Chapter- 2: Methods and Instrumentation

This chapter summarises various sample preparation techniques, including coprecipitation, hydrothermal, sol-gel, ion exchange, urea hydrolysis, oxide, and microchemical methods. Characterisation methods are applied to confirm physical and chemical structures, with x-ray diffraction and Fourier-transform infrared spectroscopy used for structural analysis, scanning and transmission electron microscopy for morphology, BET measurements for textural properties, and Uv-visible spectroscopy for pollutant concentration analysis in aqueous solutions. This chapter comprehensively covers all essential synthesis and characterisation techniques.

(1) Firstly, the synthesis techniques are discussed.
(2) The second section discusses the whole characterisation and usable instrument.

2.1. The synthesis of the hydrotalcite

Various methods can synthesise the materials depending on the specific requirements and desired properties. This chapter summarises all possible sample preparation synthesis methods, including coprecipitation, hydrothermal, anion exchange, microchemical synthesis, sol-gel, electro-synthesis, and salt oxide.

2.1.1. The coprecipitation method

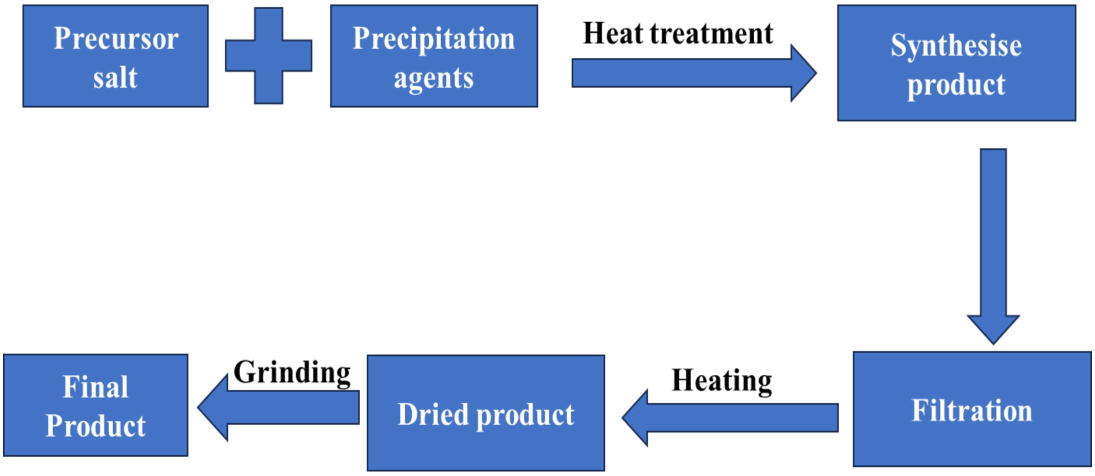

Figure 2.1: Schematic diagram of Co-precipitation method.

The coprecipitation method is widely used for synthesising hydrotalcite-like compounds because it generates a large quantity of product and is economically feasible to handle in a laboratory environment. It involves two solutions: the first is a metal solution, and the second is an alkaline solution containing precipitating agents (such as Na_2CO_3 or NaOH). The purpose of the alkaline solution is to maintain a constant pH to initiate the coprecipitation process. The metal cations will coprecipitate, and then the solution reaches supersaturation. Supersaturation occurs when the alkaline solution is added, causing an increase in the solution's pH. After maintaining the pH, the required temperature is applied to start the synthesis process. This method allows multiple cations to be used by carefully controlling the pH and supersaturation conditions [97]. The solution's pH exceeds a specific limit, at which point the most soluble hydroxide of the metals in the solution precipitates, and then the LDH will also precipitate. However, anions like OH^- may be competitively intercalated into the interlayers of the LDH. The precipitate is allowed to age at the operating temperature for 24 hours, followed by centrifugation, washing with deionised water, and vacuum drying to obtain the desired products [98]. The coprecipitation mechanism involves condensing hexa-aqua complexes in solution, forming layers with uniformly dispersed metallic cations and solvated interlayer anions. The coprecipitation process indicates that the brucite-type layers and the interlamellar regions of hydrotalcite-like compounds are formed in the early stages. The most crucial feature of this method is its ability to control the particle size of the material by regulating nucleation conditions, ageing time, or ageing temperature, viz., smaller particles are obtained by less ageing [99]. The synthesis method can achieve maximum crystallinity of the materials by carefully controlling the charge density of the hydroxide layers. Conversely, coprecipitation under high saturation reduces crystallinity due to the constant fluctuation in solution pH [100–104].

2.1.1.1. Synthesis of Ternary Layered Double Hydroxide

Chemicals: All chemicals used in this study are of analytical grades and were used without further purification. All chemicals are present in the nitrate form and purchased from SRL chemicals. Cobalt Nitrate Hexahydrate ($Co\ (NO_3)_2.\ 6H_2O$), Magnesium Nitrate Hexhydrate ($Mg\ (NO_3)_2.\ 6H_2O$), Zinc Nitrate Hexahydrate ($Zn\ (NO_3)_2.\ 6H_2O$), Nickle Nitrate Hexahydrate ($Ni\ (NO_3)_2.\ 6H_2O$), Aluminium Nitrate Nonahydrate ($Al\ (NO_3)_3{\cdot}9H_2O$), Ferric Nitrate Nonahydrate ($Fe\ (NO_3)_3{\cdot}\ 9H_2O$), Sodium Hydroxide (NaOH) and Sodium Carbonate (Na_2CO_3) were used.

