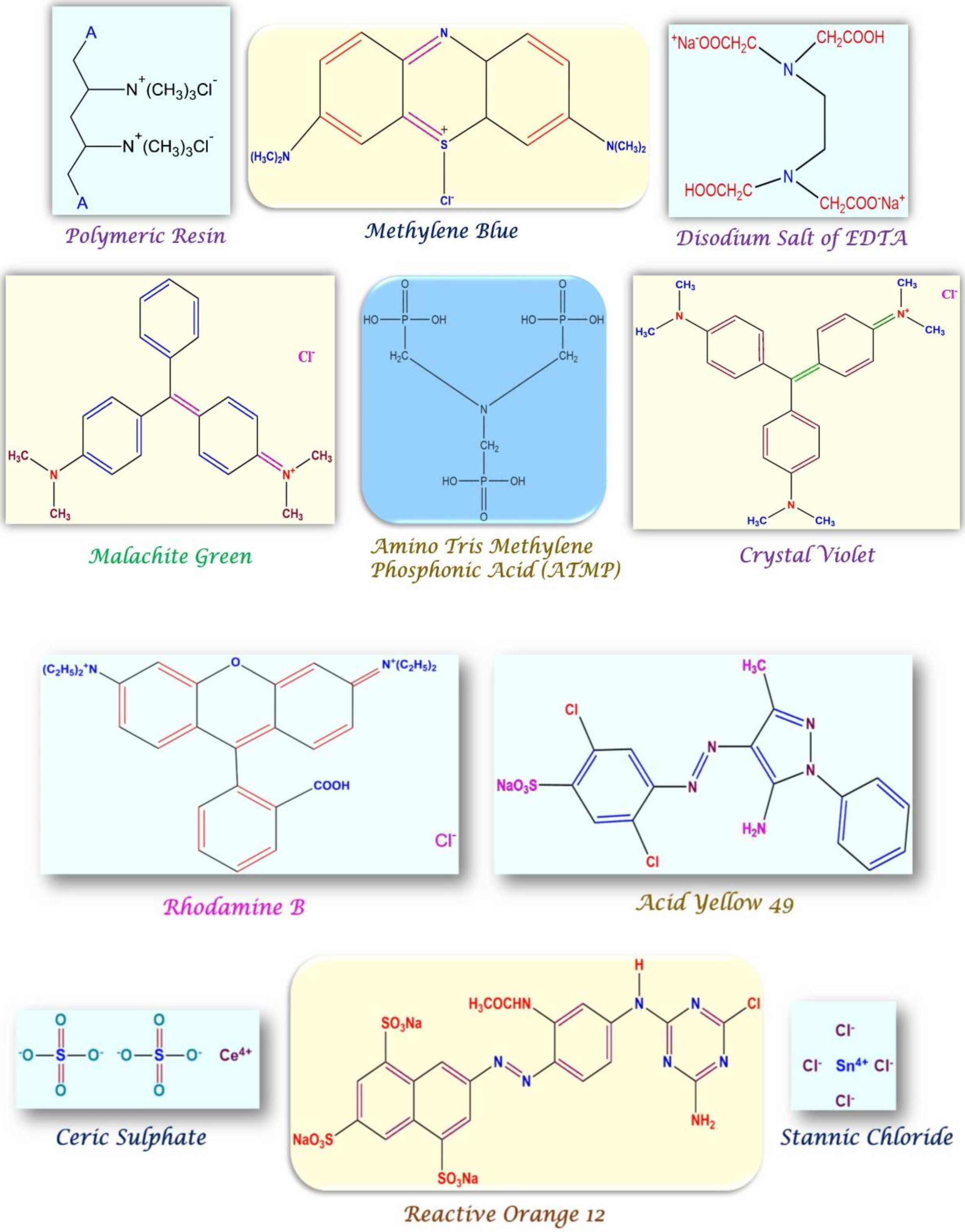
This chapter contains a full list of the materials used to produce the adsorbent. The improved adsorbent's sol-gel procedures have also been explained. This chapter also describes the various characterization methods applied in this investigation.

2.1. Materials

Amberlite IRA-400(Cl^-) resin (purchased from Merck India), disodium salt of ethylene diamine tetra acetic acid (Na_2EDTA) [M_w = 372.24 g/mol] (from BIRCH), metal salts (cobalt(II)sulphate [M_w = 154.99 g/mol], nickel nitrate [M_w = 332.24 g/mol], cupric acetate [M_w = 199.65 g/mol], zinc sulphate [M_w = 332.24 g/mol], lead nitrate [M_w = 332.24 g/mol], cadmium nitrate [M_w = 332.24 g/mol], mercury nitrate [M_w = 332.24 g/mol] (from S d fine-chem. Limited) indicators (xylenol orange, fast sulphone black-T, murexide), ceric sulphate [M_w = 332.24 g/mol], stannic chloride [M_w = 260.5 g/mol], methylene blue (MB) [M_w = 319.85 g/mol], malachite green (MG) [M_w = 364.911 g/mol], crystal violet (CV) [M_w = 407.979 g/mol], rhodamine B (RB) [M_w = 479.02 g/mol], acid yellow 49 [M_w = 426.3 g/mol], reactive orange 12 [M_w = 739.00 g/mol] microscopic grade (98%), hydrochloric acid [HCl] (99%, AR grade) [M_w = 36.46 g/mol], nitric acid [HNO_3] (99%, AR grade) [M_w = 63.01 g/mol], sulphuric acid [H_2SO_4] (99%, AR grade) [M_w = 98.07 g/mol], oxalic acid (99.5%, AR grade) [M_w = 126.07 g/mol], sodium acetate (99%, AR grade) [M_w = 136.08 g/mol], sodium hydroxide [NaOH] (99%, AR grade) [M_w = 40 g/mol], ammonium nitrate (98%, AR grade, extra pure) [M_w = 80.04 g/mol], perchloric acid (70%, AR grade) [M_w = 100.46 g/mol], acetic acid (99.5%, AR grade) [M_w = 60.05 g/mol] have been acquired from Loba Chemicals, India. Hydro-Chem India Private Ltd. furnished ATMP (amino tris-(methylene phosphonic acid) [M_w = 299.07 g/mol]. Glassware's were washed, cleaned and rinsed with dilute hydro chloric acid, distilled water and de-ionized water (D/W), respectively. All reagents used in the present work were of analytical grade and solutions were prepared in de-ionized water. In **Scheme 2.1**, some of the study's material structures are depicted.



