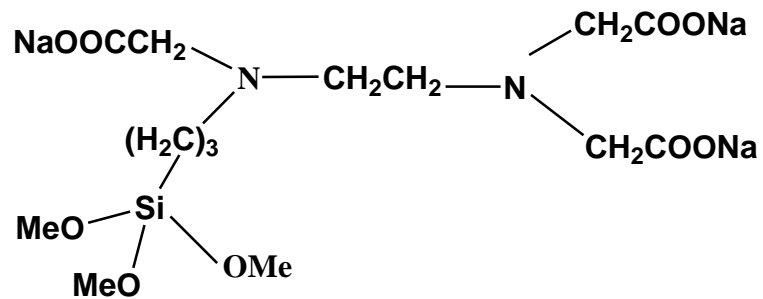
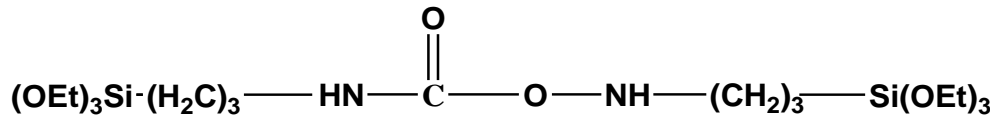


Figure 1.2: Examples of Organosilicon derivatives used in the preparation of ion-exchange films.

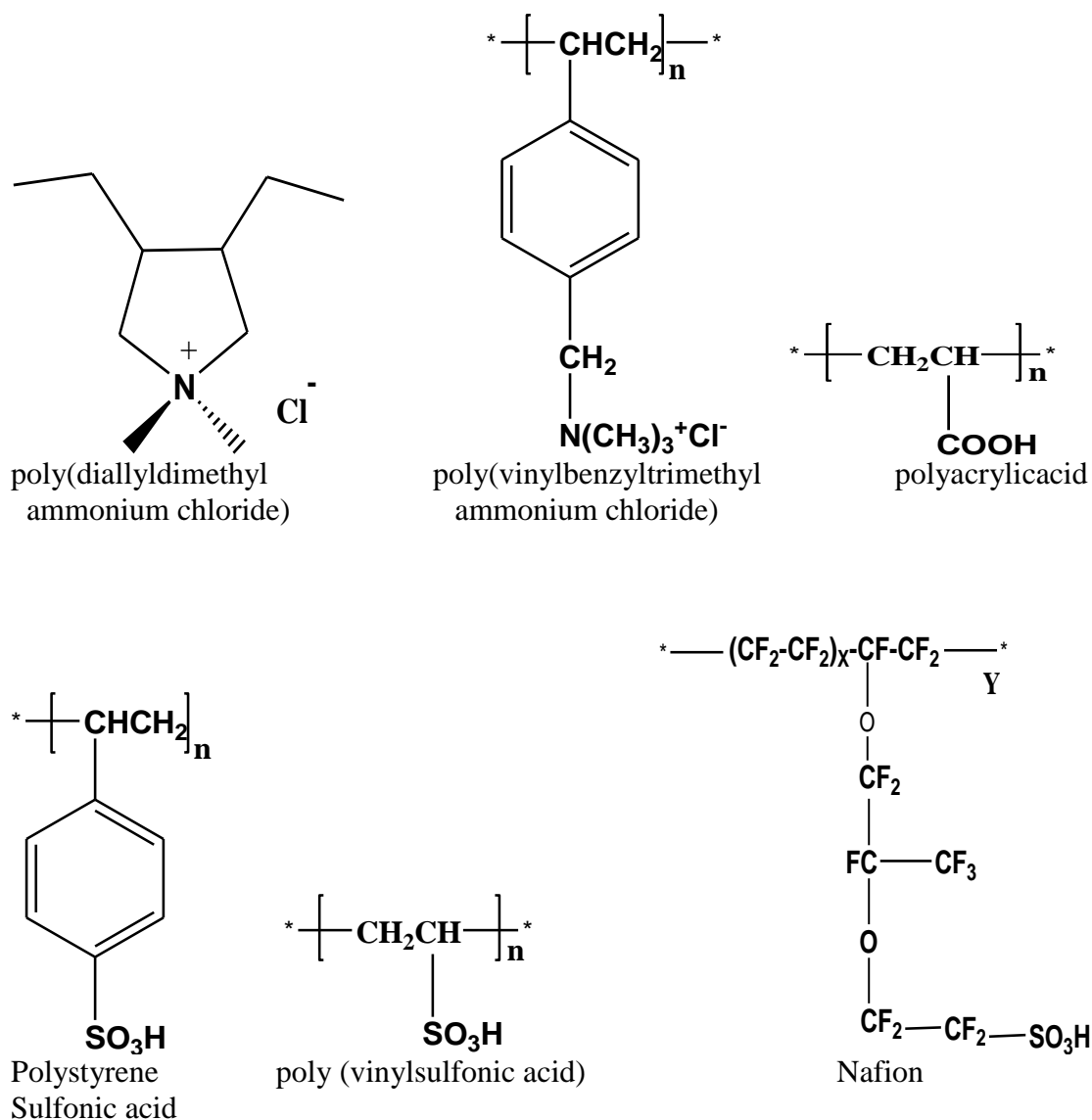


Figure 1.3: Examples of polyelectrolyte's incorporated in sol-gel derived films for ion-exchange applications.

Conclusion

The sol-gel method is a fascinating new method for the generation of new materials. This is because the main advantage of the sol-gel process is that it allows careful control of the size and morphology of clusters/particles in the sol or gel during the early process stage, so that high quality end products (in the form of powders, films or coatings) can be developed to fulfil specific demands. The mild reaction conditions allow the incorporation of organic moieties into inorganic networks. These organic-inorganic hybrid materials are particularly useful because components with different combinations of properties can be blended together. The general properties of materials synthesized by the sol-gel method are high purity, better homogeneity, controlled porosity combined with the ability to form large surface area materials at low temperatures, possibility of preparing multi-component systems with broad ranges of compositions and good dispersion of minor components. The inherent preparative advantages offered by the sol-gel method have prompted us for synthesising new and novel ion exchange materials for recovery of heavy metals and dyes from the aqueous environmental systems.

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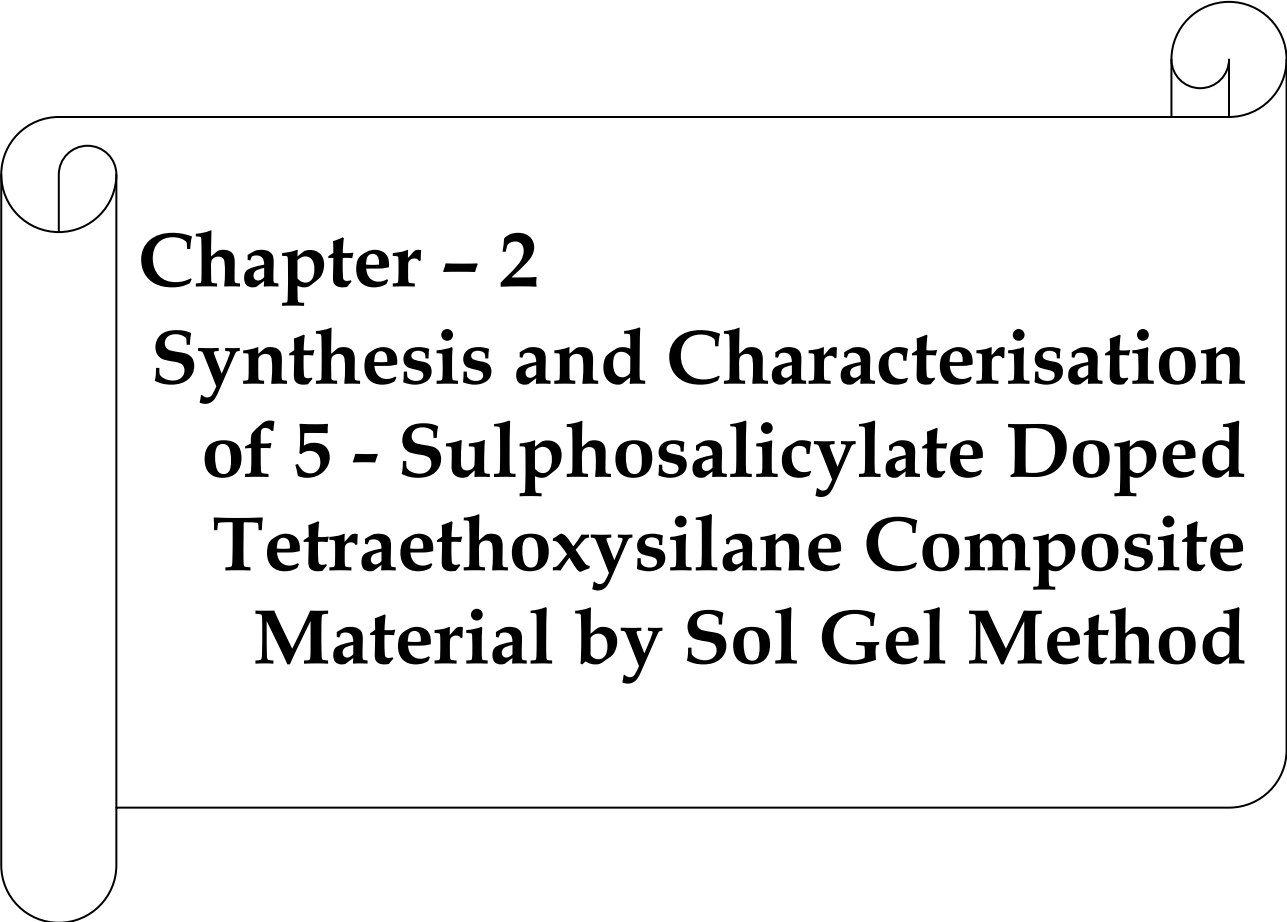
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Chapter - 2
Synthesis and Characterisation
of 5 - Sulphosalicylate Doped
Tetraethoxysilane Composite
Material by Sol Gel Method