Ternary layered double hydroxides (LDHs) are synthesized using the coprecipitation method, the schematic diagram of this method is shown in Figure 2.1. We have synthesized $[Co_{0.5}^{2+}Al_{0.25}^{3+}Fe_{0.25}^{3+}(OH)_2].(CO_3^{2-})_{0.125}.H_2O$ (CoAlFe),

$[Mg^{2+}_{0.5}Zn^{2+}_{0.25}Fe^{3+}_{0.25}(OH)_2].(CO_3^{2-})_{0.125}.H_2O$ (MgZnFe), $[Mg^{2+}_{0.5}Zn^{2+}_{0.25}Al^{3+}_{0.25}(OH)_2].(CO_3^{2-})_{0.125}.H_2O$ (MgZnAl), $[Mg^{2+}_{0.5}Ni^{2+}_{0.25}Al^{3+}_{0.25}(OH)_2].(CO_3^{2-})_{0.125}.H_2O$ (MgNiAl) LDH.

Two solution is used for preparation, where one solution is precursor salt and another is precipitating solution with sodium carbonate for charge balancing, which incorporate as a intercalated anion in the LDH.

- CoAlFe LDH was synthesized via the co-precipitation method at a constant pH of 10.5. A total volume of the cationic salts solution of 20 ml containing 0.5 mol of $\mathrm{Co(NO_3)_2 \cdot 6H_2O}$, 0.25 M of $\mathrm{Al(NO_3)_3 \cdot 9H_2O}$, and 0.25 M $\mathrm{Fe(NO_3)_3 \cdot 9H_2O}$ salts were mixed to prepare a solution. Then, the alkaline solutions of 2 M NaOH and 0.125 M $\mathrm{Na_2CO_3}$ were added dropwise into the salt solution. The entire mixing process was done at room temperature. The solution was kept stirring for 6 h at 60 °C. To study the effect of synthesis time variation on the physiochemical properties of the LDH. The LDHs with the same composition were prepared following the above-mentioned co-precipitation route at a constant temperature of 60 °C with a synthesis or ageing time duration of 12 h, 18 h, and 24 h.
- The ternary MgZnFe LDH was synthesised using the coprecipitation method. In detail, 0.50 M of $[\mathrm{Mg(NO_3)_2.6H_2O}]$, 0.25 M of $[\mathrm{Zn(NO_3)_2.6H_2O}]$ and 0.25 M $[\mathrm{Fe(NO_3)_3.9H_2O}]$ were mixed in 100 ml of deionised water with molar ratio ${}^{Mg^+}/_{Zn^+} = 2$ and ${}^{Zn^+}/_{Fe^+} = 1$. It was continuously stirred for 2 h to achieve a fully dissolved homogeneous solution. An aqueous solution of 2 M $\mathrm{Na_2CO_3}$ and 1 M NaOH was added slowly to maintain the pH of the total solution between 10 and 11. After getting the constant pH of the solution, the slurry was kept for 24 h at 60 ° C. After completing the reaction, the slurry was kept at 60 °C for 24 h for ageing to improve the material's crystallinity. Then, the slurry was washed with DI water to separate the organic compound until the pH was reached $6 - 7$. Finally, it was dried at 60 °C in a digital oven for 24 h and labelled as MgZnFe LDH. After that, it was heated at 500 °C for 4 h in a furnace and obtained the product name as calcined LDH. The Congo-red, a textile industry's azo dye, was dissolved in DI water used in the experiment.
- The coprecipitation method was utilized to synthesize the MgZnAl layered double hydroxide. In detail, metal solution of 0.50 M of $[\mathrm{Mg(NO_3)_2.6H_2O}]$, 0.25 M of

$[\mathrm{Zn(NO_3)_2.6H_2O}]$ and 0.25 M $[\mathrm{Al(NO_3)_3.9H_2O}]$ were dissolved in 100 ml deionised water with molar ratio $^{Mg^{2+}}/_{Zn^{2+}} = 2$ and $^{Zn^{2+}}/_{Al^{3+}} = 1$. It was continuously stirred for 2 h to achieve a fully dissolved homogeneous solution. An aqueous solution of 2 M $\mathrm{Na_2CO_3}$ and 1 M NaOH was added dropwise to maintain the pH of the total solution between 10 to 11. After achieving the constant pH of the solution, the slurry was kept at 70 ° C for 24 h. Then, the slurry was washed with DI water and ethanol to remove the organic compound until the pH reached $6 - 7$. Finally, it was dried at 70 °C in a digital oven for the whole night and marked as MgZnAl LDH. After that, it was calcined at 500 °C for 4 h in a muffle furnace, and the product was obtained and marked as calcined LDH. The methyl-orange, a textile industries azo dye, was dissolved in DI water and used in the experiment.