Polymeric Resin

Methylene Blue

Disodium Salt of EDTA

Malachite Green

Amino Tris Methylene Phosphonic Acid (ATMP)

Crystal Violet

Rhodamine B

Acid Yellow 49

Ceric Sulphate

Reactive Orange 12

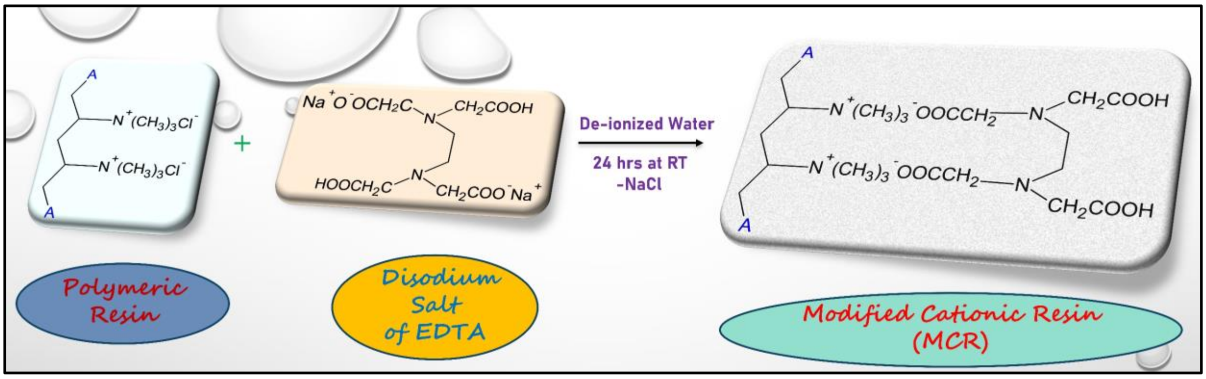
Stannic Chloride

Scheme 2.1. Chemical structures of material used.

2.2. Methods

2.2.1. Modification of Amberlite IRA-400(Cl$^-$) resin

MCR was prepared by treating 100 g of Amberlite IRA-400(Cl$^-$) resin with 1,000 mL of aqueous solution of 0.01 M (Na_2EDTA) solution in a round bottom flask. Contents of flask were left for 24 h with constant shaking to ensure the complete modification. The MCR was separated from the aqueous solution and washed several times with de-ionized water until the supernatant liquid was found free from chloride ion, the resin was dried in an electric oven (60°C). Step by step procedure is shown in **Scheme 2.2** and **Figure 2.1**.



Scheme 2.2. Synthesis of Amberlite IRA-400(Cl$^-$) resin.

2.2.2. Synthesis of Metal (IV) phosphonates

Tetravalent metal phosphonates are synthesized through sol-gel technique.

2.2.2.1. Sol-gel method

Solid materials can be made from tiny molecules using a technique called the sol-gel process in materials science. To create inorganic materials like glasses and ceramics, sol-gel chemistry has developed into a potent technique [1–3]. The procedure is called "sol-gel" since of the unique rise in viscosity that takes place at a specific stage in the process flow. This wet-chemical method of making materials begins with a solution of chemical or colloidal components (sol for solution or nanoscale particle). Low temperatures are employed to generate an interconnected network (gel). The creation of a sol, its gelation, and the solvent's removal can all be considered steps in the sol-gel process. The different phases of the sol-gel process are illustrated in **Figure 2.1**. The typical feature of sol-gel processing is a rapid increase in viscosity, indicative of the beginning of gel formation. The sol-gel method is distinct from precipitation in that it might stabilize a finely dispersed (mostly colloidal) phase in solution.

When the metal centers are joined by oxo (M-O-M) or hydroxo (M-OH-M) bridges, metal-oxo or metal-hydroxo polymers appear in solution, where M is the metal atom. This is the general process of forming a metal oxide [4,5]. Materials generated from sol-gel frequently exhibit distinctive chemical (stability of solvents and hydrophobicity) and physical properties (morphology, porosity, transparency, mechanical and thermal stability). By applying the sol-gel technique, a variety of complex material forms, such as bulk, powder, thin film, aerogel, wire, fibers, particulates, composites, etc., have been produced [6,7]. The theory and application of sol-gel science are the exclusive focus of a number of textbooks and reference sources that are comprehensible [8–10].