Synthesis and Characterization of 5-Sulphosalicylate Doped Tetraethoxysilane Composite Material by Sol-gel Method

ABSTRACT

The sol-gel process provides a versatile method to prepare size, shape and charge selective materials for analysis. We report the synthesis and characterization of a new sulphosalicylate doped tetraethoxysilane composite material by sol-gel method. The synthetic conditions such as reactant concentrations and precipitating agents were varied to optimize the ion exchange properties of this material. The material has an ion exchange capacity of 0.64meq/g(dry) for sodium ions, 0.60meq/g(dry) for potassium ions, 1.84meq/g(dry) for magnesium ions, 1.08meq/g(dry) for calcium ions and 1.36meq/g(dry) for strontium ions. Its X-ray diffraction studies suggest that it is crystalline in nature. The material has been characterized by SEM, IR, TGA and DTG so as to identify the various functional groups and ion exchange sites present in this material. Further, various ion exchange studies such as determination of ion exchange capacity, elution behaviour, pH titration, distribution behaviour towards ion exchange and adsorption behaviour towards certain important dyes have been performed on this material. This material shows selectivity for Mg (II) among alkaline earth metal ions and Ni (II) among the transition metal ions in aqueous solutions. This material, therefore, has potential application for removal of these metal ions from aqueous systems. The material shows remarkable adsorption behaviour towards environmentally important representative dyes like malachite green and methylene blue.

INTRODUCTION

Ion exchange resins comprise one of the most important scientific developments of the 20th century. The early ion exchangers were largely inorganic in origin. Subsequently, the synthetic organic resins, because of the reproducible preparations, dominated the ion exchange scene with excellent mechanical and chemical stability. Synthetic ion exchangers of single and double salts as well as organic resins are being increasingly used for separation of metal ions. The organic resins have qualities of uniformity, chemical stability and stability towards high temperature and radiations¹⁻³. Selectivity towards particular metal ions by inorganic ion exchangers⁴⁻⁹ is one of the important factors for their development and are having extensive applications in separation science especially of heavy metals¹⁰⁻¹⁴. That is the reason why inorganic ion exchangers are of current interest and in addition, these inorganic ion exchangers are resistant to heat and radiation. They are useful in environmental analysis¹⁵ and can also be utilized as solid electrolytes and catalysts¹⁶. Silicates form one of the most important classes of these materials as they have added the advantage of being resistant to thermal and chemical attack^{17, 18}.

Incorporation of a polymer material into an inorganic ion exchanger provides a class of hybrid ion exchangers with good ion exchange capacity, high stability, reproducibility, and selectivity for heavy metal ions. The intrinsic multifunctional character of these materials makes them potentially useful in multiple fields. Illustrative examples of this versatility are their high added value applications such as adsorbent for toxic compounds, catalysts, coatings for corrosion etc.

Organic inorganic hybrid materials prepared by the sol gel method have rapidly become a fascinating new field of research in material sciences. The explosion of activity in this area in the past decade has made tremendous progress in both the

fundamental understanding of the sol gel process and the development and applications of new organic inorganic hybrid materials. The sol-gel process has so far been one of the most attractive ways of synthesizing these porous materials because of the mild synthesis conditions.

Recently, some efforts have been made in our laboratory to synthesize new hybrid types of ion exchange materials, i.e. obtained by the combination of organic polymeric species and inorganic- ionogenic groups/moieties. Sulphosalicylic acid, maleic acid, acrylonitrile, acrylamide and ethyl acrylate when combined with these inorganic moieties produced materials possessing promising ion-exchange characteristics and better stability than their inorganic counterparts. The present paper summarizes our studies on new, novel and crystalline sulphosalicylic acid doped tetraethoxysilane composite polymer material by sol-gel method.

The effluents from textile, leather, food processing, dyeing, cosmetic, paper and dye manufacturing industries are important sources of dye pollution. Many dyes and their breakdown products may be toxic for living organisms. It is, usually, difficult to remove the dyes from the effluents, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater treatments. Therefore, adsorption of dyes is important aspects of wastewater treatment before discharge. Adsorption is believed to be the simplest and most cost effective technique. We have attempted to explore the possibility of synthesizing a low cost material suitable to address the challenges of dye adsorption and recovery from aqueous environmental samples. We found that the new composite material, 5-sulphosalicylate doped tetraethoxysilane composite material, prepared in this work possess excellent adsorption properties towards some important selective dyes such as malachite green and methylene blue.

EXPERIMENTAL

Reagents and Chemicals:

The main reagents used for the synthesis of the sulphosalicylic acid doped tetraethoxysilane composite material were tetraethoxysilane (Merck Germany), hexadecyltrimethylammonium chloride (Merck Germany), sulphosalicylic acid (Glaxo Laboratories India Ltd.) and ethyl alcohol. All the starting reagents were of A. R. grade and were used as purchased.

Instrumentation:

pH measurements were performed using an Eutech Instrument PC 5500. X-ray diffraction spectra was recorded on a Bruker D8 advance diffractometer. Analysis of C, H, S and N were determined on an Elemental Vario Micro CHNS analyzer. IR spectra were recorded as KBr discs on an Interspec-2020 FTIR spectrophotometer in the 4000-450 cm^{-1} range. Electron micrographs were recorded with a Saatchi-S 3000H Scanning electron microscope. An incubator shaker Yellow Line OSC with a temperature variation of $\pm 0.5^{\circ}\text{C}$ was used for equilibrium studies. Exstar 6000 TGA/DTG instrument from SIINT, Japan was used for thermal studies.

Synthesis of the ion exchange material:

A number of samples of the composite ion exchange material were prepared from silica sol using sol gel method. The silica sol was prepared from tetraethoxysilane, deionised water, ethanol, hexadecyltrimethylammonium chloride keeping the molar ratio as 4: 200: 50: 1 respectively and using 0.01M HCl as the catalyst. The resulting solution was heated at 35°C with continuous stirring leading to the formation of a gel.

Prior to gelation, organic dopants were physically doped into the sol. The gelation time was maintained at 24-36 hours. The gel was dried in an oven at 50⁰C. The product was then grounded and studied as xerogel powder. The xerogel was converted into the H⁺ form by treating with 1M HNO₃ for 24 hours. The material obtained was finally washed with deionised water and then dried at 45⁰C. On the basis of Na⁺ ion exchange capacity, appearance and percent yield, sample No. 22 (table 2.1) was selected for further studies. The reproducibility was checked by preparing the samples several times following the same procedure and determining the ion exchange capacity of the material every time, which varied negligibly.

