

# CHAPTER 1

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## INTRODUCTION

This chapter presents a detailed overview of heterogeneous catalysis and transition metal-based layered double hydroxides (LDHs). The technological developments in the smart design and synthesis of transition metal based LDHs is studied over the years with the emphasis on the exploration of pertinent heterogeneous materials for different field of prospects. The suitable synthesis strategy for the fabrication of transition metal-based LDHs along with their applications in various promising fields is briefly reviewed.

### 1.1 Background

Catalysis is considered as a key revolutionary trait in the domain of science and technology. Typically, it is defined as the phenomenon of increasing the rate of a chemical reaction on addition of a small quantity of an external substance known as the catalyst. A catalyst is a substance which increases the rate of a chemical reaction without itself being undergone any chemical change or consumed in the reaction [1]. The term catalysis was first introduced in 1836 by Berzelius, a Swedish chemist, but scientifically defined firstly by Ostwald in 1894 [2]. The “catalysis” word originally came from Greek words *kata* (cata) which means down and *lyein* (lysis) means loosen. A catalyst provides an alternative pathway for the reaction by lowering the activation energy barrier. The catalytic reactions are carried out under milder conditions and thus saving the energy. The reactions are very fast and reach the desired product(s) through a selective route using fewer resources; and thus minimize the waste.

Catalysis is classified into two major types: homogeneous and heterogeneous catalyses. In homogeneous catalysis, the catalyst is present in the same as the reactant forming a single phase. For examples, acid-base and enzyme catalysis are considered as the most important homogeneous catalysis. In heterogeneous catalysis, the catalyst is present in different phase as that of the reactant and usually these are solid materials. The surface reactions fall into this category. The heterogeneous catalysts have several advantages over homogeneous catalysts and these are presented in Table 1.1 [3]. The major advantages of heterogeneous catalysts are the easy separation after the completion of reaction and reusability. In case of solid-gaseous systems, the catalyst can be easily

separated and cleaned, and in liquid-solid systems, it can be separated simply by filtration. But separation of homogeneous catalysts from the reaction mixture is quite difficult as they are in one phase with the reactants. Moreover, high cost, toxicity, corrosion, generation of huge amount of solid wastes products etc. make the homogeneous catalytic reactions environmentally and economically unsuitable for industrial applications.

**Table 1.1.** Advantages of heterogeneous catalysts over homogeneous catalysts.

<b>Homogeneous catalysts</b>	<b>Heterogeneous catalysts</b>
Difficult in separation and expensive	Easy in separation and cheap
Single active site	Multiple active sites
Poor thermal stability	Good thermal stability
Non reusable	Reusable

A numerous chemical processes have been carried out in industry following catalytic route and major production of bulk chemicals involves the use of solid heterogeneous catalysts. Since, the catalytic reaction occurs at specific surface sites, called active sites, heterogeneous catalysts are often regarded as the surface catalysts. The heterogeneous catalytic reaction involves the following steps [4]:

- (i) Diffusion of the reactant from its bulk to the surface of the catalyst,
- (ii) Chemisorption of the reactant on the catalyst surface,
- (iii) Chemical reaction on the surface,
- (iv) Desorption of the reaction products from the surface, and
- (v) Diffusion of the product molecules from near the surface into the bulk.

Thus, the adsorption is considered to be the important step for any heterogeneous catalytic reaction. An alternative sequence of elementary steps can be acquired due to the presence of a catalyst to obtain the desired product. The efficiency of a heterogeneous catalyst can also be understood in terms of activity and selectivity with morphological characteristics like, crystallinity, surface area and active surface sites per unit area [5]. Heterogeneous catalysts have thus played vital role in different field of prospects. Some of the popular heterogeneous catalysts are layered double hydroxides (LDH), zeolites, clays

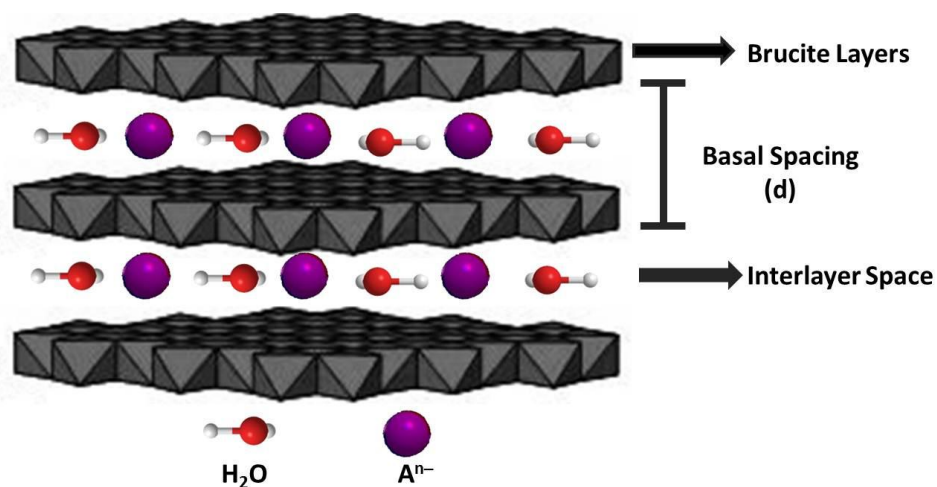
and mesoporous materials. However, in the recent years LDHs with exchangeable interlayer anions, flexible tunability and uniform distribution of metal cations in the brucite-like layers have found their applications in various fields as potential adsorbents, stable and recyclable catalysts or catalyst supports with high academic and industrial importance [6]. In view of these, we have presented herein a comprehensive overview on the use of layered double hydroxides and mixed metal oxides derived from them as heterogeneous catalytic system for various applications.

## 1.2 Layered double hydroxides (LDHs) and its structure

Layered double hydroxides (LDHs) are inorganic lamellar compounds represented by the general formula as  $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} (A^{n-})_{x/n} \cdot nH_2O$ , where,  $M^{2+}$  is divalent metal cation such as  $Mg^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ ; and  $M^{3+}$  is trivalent metal cation such as  $Al^{3+}$ ,  $Fe^{3+}$  and  $Cr^{3+}$ ;  $x$  is the charge density whose value lies in the ranges of 0.2–0.33;  $A^{n-}$  is the interlayer anion such as  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $F^-$  and  $Cl^-$  [7–9]. Simplicity, low cost preparation and easy handling make these materials more suitable for the researchers. These are commonly known as hydrotalcite-like compounds due to their structural similarities to naturally occurring hydrotalcite mineral,  $[Mg_6Al_2(OH)_{16}(CO_3)_4 \cdot 4H_2O]$  whose structure is consisting of positively charged framework, with cations occupying the octahedral sites between the sheets.