- MgNiAl LDH was synthesised by a simple coprecipitation method. In detail metal solutions of 0.04 M $[\mathrm{Mg(NO_3)_2.6H_2O}]$, 0.02 M $[\mathrm{Ni(NO_3)_2.6H_2O}]$, and 0.02 M $[\mathrm{Al(NO_3)_3.9H_2O}]$ were dissolved in 60 ml of deionised water with molar ratio $\frac{\mathrm{Mg+}}{\mathrm{Ni+}} = 2$ and $\frac{\mathrm{Ni+}}{\mathrm{Al+}} = 1$. It was continuously stirred at 60° C for 3 h to achieve fully homogeneous solutions. An aqueous solution containing $\mathrm{Na_2CO_3}$ ($\mathrm{CO_3^{2-}}$/$\mathrm{Al^+}$= 2), and 1 M NaOH dropwise added with the metal solution until a pH of $10 - 10.5$ was obtained. The resulting slurry was allowed to stand for 24 h at a temperature of 60° C. The product was extracted and washed with deionised water and ethanol several times to remove the organic impurities until the pH was reached a value of $6 - 7$. Finally, it was dried at 70° C for 24 h in a vacuum oven and labelled as $\mathrm{MgNiAl - CO_3}$ LDH. After calcining the $\mathrm{MgNiAl - CO_3}$ LDHs at 500° C for 4 h in a muffle furnace, the obtained product was $\mathrm{C - MgNiAl}$. The Congo red (CR), a textile dye, was dissolved in deionised water to create solutions for this experiment.

2.1.2. Hydrothermal treatment

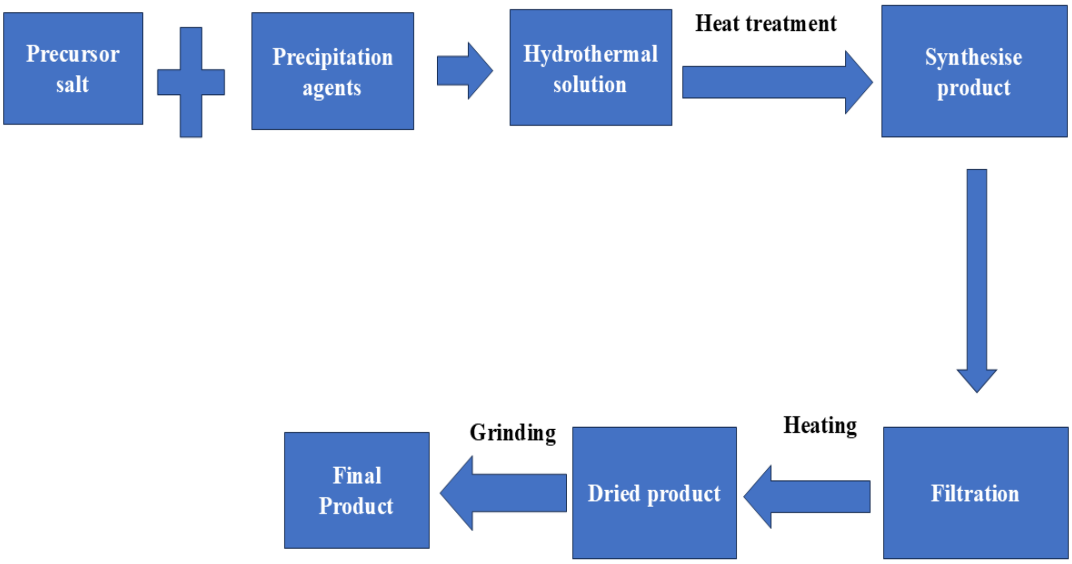

Figure 2.2: Schematic diagram for hydrothermal method.

Hydrothermal is a well-known synthesis method for preparing layered double hydroxide (LDH). Under very mild conditions, this method has been employed to enhance the crystallinity and particle size during LDH synthesis, with the temperature being raised gradually [105]. This method's reaction temperature can control material crystallinity, crystallite size, and compactness. In cases where an organic species with low affinity to LDH needs to be intercalated, anion exchange reactions and co-precipitation techniques are ineffective. Thus, hydrothermal synthesis has proven effective because it ensures that no competing anions other than the intended ones are present in the interlayer. This is achieved using insoluble hydroxides as the inorganic source [106]. Two solutions are necessary to prepare the material: one containing the metal and another serving as the precipitation agent to adjust the pH of the hydrothermal solution. Commonly used precipitation agents include NaOH, NH4OH, and urea. The properties of the synthesised materials would change depending on the choice of precipitation agent used [107]. The hydrothermal method has been observed to enhance the material's crystallinity. Still, its primary disadvantage is its higher energy requirement compared to other methods, and it is a time-consuming process [108].

2.1.3. Sol-Gel-Method

The sol-gel method has attracted considerable attention from chemists for its efficient approach to impart remarkable properties to synthesised materials [109,110]. This method is noted for its low cost and quick synthesis of nanomaterials, which exhibit high surface area, high purity, and high homogeneity. This method allows control over the structural properties of the final products by simply adjusting the quantities of reactants and the ageing time, as well as by adding or removing reactant species. It involves dissolving the appropriate metal salts in water at room temperature [111]. Various parameters affect the crystallinity of the LDH, such as the nature of the precursor, ageing time, and the nature of the acid used in this hydrolysis method [112–114]. One advantage of this method over others is that, unlike the coprecipitation method, the sol-gel method does not require a pH or controlled environment. It has been noticed that uniform pore size distribution and high surface area are obtained, which contribute to the catalytic or adsorption properties of the synthesis of layered material [115]. Prince et. al introduced a sol-gel technique for synthesising LDH, customised to incorporate specific metal cations. The synthesised material by this method exhibits nano capsular morphology and a high surface area of 290 m^2/g and features extremely narrow pore size distributions (3–4 nm). Nano-capsular morphology has been developed, unlike platelet-like particles produced by coprecipitation and other methods [116]. The material is synthesised via the rehydrate sol-gel method, which is applied in pharmaceutical applications, wherein synthetic hydrotalcite can be calcined and rehydrated without losing its lamellar structure [117]. The sol-gel method is considered