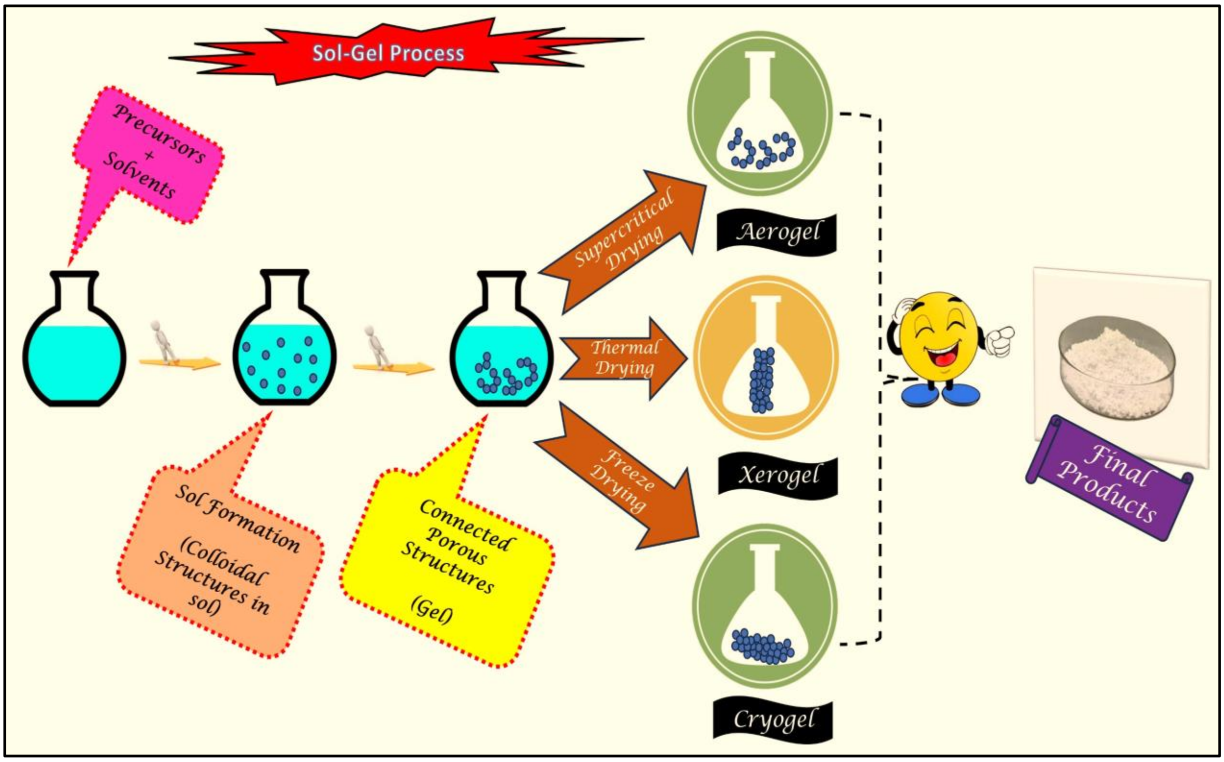


Figure 2.1. Sol-Gel Process.

The terms listed below are utilized consistently in sol-gel processing:

1. Precursors for Sol-Gel Processing

All that is recognized as the precursor are the starting materials used in the sol-gel process.

- Solubility of precursors in the reaction media is required.
- Their reactivity should to be sufficient for them to take part in the gel formation process.

Precursors include inorganic metal salts, oxides, hydroxides, complexes, alkoxides, acrylates, and amines that are soluble in the appropriate solvents [11,12]. Since alkoxides are widely accessible, they are the most often used sol-gel precursor. Metal alkoxides, a family of organic metal compounds made up of an organic base joined to a metallic or quasimetallic element, are usually used as precursors to start the sol-gel process.

2. Sol formation

A stable dispersion of polymers or colloidal particles in a solvent is known as a sol. The sol is actually a solution, or more accurately, a colloidal mixture, made up of tiny particles (sizes ranging from 1 to 100 nm) interspersed throughout the solvent phase [13,14]. The particles could have a crystalline or amorphous form. Particles in a liquid phase are called sols, and particles in a gas phase are called aerosols.

3. Gel formation

A network or framework of the substance, which can be either polymeric or colloidal (basically a concentrated sol), contains the solvent in gel, a semi-rigid solid. A solid network containing a liquid phase is the minimum composition of a gel. The term "gel" refers to a colloidal dispersed substance that, when interpenetrated by a liquid system, produces a continuous ramifying coherent network. These are viscoelastic bodies with submicrometric sized interconnecting gaps. The components of a gel are a liquid phase surrounded by a three-dimensional continuous matrix. A network consisting of aggregated colloidal particles is formed in a colloidal gel. Particles in a polymer gel have aggregates of sub-colloidal particles that form a polymeric sub-structure. The sol particles may usually interact by hydrogen bonds or van der Waals forces. Another way to create a gel is by joining polymer chains. Covalent interactions and an irreversible gel process characterize the majority of gel systems utilized in materials synthesis [15]. Gels are typically categorized based on the dispersion media that they are dissolved in; for example, water, alcohol, and air belong to the alcogel, hydrogel or aquagel, and aerogel categories. The process known as "sol-gel" converts a collection of colloidal particles in a solution into a continuous, branching, and disordered network that is permeable by liquid. Solvent separation from gels was achieved using three distinct drying techniques.

I. **Aerogel:** The solid system exhibits the least amount of change during the process of supercritical drying. The resultant material is "hollow" in correction, low strength, and has porous networks. We refer to this product as aerogel. The terms air and gel combine to form the phrase "Aerogel." When the liquid in the pore is expelled as a gas phase from the network of interconnected solid gels above its critical temperature and pressure, a low-density aerogel occurs (under supercritical or hypercritical conditions) [16]. This prevents the solid network from collapsing. It's possible that a gel with a lot of pores forms while maintaining the network structure.

II. **Xerogel:** The gel is allowed to dry spontaneously in the open air after manufacture. Xerogel is the name given to the gel that results from this drying procedure. "Dry gels" are referred to as “Xerogel”. They are produced by simply evaporating the liquid inside the gel [17].

III. **Cryogel:** The outcome of the freeze-drying process is a "Cryogel". They originate in gels when the phase of liquid is sublimated after being condensed into a solid. Vacuum pumping is applied to remove the vapor.

Drying causes the gel's liquid phase to evaporate, creating a porous material. Firing is a heat treatment that can be utilized to encourage more polycondensation and improve the material's mechanical qualities. In a standard sol-gel scenario, the salt is hydrolyzed under the right conditions to produce the matching hydroxide (Sol), and then the gel-a dense, gelatinous hydrous oxide-is formed via polycondensation.

There are various aspects that make up the sol-gel process [18]. A number of crucial phases in the synthesis of sol-gel include;

- **Phase-I [Hydrolysis]:** It entails reacting an inorganic or organometallic precursor at room temperature or slightly higher it with water or another solvent. Catalysts, either acid or base, are introduced to accelerate the process.

- **Phase-II [Polymerization]:** In this stage, nearby molecules condense, releasing water and alcohol and creating metal oxide bonds. In the liquid (sol) state, polymeric networks expand to colloidal dimensions.

- **Phase-III [Casting]:** A mold can be utilized to cast the sol. It has a low viscosity liquid. The sol shall be coated on a substrate, emulsified, or drawn into fibers.