Figure 1.1 shows the schematic diagram for structural representation of LDH. The crystal structure of LDH is analogous to that of the brucite,  $Mg(OH)_2$  that constituted by sharing the edge sheets of octahedral  $M(OH)_6$  units [10]. The structure is based on the stacking of hydroxides layers where a proportion of the  $M^{2+}$  cations are replaced by  $M^{3+}$  cations resulting in the formation of excess residual positive charges in the layers [11,12]. This resulting excess positive charge of the layers is balanced by the anions incorporated in the gallery or interlayer region of brucite-like layers [11,12]. The interlayer region also contains water molecules, hydrogen bonded to surface hydroxyl groups of the layer and/or the anions located in interlayer space [13]. The stability of LDH is depends on the electrostatic interactions and hydrogen bonding between the brucite-like layers and the interlayer contents, holding the layers together and thus establishing the crystal structure

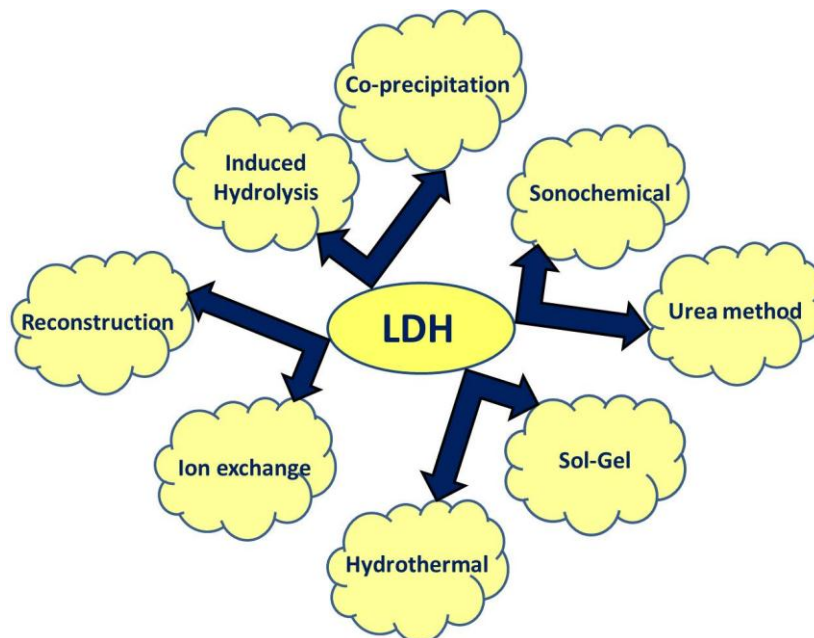
[13]. Based on the stacking of brucite-like layers on top of one another, LDHs are assigned to two forms with two layer-repeat belongs to hexagonal polytypes (2H), and three-layer repeat belongs to rhombohedral polytypes ( $3R_1$  and  $3R_2$ ) [13]. The synthetic LDHs are usually assigned to  $3R_1$  as well as  $3R_2$  form [13]. Like layered silicates, LDHs have layered structure which is significantly different from the former. LDHs are anionic clays containing positively charged brucite-layers with charge compensating anionic interlayer or gallery species [14], while the silicates are cationic clay with positively charged layers and gallery space containing cationic species.



**Figure 1.1.** Schematic diagram for structural representation of layered double hydroxide (LDH).

### 1.3 Synthetic procedures of LDHs

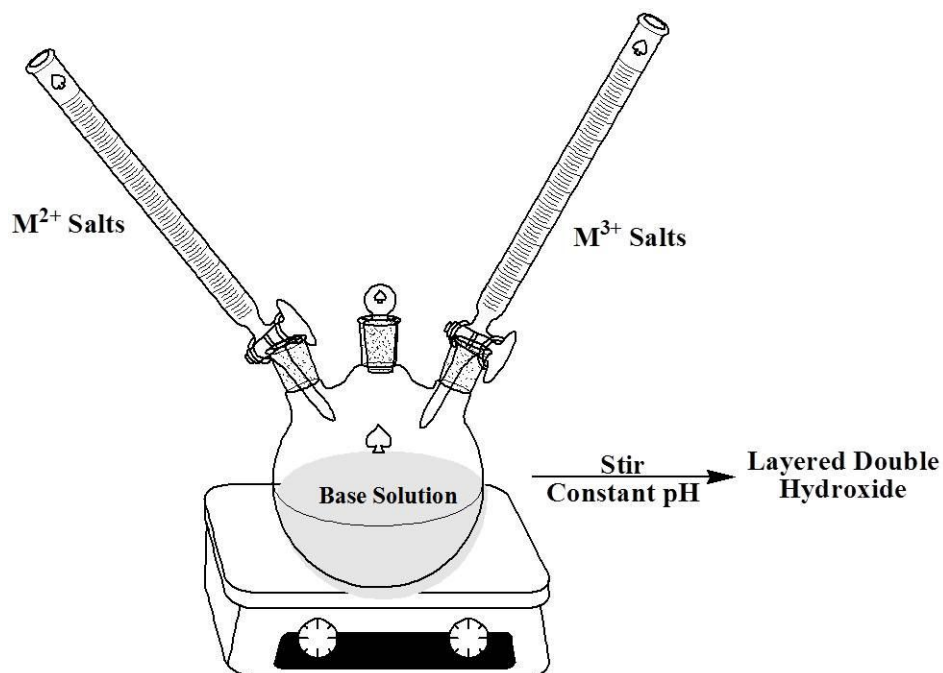
LDHs are simple and inexpensive materials which can be easily synthesized in the laboratory and industrial scales. Several methods are available for synthesis of LDHs and can be engineered with desirable physical and chemical properties for various needed applications [15]. Different methods adopted for the synthesis of LDHs are schematically presented in Figure 1.2.



**Figure 1.2.** Various synthetic methodologies of LDH.

### 1.3.1 Co-precipitation method

Figure 1.3. shows the schematic diagram of co-precipitation method for preparation of LDH. In co-precipitation method, LDHs are prepared by the addition of two solutions, one containing metal salts of  $M^{2+}$  and  $M^{3+}$ ; and another containing base, such as NaOH,  $Na_2CO_3$ ,  $NH_4OH$  and so on. In this method, initially metal hydroxides are formed and further addition of base results in the conversion of metal hydroxides into LDH through precipitation mechanism. In co-precipitation method, pH is an important factor as it adversely affects the structural and chemical properties of the LDH phases. During the addition, the pH of the solution mixture is kept at constant in the range of 8–10 in order to attain high chemical homogeneity in LDH [16]. The constant pH is maintained by the simultaneous addition of a base solution to the reaction mixture. The final solution mixture is allowed for aging for a long period of time to acquire a material of well crystallized structure. The as obtained solid precipitate is collected by filtration, washed thoroughly with deionized water and dried overnight.



**Figure 1.3.** Schematic diagram of co-precipitation method for preparation of LDH.

### 1.3.2 Sonochemical method

In typical method, LDHs are prepared by co-precipitation method followed by sonochemical treatment. In first step, two solutions containing  $M^{2+}$  and  $M^{3+}$  metal salts are mixed slowly with another solution containing base. During the mixing, the pH of the solution mixture is maintained at constant in the range of 8–10 depending on the nature of the metal ions. After completion of mixing, the resulting solution is subjected to ultrasound irradiation at a particular time and temperature. The solid precipitate is filtered, washed thoroughly with deionized water and dried in oven overnight. This method helps in improving the crystallinity of LDH phases [16].

The phenomenon of sonochemical method is based on the acoustic cavitation [17]. When the solution mixture is subjected to ultrasonic irradiation, rapid movement of the fluid leads to cavitation in which microbubbles are formed and collapsed [18]. This oscillating microbubbles create unique hot spot arises due to the compressional heating from collapsing of bubble and thus produces extraordinary conditions inside the bubble with extremely high temperature, pressure and cooling rates [17].

### 1.3.3 Urea method

In a typical urea method, urea is added to an aqueous solution of desired  $M^{2+}$  and  $M^{3+}$  metal salts and heated under reflux condition for several hours. The precipitate obtained is collected by filtration, washed thoroughly with deionized water and dried overnight. The rate of urea hydrolysis can be possible to increase upto 200 times by increasing the reaction temperature to 100 °C [16]. The urea molecules undergo decomposition to produce ammonium carbonate, which finally causes in the precipitation into LDH with  $CO_3^{2-}$  as interlayer anion. The urea method provides high degree of crystallinity and a narrow particle size distribution.