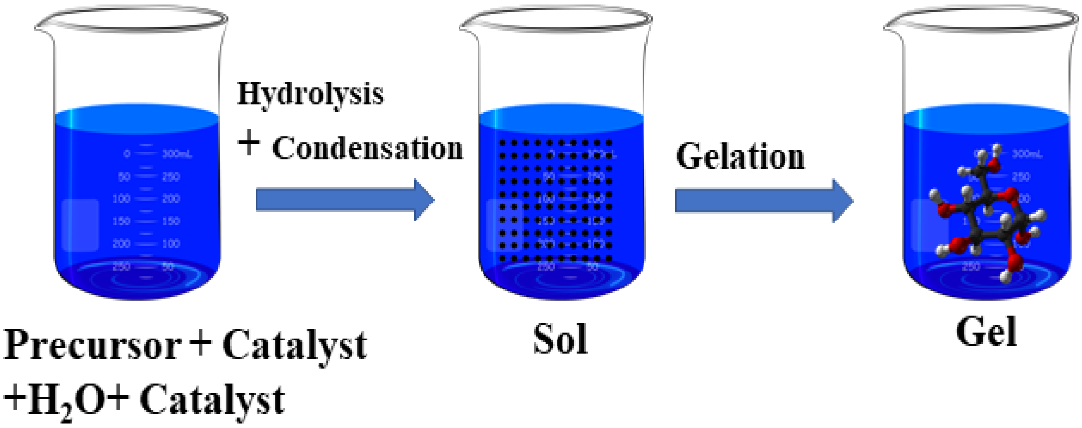

Figure 2.3: Schematic diagram of sol-gel method.

one of the best processes for synthesising the layered double hydroxide because the obtained material has a 10-25 % bigger surface than the other obtained by the coprecipitation method.

2.1.4. Ion exchange Process

The ion exchange process is utilised in cases where the intercalated anion cannot be effectively incorporated using urea or coprecipitation methods. The anion can be easily replaced by the layered double hydroxide method. Nitrate and chloride anions are commonly employed in layered double hydroxides because they can effectively replace many organic and inorganic anions. For example, Ni-Al-NO_3 layered double hydroxide (LDH) compound has been modified through an anion exchange process with benzoate ions to enhance its ability to adsorb amoxicillin drug molecules [118].

2.1.5. Urea Hydrolysis

Urea, a weak Brønsted base highly soluble in water, can be used as a precipitating agent to increase pH through thermal decomposition. The decomposition rate of urea is quite slow and started around 90 °C, resulting in an increase in pH up to 10 and a lower degree of supersaturation. During hydrolysis, carbonate anions are generated and act as interlayer anions. Urea increases the pH of the solution, leading to the formation of monodispersed LDH with high purity and crystallinity [119]. Urea hydrolysis is a combining method of coprecipitation and hydrothermal synthesis. Berber et al. reported that achieving uniform particles requires optimising the synthesis conditions by adjusting the M^{2+}: M^{3+} molar ratio, ageing time, and urea concentration [120]. Inayat et al. investigated Zn-Al-layered double hydroxides with nitrate as the charge-balancing anion in the interlayer space, created through precipitation in a homogeneous environment using urea hydrolysis. By altering synthesis times, they showed how to control whether nitrate or carbonate becomes the interlayer anion. Nevertheless, the continuous presence of carbonate from urea decomposition restricts the widespread use of this technique [121]. To tackle this problem, methods involving mineral acids or a mixture of salts and acids were implemented to exchange the carbonate particles in the LDH structure with anions like chloride [122]. The disadvantages of these techniques include increased time involvement and additional effort required for post-treatment strategies. If the treatment conditions are not adjusted correctly, there could be a reduction in crystallite size, crystallinity, and material loss due to incomplete disintegration of the LDH in acidic environments [123].

2.1.6. Oxide Method

This approach uses a divalent metal oxide and an anion intercalate alongside a trivalent metallic cation arrangement. The pH should be slightly acidic to facilitate moderate hydrolysis of the divalent metal oxide. This method requires certain conditions to be met: the divalent metal oxide should undergo gradual hydrolysis, the intercalated anion must form a soluble salt with the trivalent cation, and it must remain stable under acidic conditions.