TABLE 2.1

**DIFFERENT ION EXCHANGE SAMPLES WITH VARYING DOPANTS,
THEIR CONCENTRATIONS AND SODIUM ION EXCHANGE
CAPACITIES.**

Sample No.	TEOS (ml)	H₂O (ml)	Ethanol (ml)	Surfactant (ml)	Hcl (ml) 0.01M	Organic Dopants (ml)	Na⁺ IEC in meq/gm
3	2.504	10.08	9.08	2	1	2ml 0.1M Maleic acid	0.15
4	2.504	10.08	9.08	2	1	3ml 0.1M Maleic acid	0.16
5	2.504	10.08	9.08	2	1	2ml 0.1M Sulphosalicylic acid	0.11
6	2.504	10.08	9.08	2	1	3ml 0.1M Sulphosalicylic acid	0.14
7	1.252	5.04	4.54	1	1	4ml 0.1M Maleic acid	0.1
8	1.252	5.04	4.54	1	1	5ml 0.1M Maleic acid	0.23
9	1.252	5.04	4.54	1	1	4ml 0.1M Sulphosalicylic acid	0.24
10	1.252	5.04	4.54	1	1	5ml 0.1M Sulphosalicylic acid	0.06
11	1.252	5.04	4.54	1	1	2ml 0.1M Ethyl acrylate	0.16
12	1.252	5.04	4.54	1	1	3ml 0.1M Ethyl acrylate	0.14
13	1.252	5.04	4.54	1	1	4ml 0.1M Ethyl acrylate	0.09
14	1.252	5.04	4.54	1	1	5ml 0.1M Ethyl acrylate	0.15
15	1.252	5.04	4.54	1	1	2ml 0.1M Acryl amide	0.05
16	1.252	5.04	4.54	1	1	4ml 0.5M Sulphosalicylic acid	0.48
17	1.252	5.04	4.54	1	1	0.09ml Ethyl acrylate	0.04
18	1.252	5.04	4.54	1	1	4ml 1M Sulphosalicylic acid	0.49
19	1.252	5.04	4.54	1	1	5ml 0.5M Maleic acid	0.09
20	1.252	5.04	4.54	1	1	6ml 0.1M Sulphosalicylic acid	0.24
21	1.252	5.04	4.54	1	1	8ml 1M Sulphosalicylic acid	0.35
22	1.252	5.04	4.54	1	1	3ml 1M Sulphosalicylic acid	0.64
23	1.252	5.04	4.54	1	1	5ml 1M Sulphosalicylic acid	0.62
24	1.252	5.04	4.54	1	1	3ml 1M Ethyl acrylate	0.25

FTIR Analysis:

The IR spectrum of the prepared sulphosalicylic acid doped tetraethoxysilane composite material was measured using FTIR. The disc technique using KBr as a matrix was adopted for the recording of the spectra. 10 mg of the exchanger in H⁺ form was thoroughly mixed with 100 mg of KBr and grinded to a fine powder. A transparent disc was made by applying a pressure of 80 psi (1 psi = 6894.76 Pa) in a moisture free atmosphere. The FTIR absorption spectrum was scanned over the wave number ranging from 450 to 4000 cm⁻¹ and is given in Figure 2.1.

Thermal (TGA and DTG) Studies:

Simultaneous TGA and DTG studies of the prepared sulphosalicylic acid doped tetraethoxysilane composite material in H⁺ form were carried out by an automatic thermo balance on heating the material from 0°C to 1000°C at a constant rate (10°C per minute) in the air atmosphere (air flow rate of 200 mL min⁻¹) to investigate the degradation process and the thermal stability of the sulphosalicylic acid doped tetraethoxysilane composite material. The TGA/DTA plots are shown in Figure 2.2.

X-ray Diffraction (XRD):

The X-ray powder diffractometry was carried out using X-ray diffractometer with Ni-filtered Cu-K α X-rays of wavelength ($\lambda=1.54056 \text{ \AA}$). The finely powdered sample of the sulphosalicylic acid doped tetraethoxysilane composite material were packed into a flat aluminium sample holder, where the X-ray source was a rotating anode operating at 30 kV and 30 mA with a copper target. Data were collected between 10° and 70° in 2 θ and scan rate of 2° min⁻¹. Figure 2.3 shows the X-ray diffraction pattern of the material.

Scanning electron microscopy:

The ground sulphosalicylate doped tetraethoxysilane composite material in H⁺ form was stocked over a holder. Then it was gold sputtered before examination. Microphotographs of the original form of the composite material were obtained by the scanning electron microscope at various magnifications. Electron micrographs were recorded for the composite material by using scanning electron microscope operating at 5.0 kV at two different magnifications. The micrographs are shown in Figure 2.4 (a) and Figure 2.4 (b).

Elemental analysis:

Elemental analysis was carried out on the prepared sulphosalicylic acid doped tetraethoxysilane composite material in H⁺ form using Elemental Vario Analyzer to determine carbon, hydrogen, nitrogen and sulphur contents of the composite polymer material. The percentage composition of C, H, N, and S was found to be 39.07%, 5.988%, 1.466% and 5.266% respectively.

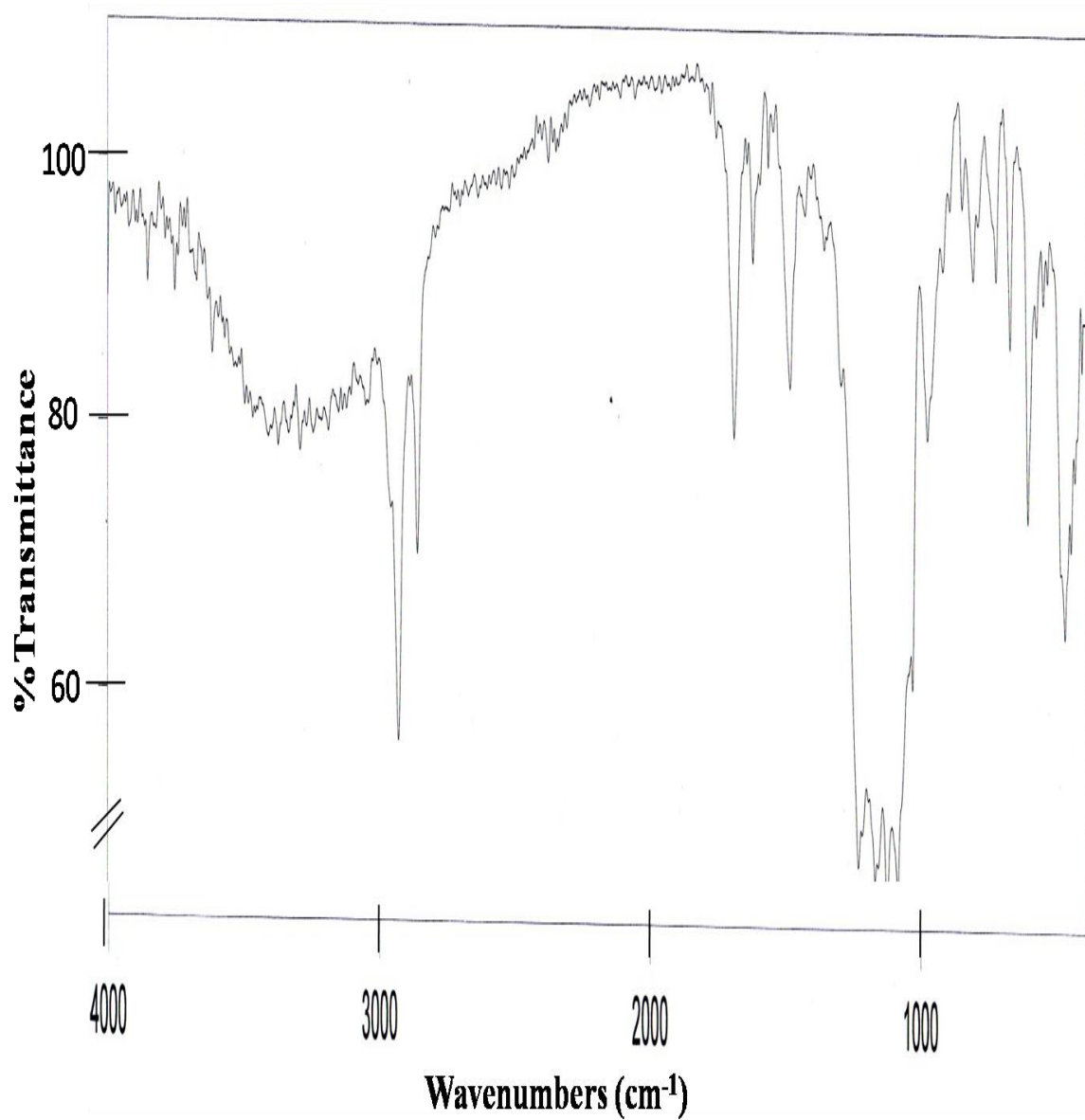


Figure 2.1: FTIR Spectrum of sulphosalicylic acid doped tetraethoxysilane composite material.