### 1.3.4 Sol-gel method

The sol-gel method was first explored by Lopez *et al.* [19] for the synthesis of MgAl LDHs. In a typical method, ethoxide solution of  $M^{2+}$  metal is added to another solution containing acetylacetonate/ tri-sec-butoxide of  $M^{3+}$  metal and heated under refluxed condition. The pH of the suspension is maintained at 10 by adding base like,  $NH_4OH$  and allowed to stir constantly until the gel like precipitate of LDH is formed. The as obtained gel like product is filtered, washed properly with deionized water and dried overnight. The LDHs synthesized using sol-gel method is thermally very stable, but less crystalline than those synthesized via the co-precipitation method.

### 1.3.5 Hydrothermal method

In a typical method, two solutions containing  $M^{2+}$  and  $M^{3+}$  metal salts are added dropwise to an another solution containing base under vigorous stirring at room temperature. Then, the suspension is transferred into a Teflon-lined autoclave and heated at higher temperature for several hours depending upon the metal ions. The pH of the supernatant ranges 8–10. The solid precipitate is collected by centrifugation washed thoroughly with deionized water and ethanol and dried overnight. The hydrothermal method is useful for synthesis of highly crystalline LDHs.



### 1.3.6 Ion exchange method

The ion exchange method is based on the exchange of anions in interlayer space with other anionic species. In typical method, the precursor LDH is suspended in an aqueous solution containing the anionic species to be exchanged. The suspension is then allowed to stir for several hours at room temperature. The precipitate is then collected by filtration, washed several times with deionized water and dried overnight.

### 1.3.7 Reconstruction method

The reconstruction method for synthesis of LDHs was first described by Miyata [20]. This method involves the reconstruction of the layered structure of brucite-like LDH by hydrating the calcined LDH. The reconstruction method is based on one of the unique properties of LDHs i.e. memory effect. In first step, the LDHs are calcined at a particular temperature to obtain mixed oxides and then subjected to rehydration in aqueous solution with the anion to be intercalated [16]. The solid precipitate is collected by filtration, washed several times with deionized water and dried overnight.

The structural recovery however, depends upon some experimental conditions such as, calcination temperature, duration and rate of heating. The reconstruction method is useful mainly in the preparation of large organic anions intercalated LDH.

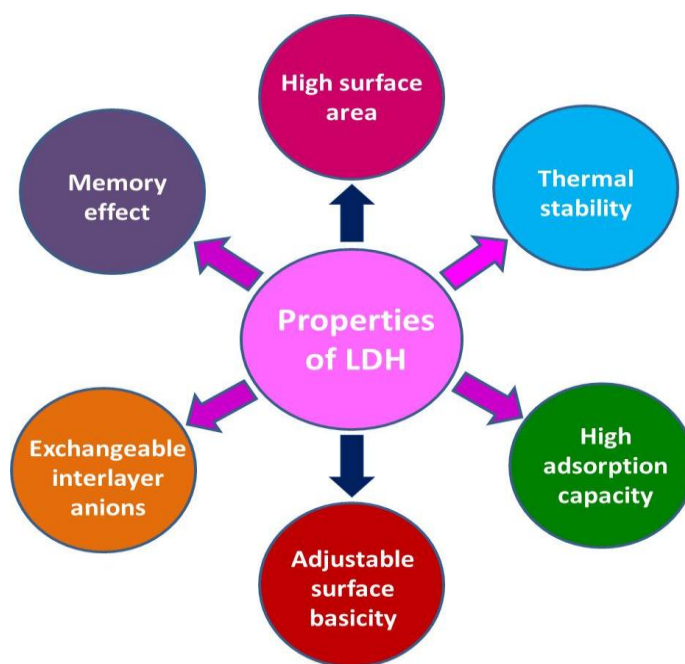
### 1.3.8 Induced hydrolysis method

In this method, metal oxides are added dropwise to an acidic solution containing  $M^{3+}$  metal salts. The metal oxides are dissolved progressively in the acidic solution and precipitated into LDH provided the pH is buffered by the oxide suspension [16]. The obtained solid precipitate is filtered, washed thoroughly with deionized water and dried overnight.

The method of induced hydrolysis can also be used for synthesis of LDH with di-valent, di-tetravalent and tri-trivalent systems.

## 1.4 Properties of LDHs

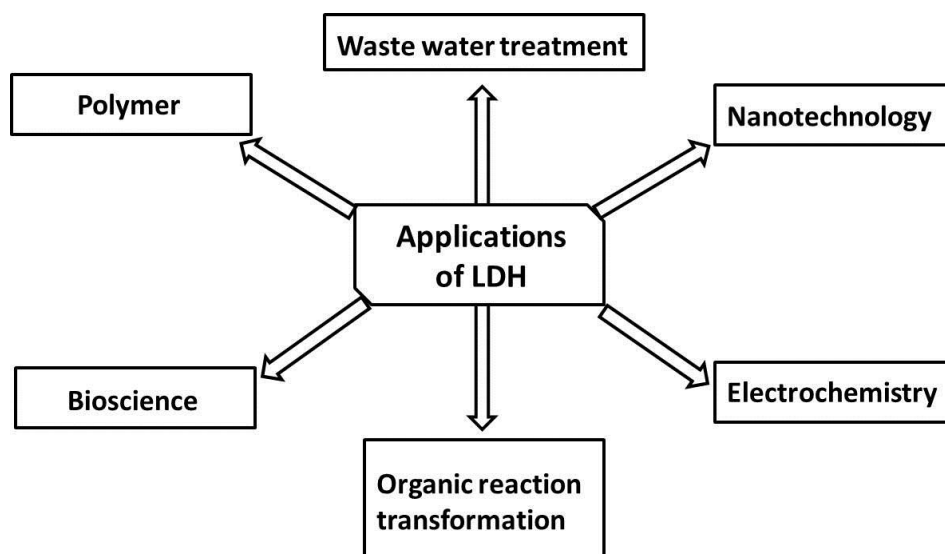
The unique properties of LDHs such as high surface area, high adsorption capacity, thermal stability, easily tailored properties with versatile metal compositions and  $M^{2+}/M^{3+}$  molar ratio, adjustable surface basicity, exchangeable interlayer anions, memory effect etc. [21,22] make them highly demandable research area for the scientist all over the globe [23]. Moreover, LDHs are environmentally and economically feasible due to their simple and easy handling, low cost, easy separation and reusability. The presence of surface hydroxyl group is another important feature of brucite-like LDHs. The efficient catalytic activity of LDHs can be understood in terms of two attractive features. The brucite-like LDHs have layered structure with an abundance of basic sites, which make these materials as potential candidate for various base catalyzed organic transformations. Moreover, the presence of two or more than two metal cations distributed uniformly at the atomic level within the brucite-like layers, enhances the catalytic activity and selectivity as one of metal cations is catalytically more active [6]. The various properties of LDH are shown in Figure 1.4.



**Figure 1.4.** Various properties of LDHs.

## 1.5 Applications of LDHs

LDHs are a class of inorganic layered compounds which have received considerable importance during the past decades due to their potential applications in various chemical and industrial processes. The various applications of LDH materials are schematically presented in Figure 1.5. LDHs have their wide use in various fields of organic reaction transformations [24,25], polymer [26], nanotechnology, electrochemistry [27], waste water treatments [28,29] and bioscience [30]. Here, we have mainly focused on applications of LDH materials in two major areas of waste water treatment and organic reaction transformations.