2.1.7. Mechanochemical Method

All the methods mentioned for preparing hydrotalcite-like materials share a similar process involving the precipitation of different metallic precursors. All required steps for obtaining the layered double hydroxide using the mechanochemical method. Recently, many researchers have used the mechanochemical method to synthesise LDH, employing techniques like grinding, milling, or crushing. These synthesis types were performed by grinding the precursor in agate or ceramic mortars or crushing it in a planetary ball mill. However, some researchers have applied wet synthesis techniques with this protocol. Mei-Gui et al. conducted hydrothermal treatment on an aground mixture of reactants to enhance the crystallinity and achieve a monodisperse LDH phase. Bhojaraj et al. introduced a mechanochemical process to execute decarbonating intercalation of anions to carry out the anion exchange from carbonate to nitrates [124–131]. The benefits of this approach compared to traditional methods have been shown in various cases. For instance, during cyclohexanone and Claisen–Schmidt condensation oxidation, yttrium-modified LDH catalysts prepared via mechanochemistry activated reagents more efficiently than those produced by the coprecipitation method [132]. Mechanochemical methods are eco-friendly, with minimal need for separating and drying the resulting products. However, there are several drawbacks to the mentioned process during the synthesis. The cost of synthesis increases to maintain parameters affecting the synthesis process, such as constant pH, controlled flow rate, and stable temperature.

In this chapter, we summarise all possible synthesis methods for sample preparation, including coprecipitation, hydrothermal, anion exchange, sol-gel, electro-synthesis, and the salt oxide method. Many techniques are involved to characterise the materials and describe their properties for application in wastewater treatment. Different techniques such as techniques X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) are used in this thesis. All characterisation techniques are discussed briefly.

2.2. Characterisation

2.2.1. Powder x-ray diffraction (XRD) method.

Max Van Laue, in 1912, discovered that a crystalline structure can act as a 3D diffraction grid for an x-ray monochromatic grid and is like the spacing of a plane in a crystal structure [133]. X-ray diffraction is a well-known technique to characterise the crystal structure and determine the spacing between atomic planes. X-ray diffraction is a very useful technique to verify the crystal phase of the material.

Working principle of the XRD: The x-ray is produced from the cathode tube, directed toward the solid, and scattered from the material's electron. This information becomes instructive and destructive interference; it depends on the atom arrangement of the material. The information will become destructive interference if the atom is organised randomly or if there is instructive interference due to the orderly atom organisation [134]. The observed diffraction pattern is strongly correlated with the periodicity of the atomic arrangement. The structural information of the crystal can be determined using the Braggs equation 1 [135].

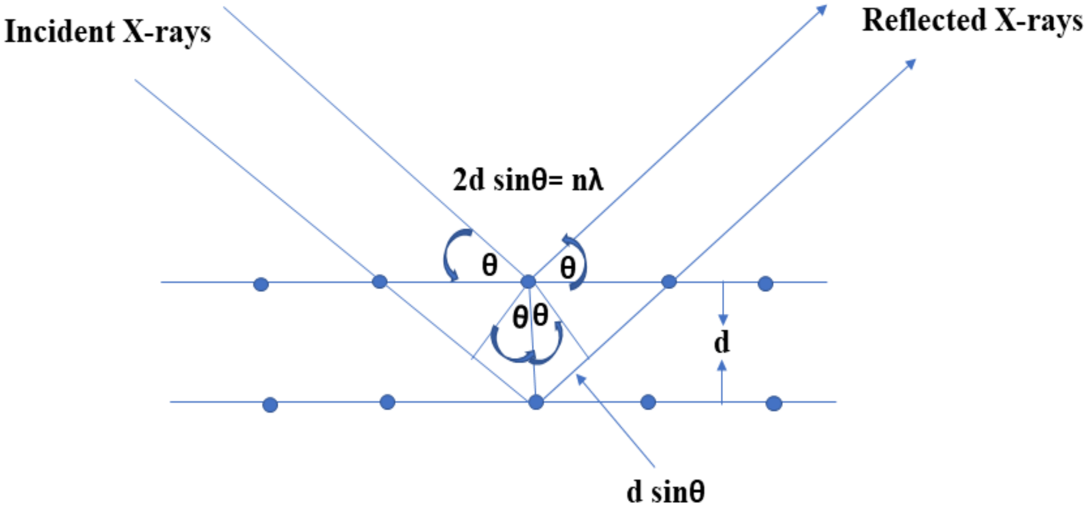

Figure 2.4: Schematic diagram of illustrating Bragg's law.

$$2d\sin\theta = n\lambda \ldots\ldots\ldots\ldots\ldots\ldots \;(1)$$

Where n is an integer number (n = 1, 2, 3…….) represents the diffraction order, λ is the x-ray wavelength, d is the interplanar distance, θ represents the diffraction angle.

The diffraction peak position gives information regarding the size and shape of the unit cell. On the other hand, the peak's intensity is utilized to determine the location of atoms within the cell and to identify the atomic number [134]. X-ray powder diffraction pattern is utilized to identify the crystalline solids. Layered materials like cationic or anionic clays frequently exhibit broad and asymmetric diffraction peaks, probably caused by structural defects or stacking errors [136]. The diffraction patterns of an ideal LDH exhibit narrow, symmetrical, and high-intensity lines at low 2θ values. Conversely, at increased 2θ values, the lines become less intense and asymmetrical [137].

The crystal structure of the LDH is mainly based on the cations, and intercalated anions are aimed. Determining the crystalline structure of hydrotalcite-like materials is challenging due to inadequate crystallization or the non-stoichiometric nature of the synthesis materials. These factors can result in asymmetry and broadening of the diffraction pattern.