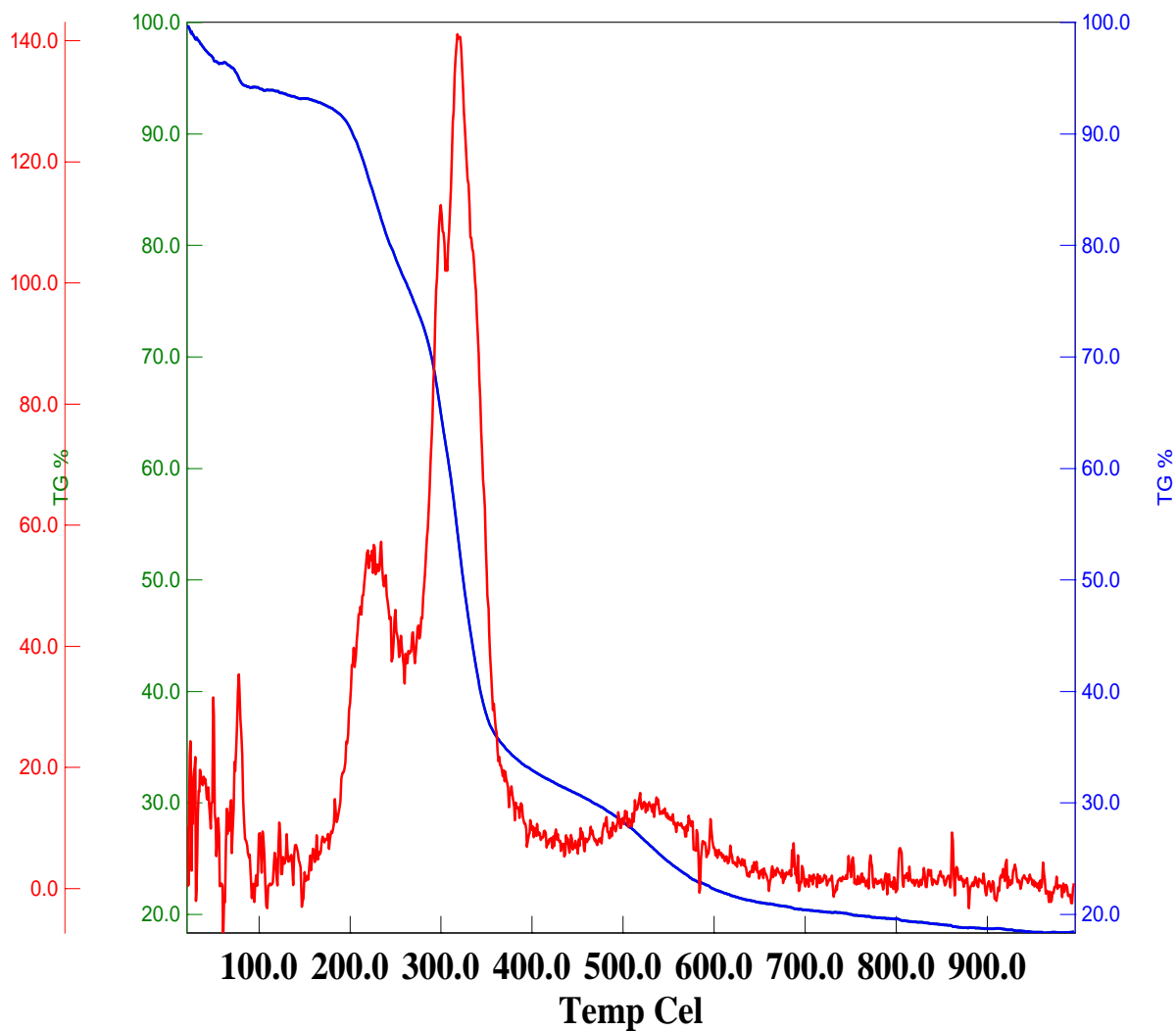


Figure 2.2: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of sulphosalicylate doped tetraethoxysilane composite material.

(Temperature range: 0-1000⁰C, Heating rate: 10⁰C min⁻¹).

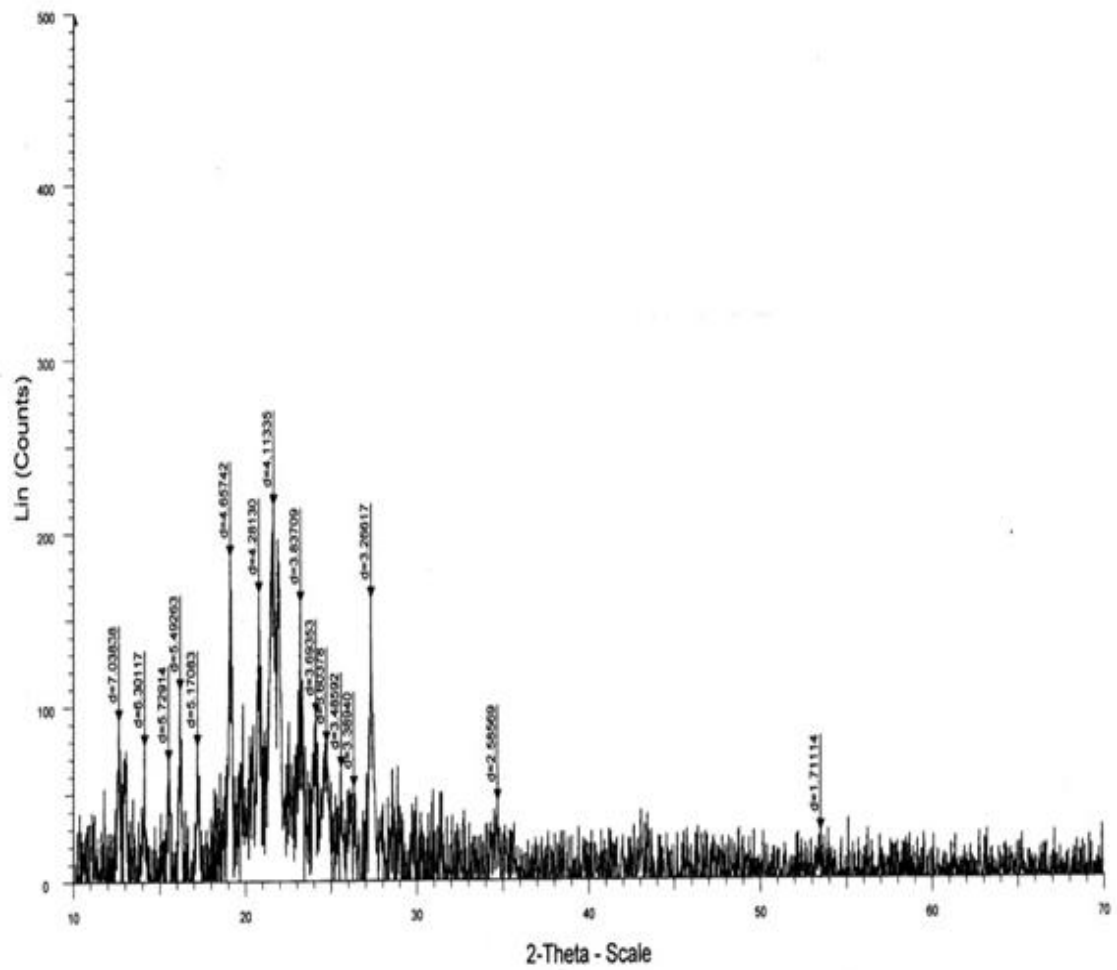


Figure 2.3: XRD of sulphosalicylic acid doped tetraethoxysilane composite material.