**Figure 1.5.** Various applications of LDH.

### 1.5.1 Waste water treatment

#### 1.5.1.1 Organic dyes and their adverse effect on environment

Dyes are colored substance that has affinity for the substrate to which it is being applied [31]. Dyes are highly soluble in water and/or an organic solvent. The color chemistry of dyes can be understood in terms of various factors. They are colored because they absorb light of wavelength in the visible range of 400–700 nm. They possess structure bearing at least one chromophoric group (color-bearing group) and a conjugated system (structure

with alternating double and single bonds). Moreover, they exhibit resonance stabilizing structure [32]. As the name implies, natural dyes are generally obtained from natural sources, such as plant roots, berries, bark, leaves, and wood; fungi, lichens etc. Throughout history, people used common and locally available materials for dyeing textiles. Some examples of natural plant-based dyes are indigo, saffron, woad and madder. On the other hand, synthetic dyes are man-made and are obtained from various synthetic resources such as petroleum by-products and earth minerals. Mauveine is the first synthetic dye, discovered in 1856 by William Henry Perkin [31,32]. It is an organic aniline dye, which was discovered from a failed attempt by Perkin in the total synthesis of quinine [31]. Organic dyes are organic compounds and these may be natural or synthetic.

Dyes can be classified based on their chemical structure and use or application method [33]. The former classification is generally adopted for practical use by the chemists and based on certain common chemical structures. The most common and important organic dyes belongs to azo ( $-N=N-$ ), carbonyl ( $C=O$ ), phthalocyanine, arylcarbonium ion, sulfur, polymethine and nitro chemical groups [34]. The classification based on use or application of dyes is mostly used by the dye users, dye technologist and attain greater interest than the former classification. Dyes belong to this classification based on application are designed carefully with a set of properties that become suitable for their particular application.

Various industries like paper, plastic, cosmetic, textile, pharmaceutical and food use different types of dyes and pigments in an extensive amount [35–37]. A large quantity of effluents is daily getting released from such industries which also contain some amount of dyes [38]. Release of such effluents along with dyes causes severe problems to the environment and health of the human body as well as on the aquatic organism [39–41]. Dyes are very stable and colorant in nature. When the dyes come in contact with water, they immediately pollute the whole water bodies. Due to their high solubility in water, presence of dyes even in a very low concentration is highly visible to the eye and hinders the passes of sunlight through the water surface [42–44]. Since sunlight is very essential for the photosynthesis phenomenon, it is very much difficult for the aquatic plants and animal to survive at that situation. Dyes are very stable with complex aromatic structure

and non degradable in nature [45,46]. Some dyes also have carcinogenic and mutagenic properties [47]. Therefore, waste water containing dyes become a serious issue because of the growing environmental pollution. So, it is very much essential to treat the effluents prior to releasing to the environment.

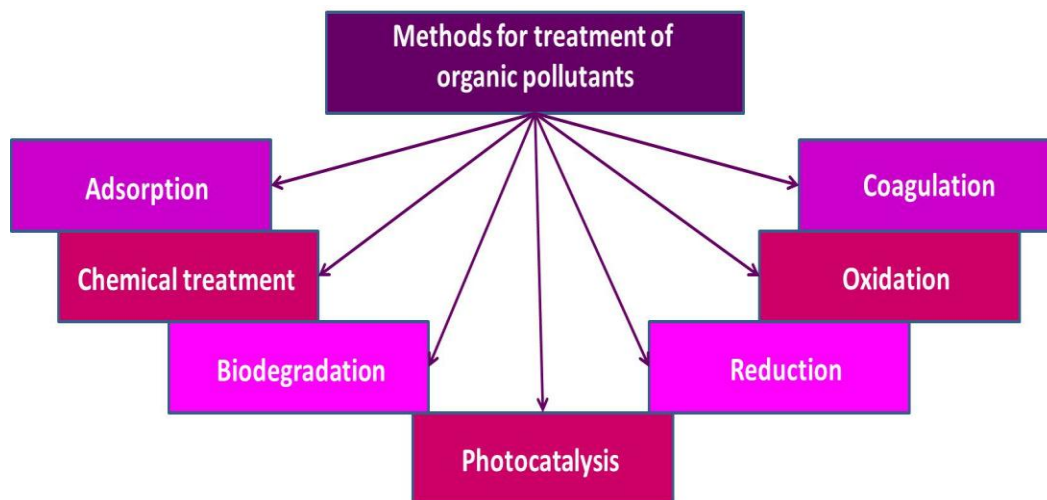
#### 1.5.1.2 Phenolic compounds and their adverse effect on environment

Among the various organic contaminants, phenol and its compounds are considered to be the major pollutants due to their toxicity causing unpleasant taste and odour when contaminating the drinking water [48–50]. Phenols have found their uses as chemical reagents in laboratory and also as raw materials in the manufacture of various organic compounds [51]. Phenolic compounds are also widely used in various industries including chemical, petrochemical, refinery, pharmaceutical, paint stripping operations, plastic and textile [52–54]. Therefore, the effluents releases from these industries are needed to treat before them being disposed to the environment; as they may contaminant both the soil and ground water. The phenolic compounds are very stable, persistent and are non-biodegradable in nature [55]. Therefore, it is difficult to remove the phenolic compounds by means of direct photolysis by sunlight. Moreover, these compounds are toxic and carcinogenic in nature, due to which it is harmful to release such compounds into the environment as they not only affect the aquatic system but also the human health [56–58]. Therefore, disposing of such toxic compounds safely is become a major concern and important area of research. As the phenolic compounds are very stable, these techniques are considered to be less effective towards the complete degradation leading to the generation of side products which make them more time consuming and also expensive [59–61]. Thus, it is essential to adopt such as techniques that are efficient in terms of time and cost in order to make them more tempting to use for industrial purposes.

#### 1.5.1.3 Methods for treatments of organic pollutants

With the increasing concern about the environmental issues related to the use of various organic contaminants, it is very challenging to develop an effective treatment for such use. Figure 1.6 shows the various methods developed for the treatment of organic pollutants from aqueous solution and they include coagulation [62], oxidation [63], reduction [64],

adsorption [65], chemical treatment, biodegradation and photocatalysis [66,67].



**Figure 1.6.** Various methods for treatment of organic pollutants.

#### 1.5.1.3.1 Adsorption

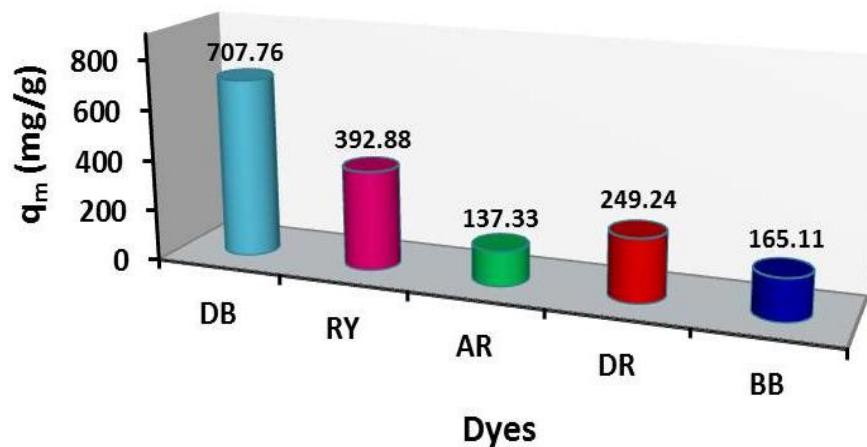
In general, adsorption can be defined as the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to surface of the adsorbent, creating a film of the adsorbate over it. This is a surface based process present in many chemical, physical, biological and natural systems and widely used in various industrial applications [68]. The adsorption process may occur through weak van der Waals forces (physisorption) or covalent bonding (chemisorption) and; also may occur due to electrostatic attraction between the adsorbate and surface of the adsorbent. It is a surface phenomenon most widely adopted in waste water treatment for removal of various organic contaminants from aqueous solution.