2.2.2. Fourier Transformed Infrared (FTIR) Spectroscopy.

Fourier-Transform Infrared Spectroscopy (FTIR) is an important technique for understanding the chemical composition of the material surface. It works by directing infrared radiation onto the sample. Molecules with functional groups absorb some infrared radiation wavelengths, effectively covalent bonds with a dipole moment. These functional groups vibrate at distinct frequencies due to the absorbed energy. FTIR produces a spectrum by measuring the absorption intensity of infrared light across various wavelengths (wavenumbers). The spectrum, which is a plot of transmittance versus wavenumber, exhibits the presence of an involved function group in the material and provides valuable information about the chemical composition of the material. In this present work, the transmission spectra were collected in the KBr and ATR mode using a Nicolet summit FTIR reflection spectrometer from a wavelength range of 4000 to 400 cm^{-1}.

2.2.3. Scanning electron microscopy (SEM).

In 1953, the German physicist Max Knoll introduced the concept of the scanning electron microscope. He believed that an image could be created by directing an electron beam onto the surface of a material. Another German physicist, Manfred von Ardenne, expanded upon the concept and established the fundamental principles of the technique. A scanning electron microscope (SEM) is utilised to take images of the surface of any materials. Some parts of an SEM instrument are very important, such as the electron column, specimen chamber, and computer con troll system. Additionally, it may have a secondary and backscattered electron detector, an energy dispersive x-ray spectrometer (EDS), and a low vacuum detector. It can capture surface images of various materials, ranging from the micrometre to the nanometre scale. In the SEM, a cathode chamber within the electron gun emits a narrow electron beam at high and low energy levels. This quality enhances the spatial resolution of the microscope while minimizing potential charging or damage to the sample. The electron gun produces the electron beam, which passes through electromagnetic lenses and then focuses it into the sample. This interaction produces various types of electrons. A detector captures secondary electrons, and analyzing the intensity differences between secondary and primary electrons produces an image of the sample surface. The interaction between the atom of the material and the electron produces different types of signals that can be detected and provide information about the morphology and composition of the sample. The electron beam scans the sample surface in a raster pattern, and an image is generated by correlating the beam position with the detected signal. In this work, the image of the material was captured using the Nova Nano SEM 450 from FEI Company USA (S.E.A.) PTE, Ltd.

2.2.4. Transmission electron microscopy (TEM).

Transmission electron microscopy (TEM) is a crucial analytical method in physics, chemistry, and biological science. TEM analysis is crucial for high-resolution imaging of material morphology and distribution in material characterisation. It also provides structural information and examines crystallographic properties using its diffraction mode.

The fundamental principle of the TEM depends on the Light Microscope, which uses electrons rather than light and electromagnetic lenses to concentrate the electrons into a skinny bean, as opposed to glass lenses, which concentrate light. TEM uses electrons as a "Light source" because of their high energy and smaller wavelength, which allows for a higher resolution than a light microscope. The electron source at the top of the microscope emits electrons that travel through the microscope's vacuum chamber and then pass through the specimen to form an image. The specimen should be an ultrathin-coated film with a thickness of less than 100 nm or a suspension on a grid. At the bottom of the microscope, the unscattered electrons hit a fluorescent screen. The screen produces a ‘shadow image’ of the specimen with its different parts shown in varying darkness depending on their density.

In TEM analysis, electrons are emitted from the electron gun, accelerated to a potential range of 50-200 kV, and operate within a vacuum chamber to prevent scattering by the atmosphere [138]. An electron gun is below the electron on two or more condenser lenses. These lenses are electromagnetic. Between the condenser lenses and the electron beam diameter control, an apparatus is present through which the electron beam passes before hitting the specimen. The electron beam interacts with the specimen, and the transmission beam passes through the objective lenses; its work is to form the image of the specimen or diffraction pattern of the specimen. The electron diffraction pattern of the material is used to identify its crystallographic structure. After the beam passes through the objective lenses, a 50–100 times magnified image is produced. This image is then further magnified by a series of intermediate lenses and is finally recorded on a fluorescent screen [138].

The samples were prepared using the following steps for TEM characterization: (1) The sample is dispersed in a solvent and dissolved through sonication for a few minutes. (2) The resulting solution is drop-cast onto a copper grid using a syringe and then allowed to air dry or dry under a bulb, ready for TEM analysis.

2.2.5. X-ray photoelectron Spectrometer (XPS).

X-ray Photoelectron Spectroscopy (XPS) is a technique used to analyse the surface chemistry of materials. XPS is based on the photoelectric effect, which was first discovered by Heinrich Hertz in 1887 when he observed that light irradiation caused electrons to be emitted from surfaces. Albert Einstein formally explained this phenomenon in 1905 and received the Nobel Prize in Physics in 1921 for his work. The observation of photoemission resulting from X-ray irradiation was first made by

Robinson and Rawlinson in 1914, and the use of photoemission as an analytical method was introduced by Steinhardt and Serfass in 1951 [139]. XPS is a powerful tool for surface analysis because it provides information about the elemental composition, chemical state, and electronic state of the atoms within the top few nanometers of the material's surface. Since most heterogeneous catalytic reactions occur on the catalyst's surface, acquiring information about the elemental atomic surface composition through XPS has become essential. The solid is exposed to soft x-ray irradiation under high vacuum conditions. The incident x-ray is absorbed by the surface electrons of the sample, leading to their ejection from the sample with a specific kinetic energy. The surface electrons, each possessing varying kinetic energies, are then analysed by a detector and plotted according to their electron counts. This thesis utilised x-ray photoelectron spectroscopy (XPS) to ascertain the chemical state of the elements on the material surface. A Thermo Fisher Scientific instrument was used for XPS survey and high-resolution XPS spectra acquisition. The survey scans were recorded using a K-alpha electron gun [140,141].