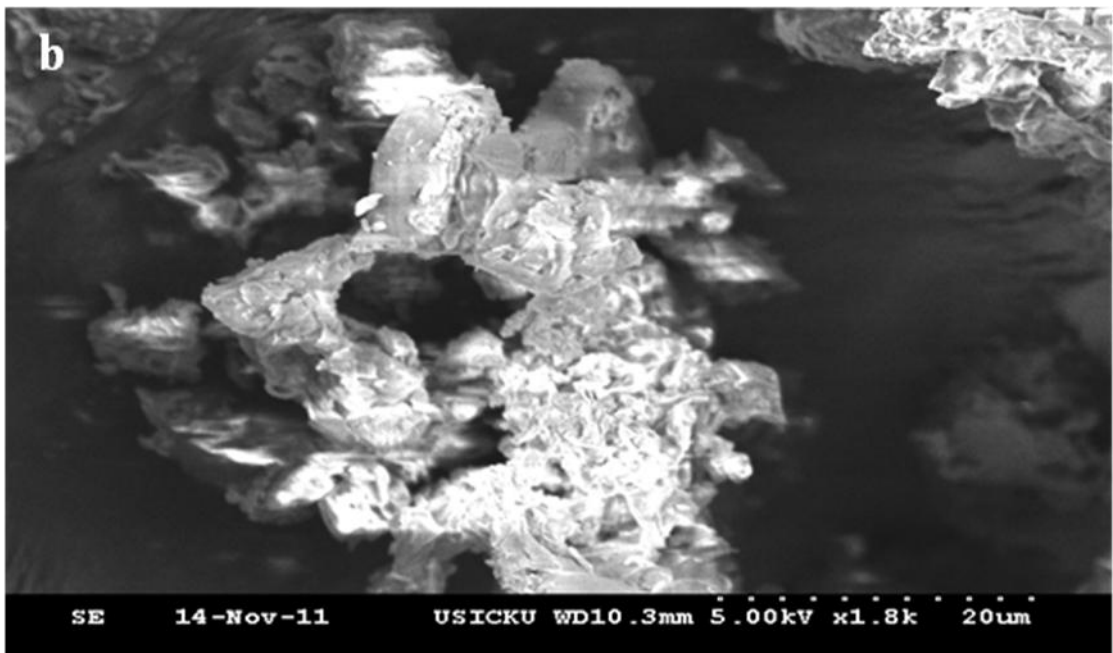
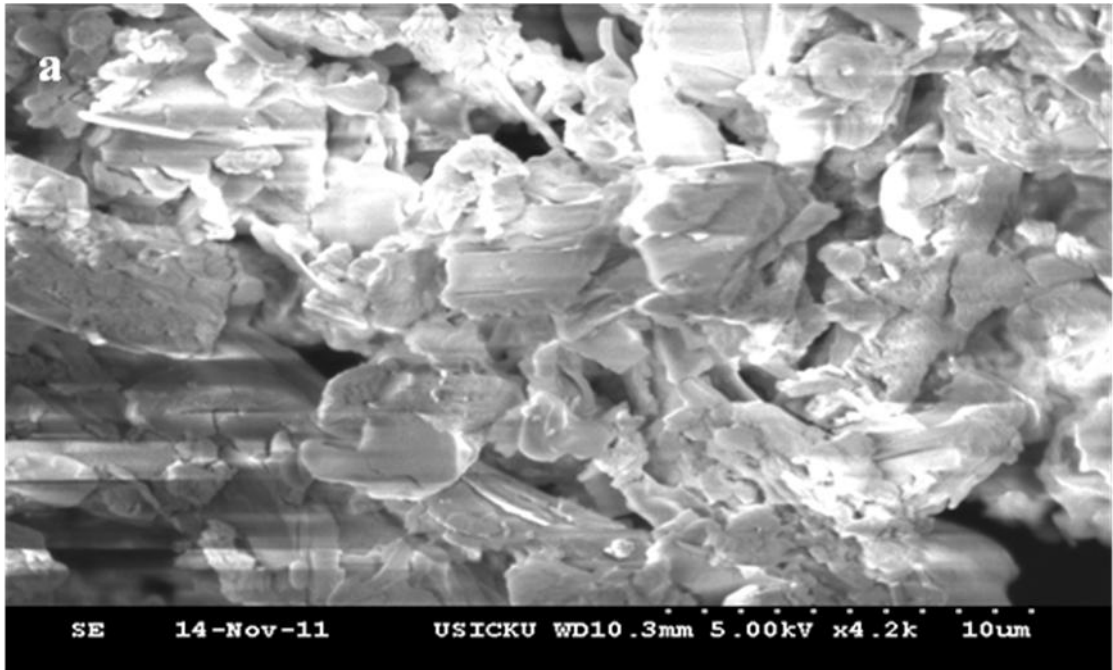


Figure 2.4: SEM pictures of sulphosalicylic acid doped tetraethoxysilane composite material at (a) 10µm and (b) 20µm

Ion-exchange capacity (i.e.c.):

The ion-exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by the sulphosalicylic acid doped tetraethoxysilane composite material was determined by standard column process. One gram of the dry composite polymer material in the H^+ form was taken into a glass column having an internal diameter ~ 1 cm and fitted with glass wool support at the bottom. 250 ml of one molar $NaNO_3$ solution was passed through it maintaining a very slow flow rate (0.5 ml min^{-1}). The effluent was titrated against a standard 0.01M NaOH using phenolphthalein indicator. The Na^+ ion exchange capacities of the various samples in terms of the milli equivalents per dry gram are shown in table 2.1.

Ion exchange capacities for different metal ions:

Ion exchange capacity of the sulphosalicylic acid doped tetraethoxysilane composite material was also determined by passing different alkali and alkaline earth metal nitrate solutions through the composite material column in the H^+ form by the method described above. The results are shown in table 2.2.

Elution behaviour:

The column containing one gram of the sulphosalicylic acid doped tetraethoxysilane composite material in the H^+ form was eluted with 1M $Mg(NO_3)_2$ solution (100 ml) having a standard flow rate of 0.50 ml min^{-1} . The effluent was collected in 10 ml fractions and the amount of H^+ ions released in each fraction was determined titrimetrically using standard sodium hydroxide solution. This experiment was conducted to find out the minimum volume necessary for complete elution of H^+ ions,

which reflects the efficiency of the column. Figure 2.5 shows the elution behaviour of the exchanger.

pH titrations:

Cation exchangers in H^+ form can be considered as insoluble acids. They can, therefore, be titrated against an alkali, as usual, which gives the nature and the number of exchange sites present in the ion exchanger. The neutralization of the insoluble acid can be observed by recording the pH of the supernatant solution while the titration is in process. Hence, pH titrations on the sulphosalicylic acid doped tetraethoxysilane composite material were conducted by the non-equilibrium method as below:

Non equilibrium Process:

Portions (500 mg) of the sulphosalicylic acid doped tetraethoxysilane composite material were mixed with 100 mL of 0.01 M salt solution (NaCl). This mixture was kept for 1 h and titrated against 0.01M solutions of the respective alkali, recording the pH of the solution after each addition of 1.5 mL of the titrant till the pH became constant. The back-titration was then carried out by adding the same fractions of 0.01M HNO_3 to the solution. A blank pH titration was also run by titrating the salt solutions against respective base and HNO_3 solution before the exchanger was added. From the pH values before and after the exchange process, the milli equivalents of OH^- ions consumed were determined. Mill equivalents of OH^- ions consumed by the exchanger were plotted against the corresponding pH values (Figure 2.6.)

Distribution Studies:

The distribution coefficient (K_d) of metal ions Mg^{2+} , Ca^{2+} , Cd^{2+} , Ni^{2+} were determined by batch method in different solvents of analytical interest. Distribution coefficients were actually used to access the overall ability of the composite material to adsorb/remove the ions of interest under different sets of conditions. Various portions of (100 mg each) the sulphosalicylic acid doped tetraethoxysilane composite material in H^+ form were taken in Erlenmeyer flasks and mixed with 10 ml of different metal nitrate solution in the required medium and subsequently shaken for 4h in temperature controlled shaker at $19^{\circ}C$ to attain the equilibrium. The amount of metal ion before and after the equilibrium was determined by EDTA titration¹⁹. The distribution quantity is the ratio of the amount of metal ions in the exchanger phase and in the solution phase. In other words, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion exchange material and hence mathematically can be calculated using the formula given as

$$K_d = \frac{\text{amount of solute on ion exchanger}}{\text{Weight of ion exchanger} \div \frac{\text{amount of solute in solution}}{\text{Volume of solution, } cm^3}}$$

That is,

$$K_d = \left[\frac{I - F}{F} \right] \times \frac{V}{M} (mLg^{-1})$$

Where, I is the initial amount of metal ion in the aqueous phase (pre-equilibrium),

F is the final amount of metal ion in the aqueous phase (equilibrium),

V is the volume of the solution (ml), and

M is the amount of cation-exchanger (g).

The sorption of metal ions involves the ion exchange of the H^+ ions in exchanger phase with that of metal ions in solution phase.