- **Phase-IV [Gelation]:** Gelation is the approach of colloidal fluids settling, and it can take several forms to provide polymeric or colloidal gels. Here, the liquid's polymeric networks connect to create a three-dimensional network. The solutions' pH, dilution, and amount of water can all be changed to create polymeric or colloidal gels. The gelation point is the moment at which a sol transforms into a gel by allowing it to sustain a stress elastically. In a gel-like manner, the system gets fairly rigid. Upon reaching the gel point, a sol solidifies in a certain polymer structure. Depending on the temperature, solvent, pH, and solvent removal, this frozen-in structure may shift significantly over a period of time. Materials with substantially distinct physical appearances and frequently physical qualities emerge during the gelation step and later treatment stages.

- **Phase-V [Ageing]:** Gel aging is caused by a steady gathering of tiny polymeric units into the major network. Ageing is the term used to explain the gradual changes in a gel's structure and features caused by complete submersion in liquid. However, solvent molecules continue to exist within the gel's pores. Gel aging (syneresis), in which the gel compresses and solvent is ejected from its pores as a result of the polycondensation reactions continuing until the gel solidify into a mass.

- **Phase-VI [Drying]:** Gel drying, which occurs when water and other volatile liquids are eliminated from the gel network. Fundamental alterations in the gel's structure make this procedure difficult. Here, the solvent is eliminated at temperatures that are modest (< 470 K), leaving the residue in intact. The aerogel powders are produced by supercritically eliminating the solvent to yield large surface area and minimal bulk density pieces.

- **Phase-VII [Dehydration]:** Dehydration stabilizes the gel against rehydration by eliminating surface-bound M-OH groups. This is usually accomplished by calcining the monolith at temperatures as high as 800 °C, which destroys the chemically linked water and organic residues and produces a glassy metal oxide that has a microporosity of up to 20–30%. The following can be used to illustrate dehydration polycondensation reactions [19];

$$-M-OH + OH-M- \longrightarrow -M-O-M + H_2O \qquad (1)$$

- **Phase-VIII [Densification]:** The gels are heated to high temperatures (> 800 °C). The gel network's pores collapse, the organic species that are still present volatilize, and a thick oxide product is formed. The surface area, pore connectivity, and pore network diameters all have a significant impact on the densification temperature.

Thus, by adjusting the experimental parameters such as the selection of reagents, additives, concentration, strength of ions in reactants, pH, sequence of addition, reaction and drying conditions, the sol-gel method provides the opportunity to generate solids with pre-determined structure. Additionally, it permits the regulation of composition, surface polarity, crystallinity, pore shape, and porosity. One can choose to follow or not follow the several phases involved in the sol-gel technique as previously mentioned. But in reality, a modified sol-gel procedure is used.

Compared to conventional ceramic technologies, the sol-gel process has the following advantages and disadvantages:

A. Advantages of Sol-Gel Process

- Superior homogeneity - close blending of raw ingredients
- Producing products with excellent purity and excellent manufacturing efficiency
- Simplicity of the process
- Processing at low temperature
    - Energy conservation
    - Decrease the amount of evaporation losses
    - Preventing air pollution
    - No response from the container
- Surface coverage
- Producing intricately shaped optical components
- In multicomponent systems, a more consistent phase distribution
- Novel crystalline phases derived from novel non-crystalline solid materials
- Superior glass products derived from unique gel qualities
- Custom-made materials provide enhanced and preferred characteristics
- Porous materials with the aid of templates

B. Disadvantages of Sol-Gel Process

- ♣ Excessive shrinking that occurs during processing
- ♣ Remaining fine pores
- ♣ Retaining hydroxyl groups when use hydroxides
- ♣ Carbon residue (derived from templates)
- ♣ Potential risks connected to organic solvents
- ♣ Prolonged processing durations

2.2.2.2. Synthesis of Ce-ATMP adsorbent

In the context of getting the materials ready, the sol-gel method was used to obtain Ce-ATMP while modulating a number of experimental components including temperature, pH, rate and mode of addition and the mole ratio of the reactants. The primary objective was to get a material with a high CEC. In each scenario, different sets of materials were performed under distinctive conditions utilizing CEC as an illustrative tool (**Table 2.1**).

$Ce(SO_4)_2.4H_2O$ [0.1 M, 150 mL in 10 % (w/v) H_2SO_4] was made, to which an aqueous solution of ATMP (0.1 M, 20 mL) was added drop-wise with continuous stirring for an hour at room temperature, resulting in the creation of gelatinous precipitates (Step I). This procedure was carried out under the optimum circumstances for the synthesis of Ce-ATMP. Following a 5-hour aging period at room temperature, the resulting gelatinous precipitates were filtered, cleaned with DI water to get rid of any remaining clinging ions, and dried at room temperature (Step II). The aforementioned dried materials from Step-II were broken to the appropriate particle size [30-60 mesh (ASTM)] by pulverizing and sieving. This material, 5 g, was exposed to 50 mL of 1 M HNO_3 for 30 min while being sometimes shaken. The substance was then decanted to eliminate the acid, and any remaining acid was then washed out with double-distilled water. All of the materials underwent the acid treatment at least five times. When the final wash was complete, the material was dried at room temperature [20] **(Figure 2.2)**.

Table 2.1. Optimization of parameters for synthesis of Ce-ATMP.