2.2.6. Brauner-Emmete-Teller (BET) measurement.

The Brunauer-Emmett-Teller (BET) method is frequently used to determine the specific surface area by analyzing nitrogen adsorption isotherm measurements at 77 K.

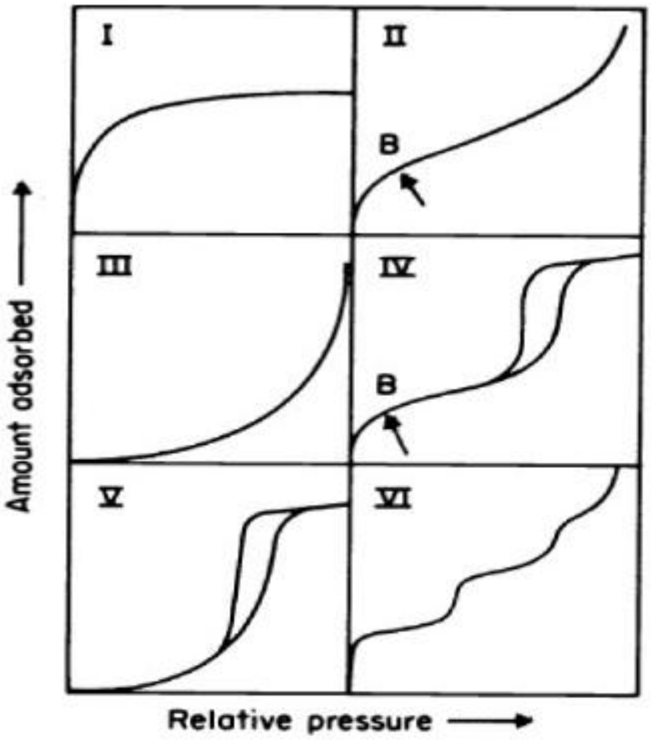

Figure 2.5: Adsorption-desorption isotherm classified by IUPAC [129].

The schematic diagram is depicted in Figure 2.4, and in this thesis, we employed BET using a Microtrac Bel (Model: BELLSORP MAX II & BELCAT-II) with a nitrogen adsorption and desorption process at a temperature of 77.3 K. The BET technique physically adsorbs nitrogen gas onto solid materials to gather data on surface area, pore volume, and pore diameter, which are crucial for understanding the material's characteristics. This physical adsorption depends on the force of the Vander walls between the gas and materials. The instrument provides information about the material's textural properties based on the amount of gas adsorbed after the adsorption and desorption processes. The process is conducted constantly and maintained by the liquid nitrogen gas while the pressure or concentration of the adsorbate gas gradually increases. Therefore, a graph is generated that correlates the relative pressure of the gas with the amount adsorbed by the material [142,143].

The BET measurement involves three steps:

(i) Standardization of the reference cell.
(ii) The sample is heated at a specific temperature and can be varied with sample properties.
(iii) The whole process undergoes under the isotherm condition.

Different types of adsorption-desorption isotherms have been discussed by Brunauer and the IUPAC [144]. This classification connects the type of porosity on the material's surface with the isotherm's form and the interaction strength between the gas and the solid surface. Isotherm type I is associated with microporous solids, while types II and IV represent mesoporous solids. Finally, type VI isotherms are associated with groups of adsorption sites that are homogeneous in energy [145]. These isotherms are shown in Figure 2.4. Different methods were created to describe the isotherm. The most well-known model, created by three professors Brunauer, Emmett, and Teller is the BET model. It derives information about the surface from type II and type IV isotherms, which consistently increases the gas adsorbed on the surface [142,143].

2.3. Magnetic Stirrer with a hot plate

A magnetic stirrer with a hot plate synthesised material with a range of 400 to 800 rpm. The stirrer works on a 220/230-volt AC supply with 0 to 100 °C temperatures. The synthesis process of the material is directly dependent on the stirring speed and synthesis temperature.

2.4. Centrifuge

Centrifugation is a useful technique for separating mixtures by utilizing centrifugal force. A centrifuge is a machine, usually operated by an electric motor, that rotates an object, like a rotor, around a stationary axis. This technique employs centrifugal force to separate particles from a solution according to their size, shape, density, the medium's viscosity, and rotor speed.

A centrifuge (Remi Laboratory) is used in the present research work. To prepare the materials, dissolved solutions were put in tubes centrifuged at 4000 rpm for a few minutes. This procedure was repeated once or multiple times for improved separation. The centrifuged materials are dried and further used for characterization.