Adsorption Capacity of the Composite Material towards Some Selective Dyes:

Adsorption capacity of the sulphosalicylic acid doped tetraethoxysilane composite material towards some selective dyes was carried out by passing aqueous solutions of dyes of varying concentrations through SATEOS adsorbent column. The basic dye, malachite green having chemical formula $C_{23}H_{25}N_2Cl$, molecular weight 364.63 g/mol, and methylene blue having molecular formula $C_{16}H_{18}N_3SCl$ and molecular weight of 319.85 were used. Sample solutions of the desired concentration were prepared in double distilled water.

In each experiment, a definite amount (250ml) of the dye solution was passed through the column loaded with 1gram of the composite material in H^+ form. Absorbance values were measured before and after passing the dye solutions through the column loaded with the composite material, with UV-Visible spectrophotometer (Schimadzu UV 3600) using a quartz cell of 1 cm path length. The dye concentration was varied to investigate the effect on adsorption capacity. Figure 2.7 and Figure 2.8 indicate the adsorption of the composite material towards malachite green and methylene blue dyes respectively. The concentration changes of the sample solutions after passing through the column of the composite materials are reported in Table 2.5.

TABLE 2.2**ION EXCHANGE CAPACITY OF SULPHOSALICYLIC ACID DOPED
TETRAETHOXYSILANE COMPOSITE MATERIAL FOR DIFFERENT
METAL IONS.**

S. No.	Cation	Salt used	Ionic radii (A^0)	Hydrated ionic radii (A^0)	IEC in meq/g
1	Na^+	NaNO_3	0.97	2.76	0.64
2	K^+	KNO_3	1.33	2.32	0.68
3	Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	0.78	7.00	1.84
4	Ca^{2+}	$\text{Ca}(\text{NO}_3)_2$	0.94	6.30	1.08
5	Sr^{2+}	$\text{Sr}(\text{NO}_3)_2$	1.06	6.10	1.36

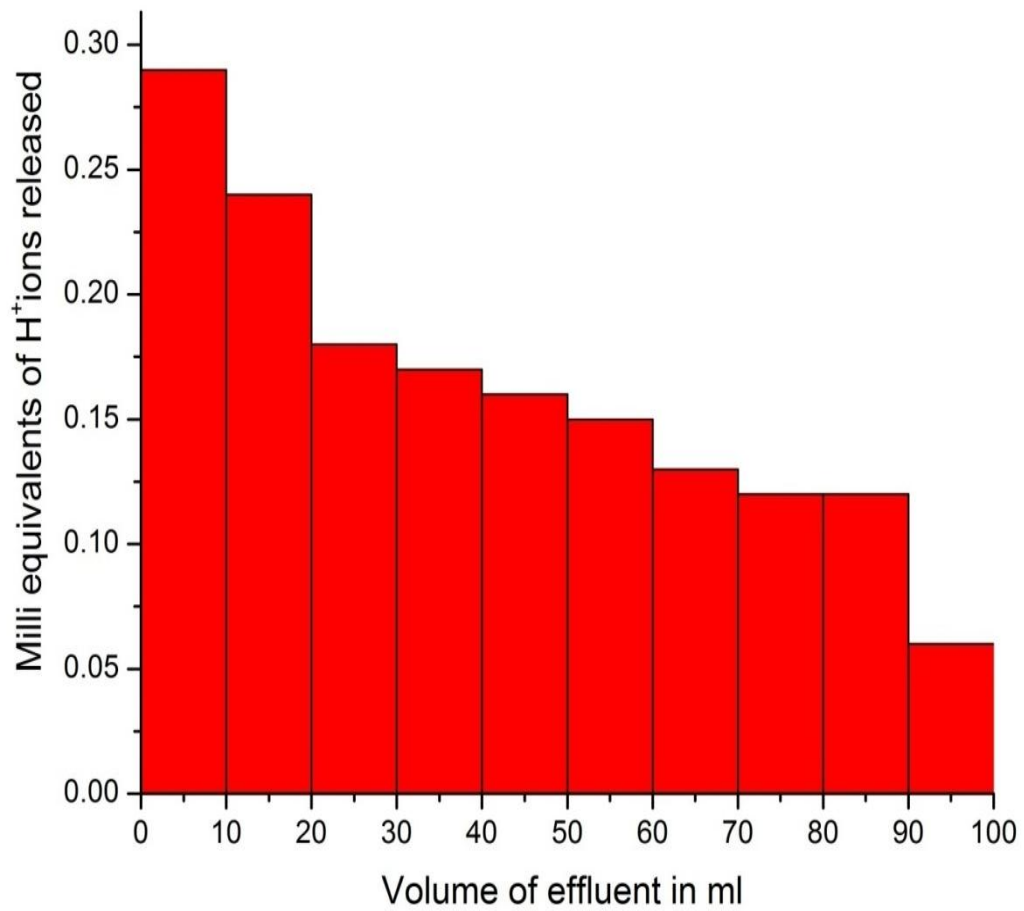


Figure 2.5: Histogram showing elution behaviour of Sulphosalicylic acid doped tetraethoxysilane composite material with 1M Magnesium Nitrate.

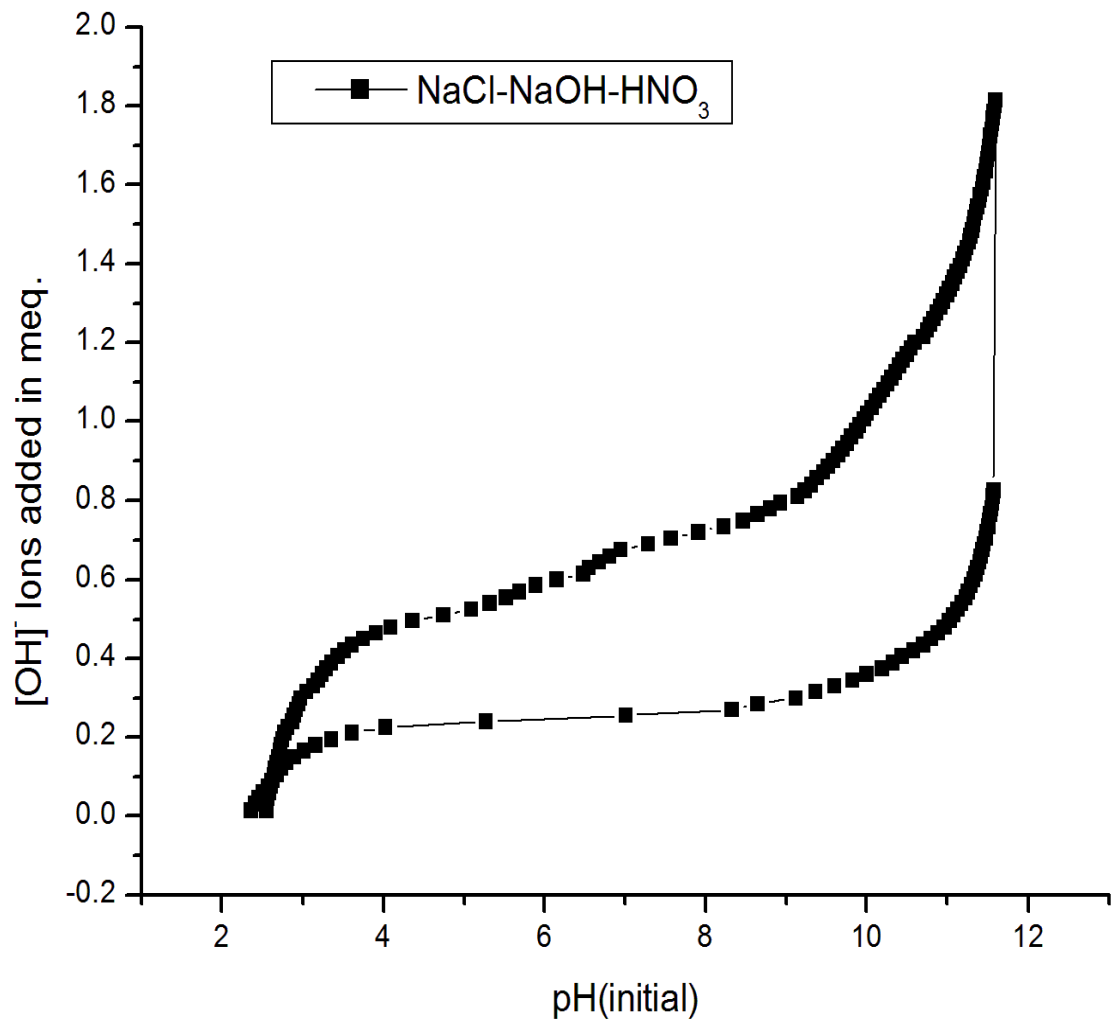


Figure 2.6: Non equilibrium pH Titration curve of Sulphosalicylic acid doped tetraethoxysilane composite material.