Parameters Varied	No.	Concentration M:A (M)	Volume M:A(mL)	pH	Temp. (±2°C)	Stirring Time	Aging Time	CEC meq.g^{-1}
Concentration	1	0.1:0.1	50:50	1:1	30	1 hr	15 hr	-
	2	0.2:0.1	50:50	2:1	30	1 hr	15 hr	-
	3	0.3:0.1	50:50	3:1	30	1 hr	15 hr	0.9
Volume	4	0.1:0.1	100:20	5:1	30	1 hr	15 hr	2.30
	5	0.1:0.1	150:20	7.5:1	30	1 hr	15 hr	2.60
Temperature	6	0.1:0.1	150:20	7.5:1	30	1 hr	1 hr	1.82
Aging Time	7	0.1:0.1	150:20	7.5:1	30	1 hr	1 hr	2.12
	8	0.1:0.1	150:20	7.5:1	30	1 hr	3 hr	2.34
	9	0.1:0.1	150:20	7.5:1	30	1 hr	5 hr	**2.40***
	10	0.1:0.1	150:20	7.5:1	30	1 hr	7 hr	2.48
Stirring Time	11	0.1:0.1	150:20	7.5:1	30	2 hr	7 hr	2.41
pH (1:1)	12	0.1:0.1	150 20	7.5:1	30	1 hr	5 hr	2.28

*M= Metal; A=Anion; *Optimum condition*

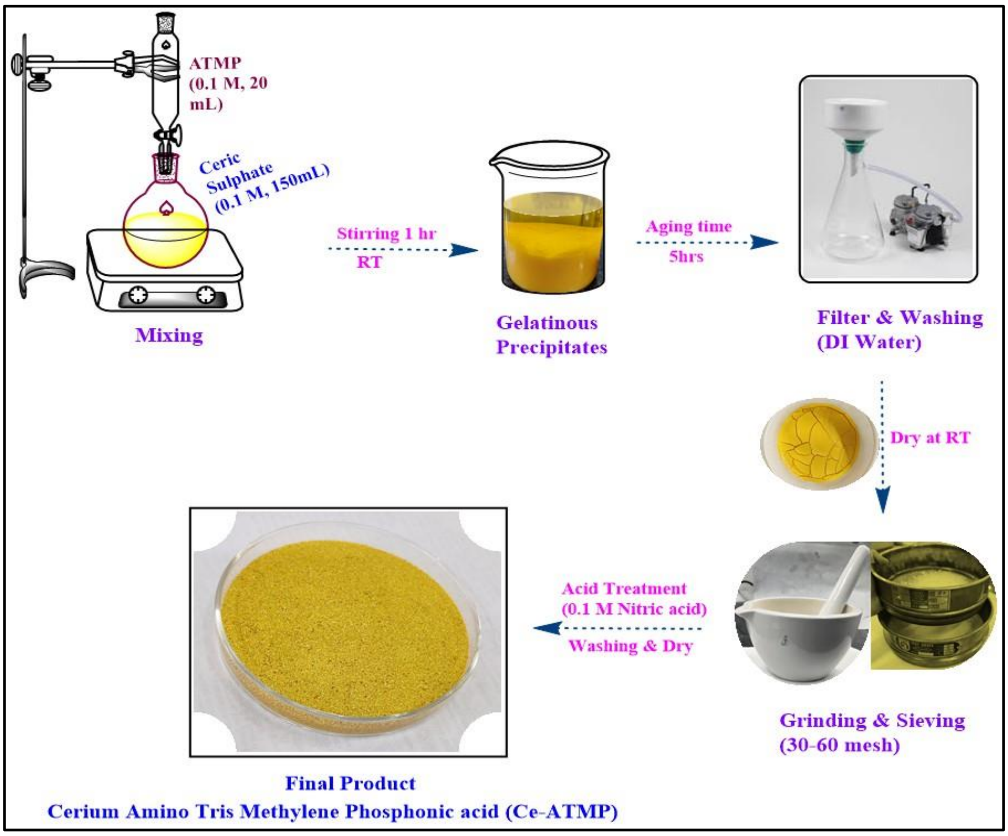


Figure 2.2. Synthesis of Ce-ATMP.

2.2.2.3. Synthesis of Sn-ATMP adsorbent

Sn-ATMP was synthesized via the process known as sol-gel, with the primary goal being to create a material with a high capacity for ion exchange. This was attained by adjusting a number of factors. CEC served as the suggestive tool in every scenario, with many sets of samples synthesized under multiple circumstances. In **Table 2.2**, the optimal parameters for Sn-ATMP synthesis are displayed.

Here, we present an optimal condition description of Sn-ATMP synthesis. At room temperature (~25°C), an aqueous solution of ATMP (0.2 M, 100 ml) was gradually added dropwise to a solution of $SnCl_4.5H_2O$ (0.1 M, 50 ml), while stirring continuously. After obtaining a gelatinous precipitate, the solution and precipitate were stirred for a further 1 hour. After having the resulting gelatinous precipitate aging for 1 hr, it was filtrated, washed with double distilled water to be eliminate of any remaining chloride ions, and then allowed to dry at room temperature. After being grinded and sieved to the required particle size of 30–60 mesh (ASTM), 5 g of the substance was treated with 50 ml of 1 M HNO_3 for 30 minutes while being shaken intermittently to turn it into an acid. Following a decantation to separate the material from the acid, adherent acid was removed by washing with double-distilled water. A minimum of five repetitions of the acid treatment procedure were carried out. The content was permitted to air dry at room temperature following the final washing. For each investigation, this substance was used [20] **(Figure 2.3)**.

Table 2.2. Optimization of parameters for synthesis of Sn-ATMP

Parameters Varied	No.	Concentration M:A (M)	Volume M:A(mL)	Temp. (±2°C)	Stirring Time	Aging Time	CEC $meq.g^{-1}$
Concentration	1	0.1:0.1	100:100	32	1 hr	15 hr	2.74
	2	0.1:0.2	100:100	32	1 hr	15 hr	3.30
	3	0.2:0.1	100:100	32	1 hr	15 hr	3.26
Volume	4	0.1:0.2	50:100	32	1 hr	15 hr	3.84
	5	0.1:0.2	100:50	32	1 hr	15 hr	2.70
Temperature	6	0.1:0.2	50:100	50	1 hr	15 hr	3.70
	7	0.1:0.2	50:100	70	1 hr	15 hr	3.40
Aging Time	8	0.1:0.2	50:100	32	1 hr	5 hr	3.04
	9	0.1:0.2	50:100	32	1 hr	1 hr	2.40
	10	0.1:0.2	50:100	32	1 hr	3 hr	2.64
Stirring Time	11	0.1:0.2	50:100	32	2 hr	15 hr	3.16
	12	0.1:0.2	50:100	32	4 hr	15 hr	2.84
Mode of addition	13	0.1:0.2	50:100	32	1 hr	15 hr	**3.84***
pH (1:1)	14	0.1:0.2	50:100	32	1 hr	15 hr	3.50
pH (1:2)	15	0.1:0.2	50:100	32	1 hr	15 hr	3.42