Various methods have been adopted for the removal of organic contaminants from aqueous solution, however, some of the methods are expensive, effective only in case of lower dye concentrations, time consuming and also produce toxic and harmful by-products. Adsorption is the most effective and reliable one as it is fast, highly efficient, less expensive, easy handling and recyclable [69–71]. Moreover, a variety of adsorbents are available which make the adsorption process a popular one and these includes fly ash [72], activated carbon [73], clays [74], zeolites [75] etc. Activated carbon is considered as effective adsorbents but economically not a feasible one [76]. Various other adsorbents

were studied by different groups over the years with efficient adsorption efficiencies. The effective absorption of methylene blue (MB) using graphene oxide was reported by Yang *et al.* [77] with removal efficiency higher than 99%. A study on preferential and enhanced adsorption of different dyes, such as erichrome black T (EBT), bromocresol green (BCG), bromophenol blue (BPB), fluorescein (FLU), methyl red (MR), methylene blue (MB) and methyl orange (MO) on iron oxide nanoparticles was explored by Saha *et al.*[78]. They reported that the group of dyes, EBT, BPB, BCG, and FLU containing hydroxyl (–OH) groups were adsorbed more on the surface of the adsorbent. Geng *et al.* [79] synthesized reduced graphene oxide (RGO)–Fe<sub>3</sub>O<sub>4</sub> nanoparticles and employed for efficient adsorption of a series of dyes, Rhodamine B (RhB), Rhodamine 6G (R6G), acid blue 92 (AB92), orange (II) (OII), malachite green (MG) and new coccine (NC). Again, the use of graphene as adsorbent was demonstrated by Liu *et al.* [80] for removal of methylene blue from aqueous solution with maximum adsorption capacity of 153.85 mg/g at 293K.

Owing to various advantages like simplicity, economical feasibility and high efficacy, layered double hydroxides (LDHs) have been widely adopted as adsorbents in the field of waste water treatment towards the removal of dyes from waste water [6,81,82]. Ai *et al.* [10] studied the efficient adsorption of organic dye, methyl orange (MO) from aqueous solution using Mg–Al LDH synthesized via hydrothermal route with monolayer adsorption capacity of 0.453 mol·kg<sup>-1</sup>. The adsorption kinetics was analysed by pseudo first-order and the equilibrium adsorption data were fitted well to both the Langmuir and Freundlich models. Zaghouane-Boudiaf *et al.* [83] reported the adsorptive removal of anionic dye, methyl orange from aqueous solution by uncalcined and calcined MgNiAl LDHs with maximum adsorption capacity,  $q_{max}$  of 118.5 and 375.4 mg/g respectively. They also reported the endothermic and spontaneous nature of the adsorption process. In another report, Wu *et al.* [84] demonstrated the adsorption of various dyes, basic blue (BB) as cationic; direct blue G-RB (DB), reactive yellow 4GL (RY) and acid red GR (AR) as anionic dyes; and disperse red 3B (DR) as nonionic dye in aqueous solution using dodecylsulfate-intercalated LDHs (LDHs-SDS). The adsorbent showed efficient adsorption activities for removal of DB, RY, AR, DR and BB dyes with maximum adsorption capacities,  $q_m$  (mg/g) of 707.76, 392.88, 137.33, 249.24 and 165.11

mg/g, respectively at 298 K (Figure 1.7). The adsorption isotherm data of the dyes were best fitted to the Langmuir model except for dye, AR and the kinetics of adsorption was well described with the pseudo-second-order model for all the dyes.



**Figure 1.7.** Maximum adsorption capacities ( $q_m$ , mg/g) for DB, RY, AR, DR and BB dyes at 298 K using LDHs-SDS.

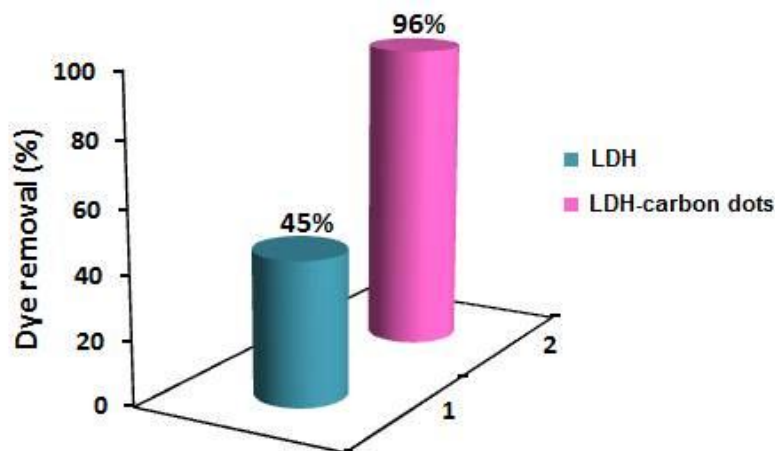
Pahalagedara *et al.* [18] reported the sonochemical synthesis of NiAl LDH for removal of reactive azo dye, Remazol Brilliant Violet (RBV-5r). They reported that NiAl-calcined at 250 °C (NiAl-C250SC) exhibited the enhanced dye removal efficiency of 100% in 6 min and with an adsorption capacity of 150 mg/g at 25 °C and at pH = 6. The adsorption of reactive brilliant red X-3B dye from aqueous solution using Ni/Al-LDH, Mg/Al-LDH and Co/Al-LDH was reported by Zhang *et al.* [85] with  $q_m$  (maximum adsorption capacity) values of 5.0350, 3.8358 and 2.3330 mg/mmol, respectively (Table 1.2). The adsorption process was well described with Langmuir isotherm model and the kinetics followed a pseudo-second-order model. They also reported that the adsorption process was spontaneous and exothermic in nature. The adsorption mechanism was associated with the electrostatic attraction and hydrogen bonding between X-3B dye molecules and LDH adsorbent with hydrogen bonding playing the main role in the adsorption process.



**Table 1.2.** Various adsorption parameters for removal of reactive brilliant red X-3B using three different LDH adsorbents.

Adsorbent	$q_m$ (mg/mmol)	Isotherm/ Kinetics	Thermodynamics
Ni/Al-LDH	5.0350	Langmuir/Pseudo-second order	Spontaneous and exothermic
Mg/Al-LDH	3.8358	Langmuir/Pseudo-second order	Spontaneous and exothermic
Co/Al-LDH	2.3330	Langmuir/Pseudo-second order	Spontaneous and exothermic

Zhang *et al.* [86] reported the fabrication of LDH-carbon dot composites for the efficient removal of anionic methyl blue dye from aqueous solution with percentage dye removal of 96% within 20 min (equilibrium time) with maximum uptake capability of methyl blue,  $q_m$  was 185 mg/g compared to the parent LDH adsorbent with only 45% dye removal (Figure 1.8). They also reported that the hydrogen bonding between carbon dots and the dye molecules along with the electrostatic attraction between anionic dye and LDH surface are mainly responsible for the enhanced adsorption capability of the LDH-dots composites for the removal of anionic methyl blue dye from aqueous solution.