TABLE 2.3

**K_d VALUES OF SOME METAL IONS ON THE SULPHOSALICYLIC ACID
DOPED TETRAETHOXYSILANE COMPOSITE MATERIAL IN NITRIC
ACID AND PERCHLORIC ACID SOLUTIONS.**

Metal Ion	K_d Values		
	0.1M HNO₃	0.01M HNO₃	0.01M HClO₄
Ca ²⁺	2×10 ²	1.5×10 ²	1.5×10 ²
Mg ²⁺	2×10 ²	1.5×10 ²	2.33×10 ²
Ni ²⁺	1.5×10 ²	4×10 ²	9×10 ²
Cd ²⁺	1.5×10 ²	2.33×10 ²	4×10 ²

TABLE 2.4**COLOUR INDEX, λ_{Max} , MOLECULAR WEIGHT OF METHYLENE BLUE AND MALACHITE GREEN DYES.**

Dye Stuff	Colour Index No.	λ_{Max}	Molecular Weight
Methylene blue	52015	660nm	319.85g/mol
Malachite green	42000	615nm	364.63g/mol

TABLE 2.5**CONCENTRATION VALUES OF THE AQUEOUS SOLUTIONS OF DYES BEFORE AND AFTER LOADING ON THE COMPOSITE MATERIAL.**

S.No.	Dye Stuff	Conc. Before loading	Conc. After loading	Conc. difference
1.	Methylene blue	5ppm	3.38ppm	1.62 ppm
		10ppm	5.88ppm	4.12ppm
		15ppm	9.34ppm	5.66 ppm
2.	Malachite green	5ppm	0.3ppm	4.7ppm
		10ppm	1.30ppm	8.7ppm
		20ppm	4.92ppm	15.08ppm

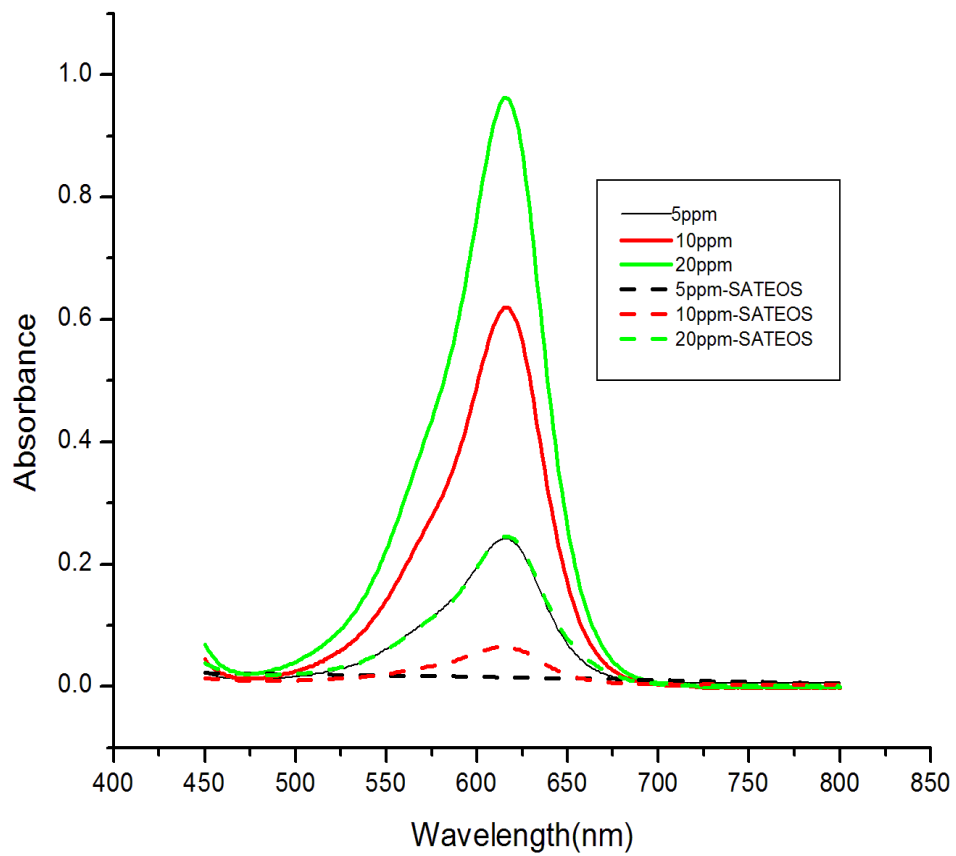


Fig 2.7: UV spectra of aqueous solutions of malachite green, of varying concentrations, before (solid lines) and after (dashed lines) passing through a column of SATEOS composite material.

(Concentration values of the solutions quoted are the initial ones, before loading on the column bed)

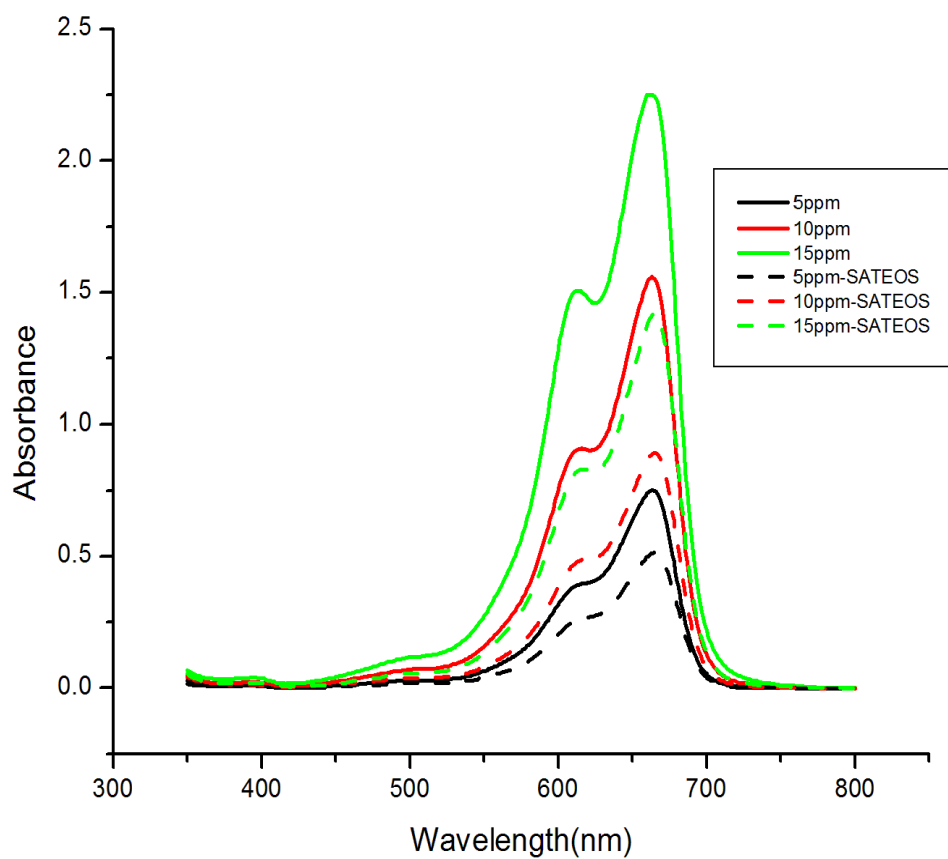


Fig 2.8: UV spectra of aqueous solutions of methylene blue, of varying concentrations, before (solid lines) and after (dashed lines) passing through a column of SATEOS composite material.

(Concentration values of the solutions quoted are the initial ones, before loading on the column bed)

RESULTS AND DISCUSSION

In this study, a number of samples of the composite material, sulphosalicylate doped tetraethoxysilane (SATEOS), were prepared by the sol gel method. Among these, the sample-22 possessed relatively better Na^+ ion exchange capacity (0.64meq/dry gram) and was, therefore, chosen for detailed studies and characterization.