*M= Metal; A=Anion; *Optimum condition*

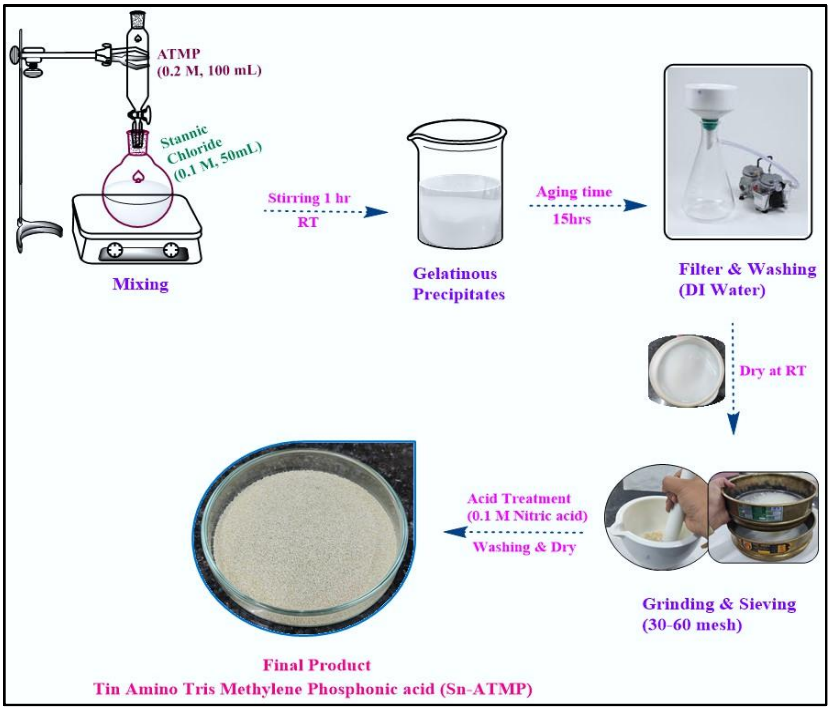


Figure 2.3. Synthesis of Sn-ATMP.

2.3. Characterization

In contemporary materials science, material characterization is a crucial component. A description of the instrumental techniques used is provided. We used ion exchange and physical characterization approaches to study the metal phosphonates Ce-ATMP and Sn-ATMP.

2.3.1. Physical and Ion exchange characteristics

Physical characteristics provide an overview of the material. It comprises appearance, particle size, apparent and actual (true) densities, moisture content percentage, exchanger type, and chemical stability. Ion exchange capacity, the impact of calcination on IEC, the concentration of fixed ionogenic groups, the void volume fraction, and volume capacity are illustrations of ion exchange characteristics.

2.3.1.1. Appearance

It comprises physical features, namely colour, opacity, transparency, hardness, and lustre (hardness).

2.3.1.2. Percentage moisture content

The capability of an exchanger to retain moisture is measured by its percentage moisture content, which is determined by its ionic form/ionogenic group content, matrix structure, and functional groups. The material, which weighed around one gram, was placed in distilled water for a whole day (24 hr) with the aim to measure its percentage moisture content. Once the surface moisture was eliminated, the material was weighed after being filtered and dried at room temperature. This material was dried for 4 hours at 110 °C, cooled, and then weighed again. The following formula is used to get the moisture percentage.

$$\%\,\boldsymbol{Solid} = \frac{\boldsymbol{Weight\ of\ Dried\ Material}}{\boldsymbol{Weight\ of\ Material\ Before\ Drying}} \times \mathbf{100} \tag{2}$$

$$\%\,\boldsymbol{Moisture\ Content} = \mathbf{100} - [\%\,\boldsymbol{Solid}] \tag{3}$$

2.3.1.2. Size of particle

In typically, ion exchange materials come in the form of tiny, rounded beads with dimensions of 0.3 to 1.2 mm. In column operations, huge beads are preferred for the advantage of pressure drop. Still, compared to smaller beads, larger beads break more frequently. The most effective ion-exchange processes take place when the liquid and exchanger can make short contact times with the majority of the functional groups. The amount of time required to access groups located deeper within the particles grows with particle size. When the particle size gets lesser, the ion exchange rate will go up. Exchanges occur more quickly because the exchanging ions' diffusion pathways to the exchanger and from the exchanged sites to the electrolyte media are shorter and have smaller sizes of particles [21].

2.3.1.3. Apparent/Bulk density (D_{col})

The most prevalent one is the apparent density, also known as bulk density or column density, which calculates the ion exchanger's weight per unit volume. The efficiency of an ion exchanger in a commercial scenario is assessed by density. After prolonged use, an alteration in density indicates the occurrence of chemical deterioration.

Accurate exchanger weights were acquired in a glass column that was calibrated in order to determine the density. Water was discharged and the exchanger was provided with time to settle after backwashing. The following equation is used for estimating apparent density;

$$\boldsymbol{Apparent\ Density\ (D_{COl})\ =\ \frac{Weight\ of\ Ion\ Exchanger}{Volume\ of\ Ion\ Exchanger\ Bed}} \tag{4}$$