**Figure 1.8.** Dye removal (%) of methyl blue from aqueous solution over LDH and LDH-carbon dots adsorbents.

Recently, Lei *et al.* [87] synthesized hierarchically porous NiFe-LDH via hydrothermal method followed by calcination to obtain LDH derived oxides (NiFe-LDO) for the removal of Congo red (CR) dye from aqueous solution. The isotherm study showed that the adsorption data were fitted well with the Langmuir model for both calcined and uncalcined samples. The obtained maximum adsorption capacities were 205 and 330 mg/g for NiFe LDH and NiFe LDO, respectively. The adsorption kinetics was well described with pseudo-second-order kinetic model. The anion exchange and reconstruction were involved in the mechanism of adsorption process. Zubair *et al.* [88] reported the efficient adsorptive removal of Eriochrome black T (EBT) dye from aqueous solution using calcined MgAl-, CoAl- and NiFe-LDHs at pH 2. Table 1.3 showed adsorption efficiencies of the calcined LDHs in terms of degradation (%) and maximum adsorption capacity,  $q_m$  (mg/g) for removal of EBT. They also reported that the adsorption of EBT followed monolayer adsorption and kinetics was well described with a pseudo-second order model for all cases. The mechanism for enhanced adsorption of EBT on calcined LDH adsorbents were explained on the basis of hydrogen bonding and electrostatic attraction between surface functional groups of the adsorbent and the dye molecule.

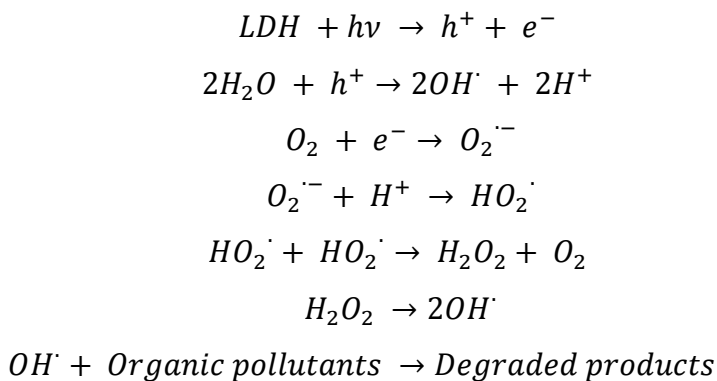
**Table 1.3.** Adsorption efficiencies of various adsorbent in terms of degradation (%) and maximum adsorption capacity,  $q_m$  (mg/g) for removal of EBT.

Adsorbent	Degradation (%)	$q_m$ (mg/g)
MgAl-CLDH	96.54	540.91
CoAl- CLDH	93.13	419.87
NiFe-CLDH	91.50	132.49

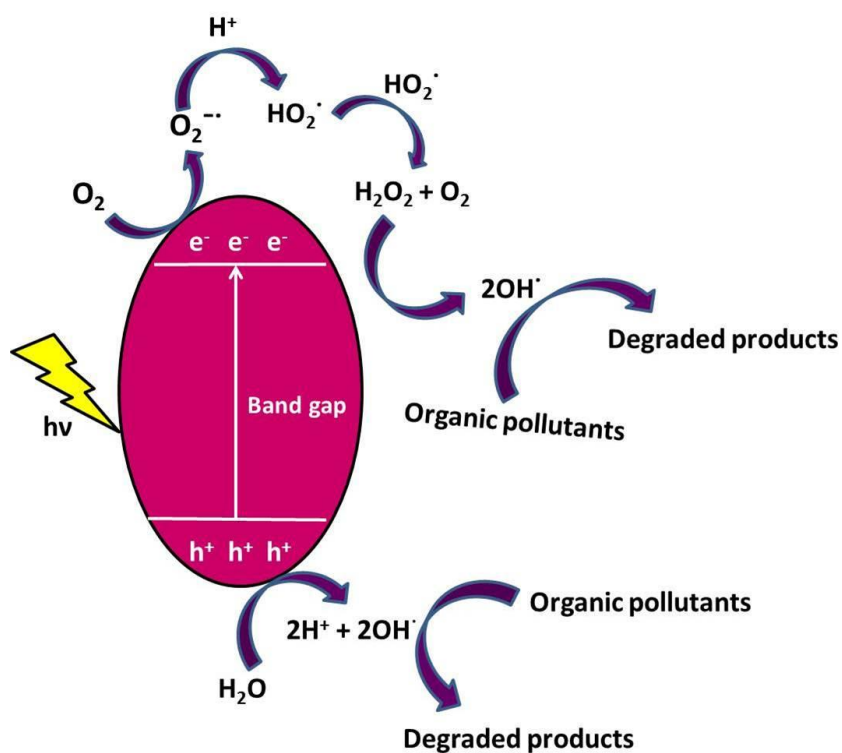
#### 1.5.1.3.2 Photocatalysis

Photocatalysis is the acceleration of a reaction by a catalyst in the presence of photon or light [89]. In photocatalyzed reaction, the activity of a photocatalyst mainly depends upon

its ability to generate electron–hole pairs which create highly active oxidative free radicals such as hydroxyl radicals ( $\bullet\text{OH}$ ), and thus able to undergo oxidative degradation process. When the catalyst is subjected to light irradiations, photons with energy ( $h\nu$ ) equal to or greater than the band gap of the catalyst excite the electrons from valence band to the conduction band leaving behind positive holes ( $h^+$ ) in the valence band and thus the pairs of positive hole and negative electron are generated to promote the degradation process [90,91]. The  $\text{H}_2\text{O}$  molecules in the reaction medium combine with the positive holes in the valence band and generates  $\text{OH}^\bullet$  radicals. The adsorbed  $\text{O}_2$  molecule on the catalyst surface form superoxide radicals,  $\text{O}_2^{\bullet-}$  by combining with the photogenerated negative electrons in the conduction band. The  $\text{O}_2^{\bullet-}$  radicals thus formed again combine with  $\text{H}^+$  ions and generates  $\text{HO}_2^\bullet$  radicals, which in return combining with another molecule of  $\text{HO}_2^\bullet$  radicals result in the formation of  $\text{H}_2\text{O}_2$ . This *insitu* generated  $\text{H}_2\text{O}_2$  finally forms the oxidizing species,  $\text{OH}^\bullet$  radicals, which are mainly considered as the active species for initiating the degradation of phenolic compounds. The overall possible degradation mechanism for photocatalytic degradation of organic pollutants over LDH can be expressed as follows,



The possible mechanism for photocatalytic degradation of organic pollutants is schematically represented in Figure 1.9.



**Figure 1.9.** Schematic diagram of the proposed mechanism for photocatalytic degradation of organic pollutants.

On increase demand of the environmental remediation, a number of studies on photocatalytic degradation of various organic pollutants have been reported. Chen *et al.* [92] reported the photocatalytic degradation of Fluoresein, Orange II and Red acid G, using a magnetically separable photocatalyst,  $\text{TiO}_2/\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$  (TSF) under visible and UV irradiation. Another report on the efficient photocatalytic degradation of phenol over  $\text{Co}_3\text{O}_4/\text{BiVO}_4$  composite was demonstrated by Long *et al.* [93] under visible light irradiation with the highest efficiency for the composite loaded with 0.8 wt % cobalt and calcined at 300 °C. Lv *et al.* [94] synthesized the microwave-assisted ZnO-reduced graphene oxide composite for efficient photocatalytic degradation of methylene blue with maximum degradation efficiency of 88% under UV light irradiation in 260 min at neutral pH. An efficient degradation of Rhodamine B (RhB) was reported by Jothivenkatachalam *et al.* [95] using  $\text{WO}_3$  supported zeolite-Y under visible, UV and solar light irradiation. At the same time, Purushothaman *et al.* [96] reported the photocatalytic activity of wafer

level GaN nanowires grown under catalytic and self-catalytic approach was investigated for the degradation of methylene blue under UV and visible light irradiation.