To confirm the presence of various functional groups and composite nature of the synthesized material, we recorded the IR spectrum of the composite material at room temperature (Figure 2.1). Some specific bands clearly point out towards the existence of the 5-sulfosalicylate and tetraethoxysilane moieties in the composite polymer. At 2927cm^{-1} an intense band appears, characteristic of a stretching vibration of the OH groups of silanols, as well as the ethanol and the water occluded in the gels after its gelation. Generally this band is present near 3400cm^{-1} ²⁰, but shifts to the low energy region in the doped material, perhaps due to intermolecular hydrogen bonding with the dopant, that weaken the $\text{SiO}_2\text{-OH}$ bonds. The presence of the hydrogen-bonded hydroxyl groups on the oxide surface or due to adsorbed molecular water is often indicated by the shift of their IR peaks relative to the isolated unperturbed hydroxyl groups on the un-doped substrate. Thus, in general, involvement of an OH group in a hydrogen-bonding interaction causes broadening and a shift to a lower wave number of the IR band associated with the OH stretching vibration. The medium intensity band at 2854cm^{-1} in the IR spectrum are assigned to the C-H stretching modes of the 5-sulfosalicylate moiety. The vibrational band due to C =O stretching mode is the most characteristic band in the IR spectra of the compounds containing a COOH group and is expected in the range $1660\text{-}1700\text{ cm}^{-1}$ ²¹. This characteristic band due to $\nu(\text{C}=\text{O})$ of 5-sulphosalicylate moiety in the composite material is observed as relatively a medium intensity band at 1682cm^{-1} in the IR spectrum, close to the

position of $\nu(\text{C}=\text{O})$ of free 5-sulphosalicylic acid ^{22, 23}. At about 1614 cm^{-1} , an OH bending vibration peak characteristic of the intercalated water molecules and hydroxylated silanol groups on the silica surface is observed. This band is important because it also provides information on the amount of water and ethanol occluded in the gel. The narrow intense peak at 1479cm^{-1} may be due to the $\nu(\text{C}-\text{O})$ stretching motion of the sulphosalicylate group. The low intensity peaks due to the in-plane bending modes $\delta(\text{OH})$ of COOH , referred as $(\delta(\text{OH})\text{c})$ and $\delta(\text{OH})$ of the hydroxyl group attached to the phenyl ring, referred as $(\delta(\text{OH})\text{h})$ in sulphosalicylate part are assigned at 1347cm^{-1} and 1288cm^{-1} respectively. The group of peak between 1348 to 1480cm^{-1} may also be due to the vibrations excited in the benzene ring. The group of overlapping peaks which constitute a broad band between 1077cm^{-1} - 1220cm^{-1} is characteristic of the SiO_2 group in different types of silicate matrix ^{24, 25}. The partially resolved peak near 1021cm^{-1} is assigned to anti-symmetrical stretching of the bridging oxygens along a parallel line to $\text{Si}-\text{O}-\text{Si}$ group with a substantial amount of silicon motion ²⁶. At 966cm^{-1} , the characteristic peak of silanol groups ($\text{Si}-\text{OH}$) appears at relatively higher intensity. The out of plane bending modes $\gamma(\text{OH})\text{c}$ and $\gamma(\text{OH})\text{h}$ are assigned at in the region 914cm^{-1} and 664cm^{-1} , respectively. The peak with moderate intensity at 599cm^{-1} may be due to SO_2 scissoring or wagging vibration. At 461cm^{-1} stretching motion of all bridging is observed, corresponding to a completely symmetric stretching motion of all bridging oxygen atoms along the bisectors of the $\text{Si}-\text{O}-\text{Si}$ angles ²⁰.

In order to analytically characterize the sample, thermo gravimetric analysis (TGA) as well as differential thermal analysis (DTA) was performed. Figure 2.2 shows the thermo gravimetric analysis (TGA) curve (temperature range: $20-900^{\circ}\text{C}$) which exhibits four distinct stages of weight loss. The first stage of weight loss of about 5%

completes at a temperature of 100⁰C, which stems from the evaporation of external water molecules and residual solvent from the surface of the composite material. The second, observed between a temperature range of 150-250⁰C, exhibit a further weight loss of about 15%, which may be due to the loss of interstitial/intercalated water molecules. The third stage of sharp weight loss of about 60% between a temperature range of 250-400⁰C may be attributed to the degradation of the sulphosalicylate moiety, incorporated surfactant molecules and the total removal of the residual organic composites from the material. Further weight loss beyond 400⁰C may be due to the condensation process taking place and seems to be completed at 900⁰C. The DTG curve (Figure 2.2) shows four distinct endothermic peaks at 100⁰C, 200⁰C, and 300⁰C, corresponding to four stages of weight loss during temperature rise from 20-900⁰C.

XRD analysis was carried out for structural identification of the composite material in the 2θ range between 10 and 70 degree, as shown in Fig. 2.3. The X-ray diffraction spectrum of the composite polymer material confirms the crystalline nature of the material. The diffractogram was indexed using powder -X software. Calculation of cell parameters reveals that this crystal belongs to hexagonal crystal structure. The cell parameters for this crystal are $a = b = 8.9876\text{Å}$, $c = 10.87654\text{Å}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$.

Scanning electron microscopy was performed to gain information about the morphological characteristics of the material. The SEM pictures of the composite polymer material at two different magnifications shows the presence of sheet like structures (Fig. 2.4).

The chemical composition data are as follows: nitrogen 1.46%; carbon 39.07%; hydrogen 5.988% and sulphur 5.266%. These results indicate the molar ratio of N, C, H, and S in the composite polymer material is 1:4:4:26.

In order to investigate the working capacity of the composite polymer material as an ion-exchanger, the ion exchange capacity of some monovalent and divalent cations were determined (Table 2.2). The ion exchange capacity increases with the decrease in hydrated ionic radii, except in case of Mg^{2+} ions. This trend in the exchange capacity suggests that the exchange of these cations take place in the hydrated form. The monovalent/divalent exchanges show that the replacement of the ions becomes progressively less favourable as the ions decrease in hydrated cation radius. This observation is in line with the previous conclusions summarized by other workers²⁷⁻²⁸ that the entropy contributions to the free energies of exchange are unfavourable to the uptake of smaller hydrated cations. The interesting feature shown by the composite polymer material is that exchange capacity of alkaline earth metals is greater than alkali earth metal ions. The material appears to have a selective affinity for Mg^{2+} ions among the alkaline earth metals as it shows a maximum ion exchange capacity (1.86 meq/dry gram) for this ion (table 2.2)

The efficiency of the exchange process on this material in the column form is studied by evaluating the elution behaviour of 1 g column bed (Figure 2.5). We found that the exchange is quite fast at the beginning of the process, as most of the exchangeable H^+ ions are eluted out in the first 70 ml of the effluent.

In order to check the reversibility of the exchange process on these materials the pH titrations were performed. The plots of mill equivalents of OH^- ions consumed vs pH, obtained during the forward and reverse pH titration under non-equilibrium conditions

are shown in Figure 2.6. It is evident from the pH titration plots that the cation exchange reaction is almost reversible.

The distribution studies (Table 2.3) for a number of metals indicate that the composite polymer material is highly selective for Ni (II) in comparison to the other metal ions studied in different solvent systems. The differential selectivity of metal ions depend on a variety of factors, such as size, charge, complex formation and the chemical conditions such as the nature of the solvent and the pH. The greater selectivity for this ion may be due to the reason that the size of this cation just matches the size of the pores of matrix, leading enhanced accessibility of Ni (II) ions to the ionogenic sites. Therefore, this cation exhibits a preferred binding to the matrix over the cations with inappropriate sizes, which form weaker bonds with the polymer framework. This behaviour can be useful for the qualitative separation of Ni (II) from other metal ions.

The SATEOS composite material exhibits remarkable adsorption behaviour towards the two representative dyes and demonstrates a promising potential for the recovery of this class of dyes from aqueous systems. However, from the adsorption capacities of the dyes towards SATEOS, we find that malachite green is adsorbed much more effectively than the methylene blue. Table 2.5 summarizes the concentration of the dye loaded and the concentration of the dye adsorbed after passing through a column loaded with SATEOS which has been calculated from the calibration curves.

CONCLUSION

The new composite materials, SATEOS, synthesized in this work by sol-gel method, possess some novel characteristics as an ion-exchanger and an adsorbent. The material is crystalline in nature and shows higher degree of selectivity for Mg (II) ions among the alkali and alkaline earth metals and for Ni (II) ions among the transition metal ions. It would be expected to usefully scavenge these metal ions from laboratory waste solutions and other polluted water samples. The remarkable efficiency of this novel material for adsorption of dyes from aqueous systems has been demonstrated, which makes it a potential candidate for useful applications in environmental clean-up and analysis.

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