2.3.1.4. True density (D_{ie})

The value of the number acquired for the wet exchanger using a pycnometer is usually referred to as the specific gravity. Another name for this is true density. The specific gravity of cation exchangers is greater than that of anion exchangers True density should be greater than 1 in order to avoid exchanger particles from floating. Commercial exchangers typically have a true density of 1.1 to 1.5 g.L^{-1}. A pre-weighed specific gravity bottle (W) containing a fixed quantity of the ion exchange material was used to find the true density. The ion exchanger (W_i) and the bottle were both weighed once again. After adding ion exchange material and water, the bottle was weighted (W_{iw}). Additionally, the weight of the water-filled specific gravity container was recorded (W_w). Equation is utilized to compute the actual (True) density:,

$$\boldsymbol{D_{ie}\ =\ \frac{(W_i-W)}{W_w-W_{iw}+(W_i-W)}} \tag{5}$$

2.3.1.5. Void volume fraction

The extent of cross-linking and the resulting network are correlated with an ion exchanger's porosity. Ion exchange characteristics, including capacity and selectivity, are also influenced by porosity assessments. Without a porous structure and with only the functional groups near the surface being active for ion exchange, the exchanger's actual capacity would be substantially smaller. The presence of active functional groups within the pores of porous materials accounts for their high ion exchange capacity [22]. Materials used in ion exchange are typically either macroporous or microporous. The term gel or gel type exchanger is more frequently used to describe microporous materials. Standard procedures are not relevant for measuring porosity in such materials. When exposed to a solvent or water, these exchanger particles swell. When the material is dry, porosity does not exist. Porosity in macroporous materials is quantifiable and does not vanish when the exchanger is dry. The concentration of fixed ionogenic groups, the void volume fraction, and volume capacity are illustrations of ion exchange characteristics.

To compute the void volume fraction, utilize the formula,

$$\boldsymbol{Void\ Volume\ Fraction\ =\ 1-\frac{D_{COl}}{D_{ie}}} \tag{6}$$

The following formula is used for estimating the concentration of the fixed ionogenic group,

$$C_r = \frac{D_{ie} \times (100 - \%\ Moisture) \times IEC}{100} \qquad (7)$$

The exchanger's volume capacity is calculated using this equation,

$$Q = (1 - Void\ Volume\ Fraction) \times C_r \qquad (8)$$

2.3.1.6. Nature of exchanger (pH titration curve)

The pH titration curve can be utilized to identify if an exchanger is weak or strong. A material's acid sites can be titrated against both an alkali hydroxide, which is used to neutralize the material, and a salt solution containing the same alkali metal, which serves as a supporting electrolyte. The term "pH titration curve" or "potentiometric curve" refers to a plot of pH against the amount of milliequivalents of OH^- ions that provides information on how acidic a material nature is, whether it is weak or strong [23].

The batch method of the Topp and Pepper method [24] was used to carry out the pH titration. In the present investigation, 0.5 g of Ce-ATMP and Sn-ATMP was placed in within a 100 mL solution of 0.1 M NaCl. The mixture of solutions was titrated against a solution of NaOH (0.1 M). There was sufficient time provided for equilibrium to be accomplished for the pH staying consistent after subsequent 0.5 mL of adding titrant. Plotting pH against volume of NaOH obtained a pH titration curve.

2.3.1.7. Chemical stability

In order to employ a material for a variety of applications in a variety of settings, it is helpful and significant to examine its chemical resistivity and stability in mineral acids, bases, and organic solvent media. By dissolving 0.5 g of Ce-ATMP and Sn-ATMP in 50 ml of each medium and letting it stand for 24 hours, researchers were feasible to examine the chemical stability of the material in a variety of acidic (HCl, H_2SO_4, and HNO_3), basic (NaOH and KOH), and organic solvent (ethanol, benzene, acetone, and acetic acid) solutions.

2.3.1.8. Ion exchange capacity (IEC)

The capacity of an ion exchange material to exchange ions is one of its most crucial characteristics. The number of ions-acid or base-that are removed or exchanged by an ion-exchange material is known as its capacity. The two fundamental implications of capacity and associated data are,

(1) Regarding the ion exchange material characterization

(2) In the numerical computation of ion exchange processes.

The entire available exchange capacity of an ion exchanger, as indicated by the number of functional groups on it, is what is meant to be described by the word "ion exchange capacity." This number, which is based on the dry amount of the ingredient in the specified form (such as H^+ or Cl^-) and is displayed in milli equivalents per gram, is invariant for a given ion exchange material. Two capacity attributes are usually employed for ion exchanger characterization: the whole static exchange capacity (batch method determined) and the dynamic exchange capacity (column method determined). The exchange capacity is determined by the number of functional groups per gram of exchanger, and the degree of ionization of the exchanger's functional groups, as well as the process's chemical and physical parameters, determine the overall exchange capacity. Similarly, for the evaluation of IEC, sodium acetate should be used for weak acid ion exchangers, NaCl for neutral ion exchangers, and NH_4Cl for acidic ion exchangers. By altering the electrolyte solution's concentration and volume at a constant flow rate to identify the ideal concentration and volume needed for full exchange, the column method [25] is typically used to measure the Na^+ IEC of materials. The IEC of exchangers is evaluated at the optimized parameters to get accurate and efficient IEC values, when the optimized parameters (volume and concentration) have been identified.

By employing the column method [26] to optimize the volume and concentration of sodium acetate solution, the Na^+ cation-exchange capacity (CEC) of Ce-ATMP and Sn-ATMP was ascertained. The first scenario involved passing a glass column containing 0.5 g of the exchanger at a steady flow rate of $0.5\ mL{\cdot}min^{-1}$ through a fixed volume (250 mL) of sodium acetate solution with different concentrations (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 M). The eluted H^+ ions-containing effluent was titrated against a 0.1 M NaOH solution. This allowed for an estimation of the optimal eluant concentration. In the second scenario, 10 mL fractions were passing through the column at a steady flow rate of $0.5\ mL\ min^{-1}$, utilizing an eluant of optimal concentration. In order to evaluate the column's efficiency, the experiment aimed to ascertain the lowest volume required for the entire elution of H^+ ions. Considering these enhanced parameters, the Na^+ CEC was calculated as follows equation,

$$CEC = \frac{a \times V}{W} \tag{9}$$

where a and V are the molarity and volume of NaOH utilized throughout the titration, W is the exchanger's weight.