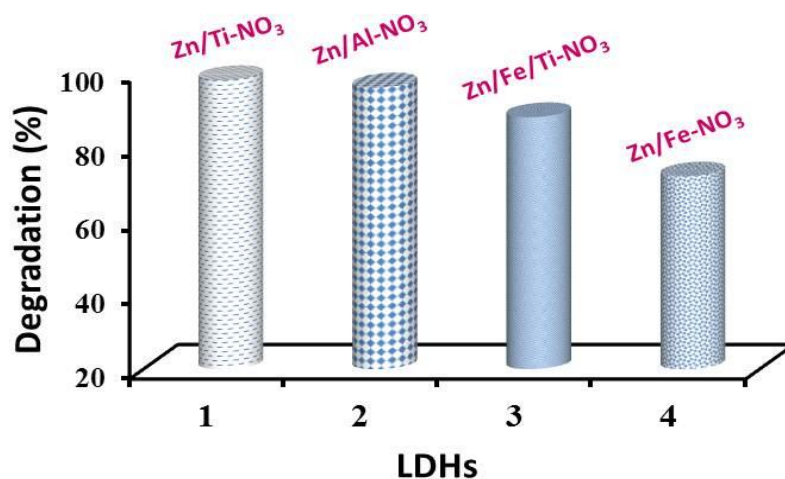
The use of layered double hydroxides (LDHs) as photocatalyst has drawn increasing attention towards the treatment of organic contaminants over the years [97–99]. The presence of surface –OH group in the LDH structure make it an interesting material of choice as photocatalyst for the oxidative degradation of organic pollutants. Seftel *et al.* [100] reported the photocatalytic degradation of the methyl-orange dye using Zn/Al-LDHs. They also reported that Zn/Al-LDH with the cationic ratio of 4 and calcined at 500 °C exhibited dye removal of 93%. Shao *et al.* [101] demonstrated the efficient photocatalytic activity of Zn–Ti layered double hydroxide for degradation of methylene blue (MB) under visible-light irradiation with % degradation of ~100% in 100 min. The synthesis of various anions such as chloride, nitrate and carbonate intercalated ZnFe layered double hydroxides were demonstrated by Parida *et al.* [102] and employed as photocatalyst for degradation of methyl violet (MV) and malachite green (MG) using solar light. They reported that the carbonate intercalated LDH (ZnFe-CO<sub>3</sub> LDH) showed the efficient photocatalytic activity with degradation (%) of 99 and 98.5%; and high apparent rate constant,  $K_{app}$  value of 0.036 and 0.032 for MV and MG, respectively compared to the other intercalated LDHs (Table 1.4).

**Table 1.4.** Degradation (%) and  $K_{app}$  values for photodegradation of MV and MG over various anion intercalated ZnFe LDH photocatalysts.

Photocatalyst	Degradation (%)		$K_{app}$ (min <sup>-1</sup> )	
	MV	MG	MV	MG
ZnFe-Cl LDH	75	72	0.012	0.009
ZnFe-NO <sub>3</sub> LDH	66	64	0.008	0.007
ZnFe-CO <sub>3</sub> LDH	99	98.5	0.036	0.032

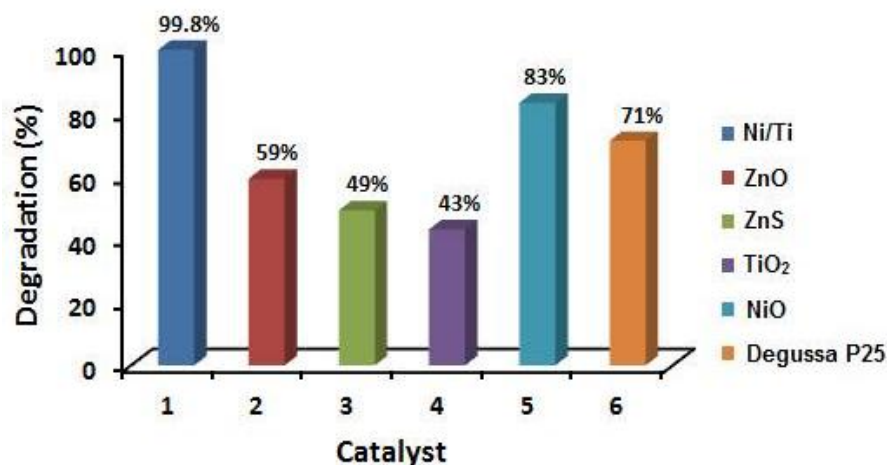
Xia *et al.* [103] reported the synthesis of a series of Zn/M–NO<sub>3</sub>-LDHs (M = Al, Fe, Ti, and Fe/Ti) and tested the catalytic activity for the photodegradation of Rhodamine B (RB) under visible-light irradiation. Figure 1.10 shows the degradation performance of

RB using Zn/M-NO<sub>3</sub>-LDHs following the order: Zn/Ti-NO<sub>3</sub>-LDHs (98%) > Zn/Al-NO<sub>3</sub>-LDHs (96%) > Zn/Fe/Ti-NO<sub>3</sub>-LDHs (88%) > Zn/Fe-NO<sub>3</sub>-LDHs (72%). The Zn/Ti-NO<sub>3</sub>-LDHs exhibit the efficient photocatalytic activity for the degradation of RB with  $k_{app}$  value of 0.0329 min<sup>-1</sup> than the other Zn/M-NO<sub>3</sub>-LDHs.



**Figure 1.10.** Degradation (%) of rhodamine B (RB) on photodegradation by Zn/M-NO<sub>3</sub>-LDHs.

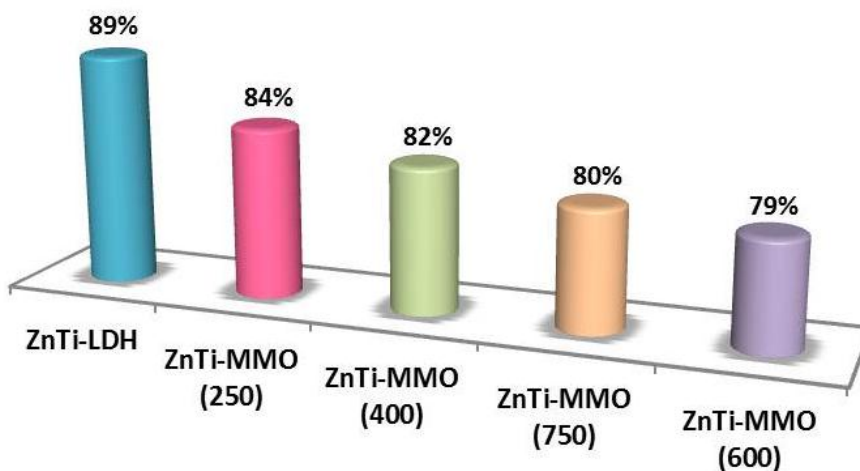
Xia *et al.* [104] reported the synthesis of three types of Ti-based LDHs; Zn/Ti-NO<sub>3</sub>-LDHs, Zn/Al-Ti/Schiff-base-LDHs and CeO<sub>2</sub>/ZnTi-LDH composite for photocatalytic degradation of methyl orange and methylene blue under visible light. Roy Chowdhury *et al.* [105] synthesized 2:1 Ni/Ti layered double hydroxide (LDH) using hydrothermal route and used as photocatalyst for degradation of methylene blue in aqueous solution under visible light. The material showed efficient photocatalytic activity for degradation of methylene blue (99.8% degradation) compared to various commercially available catalysts such as ZnO, ZnS, NiO, TiO<sub>2</sub> and Degussa P25 (Figure 1.11). The enhanced photocatalytic efficiency of the material was associated with the high surface area, narrow band gap energy and surface defects present within the layered material.