2.5. Vacuum Oven

After centrifugation, the materials are dried in the vacuum oven (Model: Vacuum oven RT-165) at 60 ° C for 24 h. The oven consists of double chambers sized 250 × 300 mm and 14 L capacity. Vacuum ovens are equipped with double-walled units, with the exterior coated in epoxy powder on MS sheets and the interior crafted from heavy gauge 304-grade stainless steel sheets, including an SS lid. The oven is worked on temperature at 5 °C to 150 °C. However, this oven can perform well on 220/230 Volts AC current without using any specialized Vacuum Pump.

2.6. Zetasizer

The Zetasizer is an instrument that measures the two characteristics of the particles or molecules: particle size and Zeta potential. This technique works over a wide range of concentrations of solution.

The particle size is determined by measuring the average size of the particles. The light is scattered due to the random motion from a suspension or solutions using the dynamic light scattering (DLS) method. The random movement of particles is related to their size, with smaller particles moving more rapidly than larger ones. Temperature also affects the rate of Brownian motion, so precise temperature control is essential for accurate size measurements. The speckle pattern generated by laser light on the particles is analysed to evaluate diffusion speed. Intensity variations are assessed with a digital autocorrelator, which creates a correlation function. This function and its resulting curve reveal details about particle size and distribution.

The Zetasizer Nano series determines the zeta potential by measuring Electrophoretic Mobility and applying the Henry equation. The generation of a net charge on the particle surface alters the distribution of ions in the adjacent interfacial region, leading to an accumulation of counterions near the surface. This creates an electrical double layer around each particle, with the zeta potential representing the potential at this boundary. The magnitude of the zeta potential reflects the stability of the colloidal system. A high absolute value of the zeta potential indicates strong electrostatic repulsion between particles, reducing the likelihood of flocculation. Conversely, a low zeta potential suggests insufficient repulsive forces, making flocculation more probable.

In this research work, the Zeta-sizer version (Malvern) UK was used to analyze the particle's average size and Zeta potential. The material should be dispersed in the solvent and properly mixed with sonication for this analysis. After preparing the solution, it is filled in the cuvette cell for size determination and in the electrode for zeta potential.

Section-II

2.7. Chemicals

This section describes the details of all the reagents used in this whole study and the methods of preparation of various solutions. Acetone and distilled water are used to wash the glassware. Double distilled water is used to prepare and synthesise the materials for the solution.

2.7.1. Magnesium Nitrate [$Mg(NO_3)_2$]

Magnesium nitrate is an inorganic compound and colourless crystalline solid. i.e. the chemical formula is magnesium nitrate hexahydrate [$Mg(NO_3)_2 . 6H_2O$]. A magnesium nitrate (SRL chemical) solution was prepared by dissolving the required amount of $MgNO_3$ with double distilled water to synthesise the required material.

2.7.2. Aluminum Nitrate [$Al(NO_3)_3$]

Aluminium Nitrate is a colourless inorganic compound, and the chemical formula is Aluminium Nitrate nano hydrate [$Al(NO_3)_3 . 9H_2O$]. Aluminium nitrate was prepared by dissolving the required amount of $AlNO_3$ with double distilled water to synthesise the required materials.

2.7.3. Nickel Nitrate [$Ni(NO_3)_2$]

Nickel Nitrate is an emerald green colour inorganic compound, and its chemical formula is Nickel Nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$]. A Nickel Nitrate solution was prepared using double distilled water to prepare the required materials.

2.7.4. Zinc Nitrate [$Zn(NO_3)_2$]

Zinc Nitrate is a colourless inorganic material, and its chemical formula is Zinc Nitrate hexahydrate [$Zn(NO_3)_2$. $6H_2O$]. This solution was prepared using the required amount of salt with the help of double distilled water.

2.7.5. Iron Nitrate [$Fe(NO_3)_3$]

Ferric Nitrate is a violet crystalline colour inorganic material, and its chemical formula is Ferric Nitrate Nano Hydrate [$Fe(NO_3)_3$. $9H_2O$]. The ferric nitrate-nano hydrate solutions are prepared by dissolving the necessary salts in double-distilled water to obtain the synthesised material.

2.7.6. Sodium Carbonate and Sodium Hydroxide [Na_2CO_3 & NaOH]

Sodium carbonate and sodium hydroxide are colourless inorganic compounds; their chemical formula is Na_2CO_3 and NaOH. These are used as precipitate agents to synthesise the required materials.

2.7.7. Methyl Orange

Methyl orange is a water-soluble mono-azo dye, whose chemical name is Sodium 4-{[4-(dimethylamino) phenyl] diazenyl} benzene-1- sulfonate. This is extensively used in the textile industry, printing, paper production, food colouring, pharmaceuticals, and various research laboratories. It serves as a pH indicator and acts as an acid-base dye. In this adsorption experiment, methyl orange is utilised, and its solution is prepared by dissolving the required amount of the dye in double-distilled water.

2.7.8. Congo Red

Congo Red is a diazo dye whose chemical name is benzidinediazo-bis-1-naphthylamine-4-sulfonic acid. This dye is also used as a pH indicator and is widely used in the textile industry, paper printing, food colouring, and pharmaceuticals. Various experiments have been conducted using this dye. This dye is used in adsorption, and the solution was prepared using double distilled water.

2.7.9. Ethanol

Ethanol is a water-miscible solvent commonly used as a versatile general-purpose solvent. The ethanol obtained from SRL chemicals is a volatile, colourless liquid with a faint odour. It was employed to test the free radicals formed in the reaction mixture.