2.3.1.9. Effect of calcination on IEC

Elevated temperatures are necessary for a number of significant ion exchange activities. In these situations, one of an ion exchanger's most crucial requirements is thermal stability. The reaction system's temperatures should not be able to destroy the exchanger that is currently in operation. Temperatures greater than those specified by the manufacturer should not be used with ion exchange materials. When the temperature limit is surpassed, both cation and anion exchange resins lose their functional groups. The higher the temperature exceeds the upper limit, more rapidly the weight loss occurs. The material's acceptability for high temperature applications could be determined by researching how calcination affects the exchanger material.

When calcining numerous 1 g portions of the material in a muffle furnace for two hours at 100°C intervals, allowing them to cool to ambient temperature, and using the column method previously mentioned to determine the Na^+ CEC, the impact of calcination on CEC was investigated [27].

2.4. Characterization by instrumental techniques

The materials developed for this research study were characterized using a variety of spectroscopic and thermal techniques including elemental analysis (ICP-AES, CHN), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (XRD), Thermogravimetric analysis (TGA), Field emission scanning electron microscopy (FESEM) and Energy dispersive X-ray (EDX). UV-visible absorption spectroscopy (UV-Vis) was utilized for studying the characteristic dye adsorption of the samples. pH of the samples was measured using ANALAB (Vadodara, India), pH meter. An electric, temperature-controlled shaker bath having a temperature variation of ±0.5°C was used and rotary shaker was also used.

2.4.1. Elemental analysis

The elemental constitution of materials can be obtained using well-known methods such as gravimetric or volumetric approaches. Wet chemical analyses, which involve solubilizing a solid using appropriate techniques and then quantitatively evaluating these solutions, are commonly performed. The chemical composition can be estimated using analyzers that use inductively coupled plasma atomic emission spectroscopy (ICP-AES). A CHN analyzer is utilized to examine the different organic components, such as carbon, hydrogen, nitrogen, etc., in hybrid (inorgano-organic) materials.

2.4.1.1. Inductively coupled plasma atomic emission spectroscopy [ICP-AES]

An analytical approach for detecting chemical elements via the creation of agitated atoms and ions that release electromagnetic radiation at wavelengths specific to an assigned element is known as inductively coupled plasma atomic emission spectroscopy (ICP-AES), which is additionally referred to as inductively coupled plasma optical emission spectroscopy (ICP-OES). The analysis for this investigation was done using an ICP-OES spectrometer, namely the Thermoscientific iCAP 6000 series.

2.4.1.2. CHN analyzer

A complex equipment used to quantify the concentration of components in a sample, specifically carbon (C), hydrogen (H), and nitrogen (N), is called a CHN Analyzer, often referred to as a Combustion Analyzer. When finding out the elemental makeup of organic components as well as other materials like solids, liquids, volatiles, and viscous samples, this analytical instrument is essential. The present investigation used the Coleman USA - CHN analyzer to determine the C, H, and N content.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

The most effective analytical method for determining the structure of molecules and the makeup of molecular mixtures is Fourier Transform Infrared Spectroscopy (FTIR), which is utilized in both academic and industrial settings.

In the current investigation, FTIR-8400S equipment, built by Shimadzu in Japan, was utilized to perform FTIR spectra in the KBr emission mode, spanning the 4000-400 cm^{-1} spectral region. Samples were incorporated with KBr and compacted to 4 tons using a hydraulic press to generate pellets. Particular incident frequencies correlated with molecular vibrations during radiation exposure. This resonance allowed energy between the incident electromagnetic wave and molecular vibrations to be transmitted, and a spectrum of absorbed frequencies was observed.

2.4.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis has been carried out to determine the crystalline or amorphous nature of the material.

In Present study, Bruker D8 FOCUS X-ray diffractometer with a Cu Kα radiation with a wavelength of 1.5406 Å was used to perform the XRD patterns of the samples and scanned in the 2θ values spanning from 5º to 80º at 0.04º per min.

2.4.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is one kind of thermal analysis in which a sample's mass is determined as an estimate for temperature. Sample weights typically range from 1 to 10 mg. In the present instance, the sample was heated at a rate of 20 ºC/min in a nitrogen environment, going from 30 ºC to 800 ºC. Weight fluctuations were monitored using an extremely sensitive microbalance.

In the present investigation, the Japanese Shimadzu TGA-50 equipment was used to record weight loss data online in relation to temperature and time.

2.4.5. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX)

The phrase "FESEM-EDS instrument" most likely describes a hybrid system comprising Field Emission Scanning Electron Microscopy (FESEM) with Energy-Dispersive X-ray Spectroscopy (EDS). With the employment of a concentrated electron beam, FESEM is an effective imaging technology that provides high-resolution images of sample surfaces. Despite the implementation of a secondary electron detection system, FESEM is able to reveal features as small as 1 nm to 5 nm on a sample surface - highly detailed imagery. However, elemental analysis is rendered feasible by EDS, a technique for analysis that finds the distinctive X-rays that a sample emits when it is exposed to an electron bombarding. Researchers can observe sample surface morphology at high magnifications and then use elemental analysis to ascertain the sample's chemical composition when the two techniques are integrated into a single device.

In this investigation, a SIGMA 500VP Field Emission Scanning Electron Microscope with EDS and EBSD Sensors was implemented for investigating the sample morphology of Ce-ATMP and Sn-ATMP. EDX OXFORD 6587 was utilized for collecting SEM and EDX data for Amberlite IRA-400(Cl^-)resin samples.

2.4.6. Ultraviolet-visible spectroscopy (UV-vis)

Ultraviolet-visible (UV-Vis) spectroscopy is an effective technique to assess light absorbance in the visible and ultraviolet bands that is applied to numerous scientific domains. A UV-Vis spectrophotometer measures the intensity of light that enters a sample solution and correlates it to the incident light to offer important details about the features of materials encompassing how they interact with light. In this research, a Carry 60 equipment was used to do the UV analysis.

2.4.7. pH Meter and Temperature-controlled shaker bath

pH of the samples was measured using ANALAB (Vadodara, India), pH meter. An electric, temperature-controlled shaker bath having a temperature variation of ±0.5°C was used for thermodynamic study. Rotary shaker utilized in dye batch sorption studies.

2.5. References

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