**Figure 1.11.** Photocatalytic efficiencies of Ni/Ti LDH and various commercially available catalysts for degradation of methylene blue in aqueous solution under visible light.

Similarly, the photodegradation of phenol and its derivatives using LDHs was also reported by various research groups. Mantilla *et al.* [106] studied the photodegradation of phenol and cresol in aqueous medium by using ZnAlFe LDH derived mixed oxides under UV light irradiation. They also reported 98 and 100% degradation of phenol and *p*-cresol in 6 and 4h, respectively. Tzompantzi *et al.* [107] demonstrated that ZnAl LDH derived mixed oxides efficiently degraded phenol and *p*-cresol using UV light with % degradation of 95% for both cases in 4 and 6h of irradiation, respectively. In another report, Paredes *et al.* [108] reported the photocatalytic degradation of phenol using TiO<sub>2</sub>/MgAl LDH mixtures. At the same time, Valente *et al.* [109] studied the highly efficient photocatalytic elimination of phenol and chlorinated phenols by CeO<sub>2</sub>/MgAl layered double hydroxides under UV light irradiation. The efficient photocatalytic degradation of various organic pollutants such as, xanthene dyes (Rhodamine B, Rhodamine 6G) and substituted phenol (4-chloro 2-nitro phenol) using Zn–Cr–CO<sub>3</sub> LDH under visible light irradiation was reported by Mohapatra *et al.* [110]. Puscasu *et al.* [111] reported the synthesis of ZnTi-Layered double hydroxides (LDHs) and their derived mixed metal oxides (MMO) for photocatalytic degradation of phenol under UV light irradiation. Figure 1.12 shows the degradation (%) of phenol over ZnTi-LDH and derived mixed oxides. They demonstrated that presence of surface –OH groups in the LDH-matrix favored the enhanced photocatalytic activity of ZnTi-LDH for degradation of phenol in aqueous solution and the

decrease in the photocatalytic efficiency of the LDH derived mixed oxides could be attributed to the loss of the –OH groups of the LDH surface on increasing the calcination temperature.

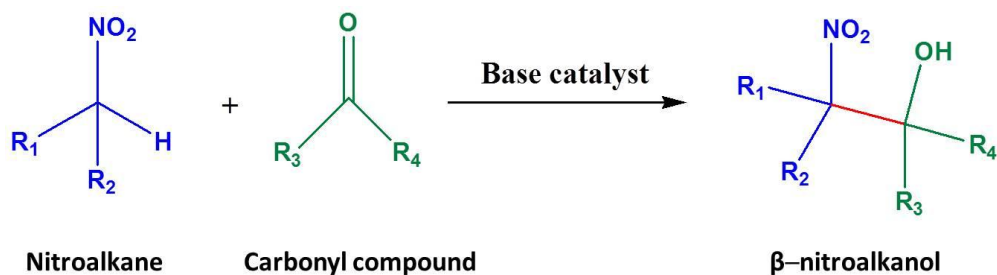


**Figure 1.12.** Degradation (%) of phenol over ZnTi-LDH and derived mixed oxides calcined at different temperatures.

### 1.5.2 Organic transformations

#### 1.5.2.1 Nitro-aldol condensation reaction

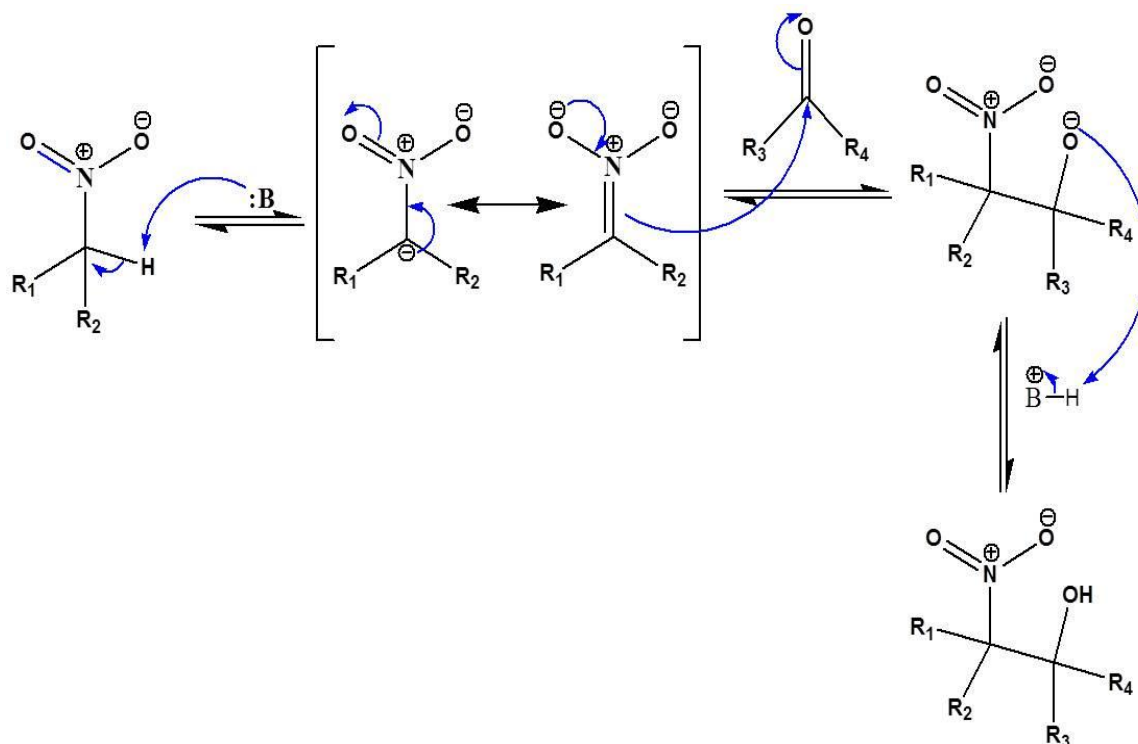
Nitro-aldol condensation reaction is one of the most important C–C bond formation reactions [112,113]. Nitro-aldol reaction is commonly known as Henry reaction after the name of the Belgian chemist Louis Henry who first discovered the reaction in 1895. It is the combination of nitroalkanes containing an  $\alpha$ -hydrogen with carbonyl compounds such as aldehydes or ketones in the presence of a base catalyst to form 2-nitro-alkanols or  $\beta$ -nitro-alkanols (Figure 1.13).



**Figure 1.13.** Schematic diagram for nitro-aldol condensation (Henry) reaction.



The general mechanism for nitro-aldol condensation (Henry) reaction is shown in Figure 1.14. The mechanism is initiated with the abstraction of a proton from nitroalkane at  $\alpha$ -carbon position by the base catalyst. It results in the formation of a resonance stabilized anion, which subsequently attacks on the carbonyl compound and form  $\beta$ -nitro alkoxide. The protonation of the alkoxide from conjugate acid of the base give the final product,  $\beta$ -nitro alcohol [114,115].

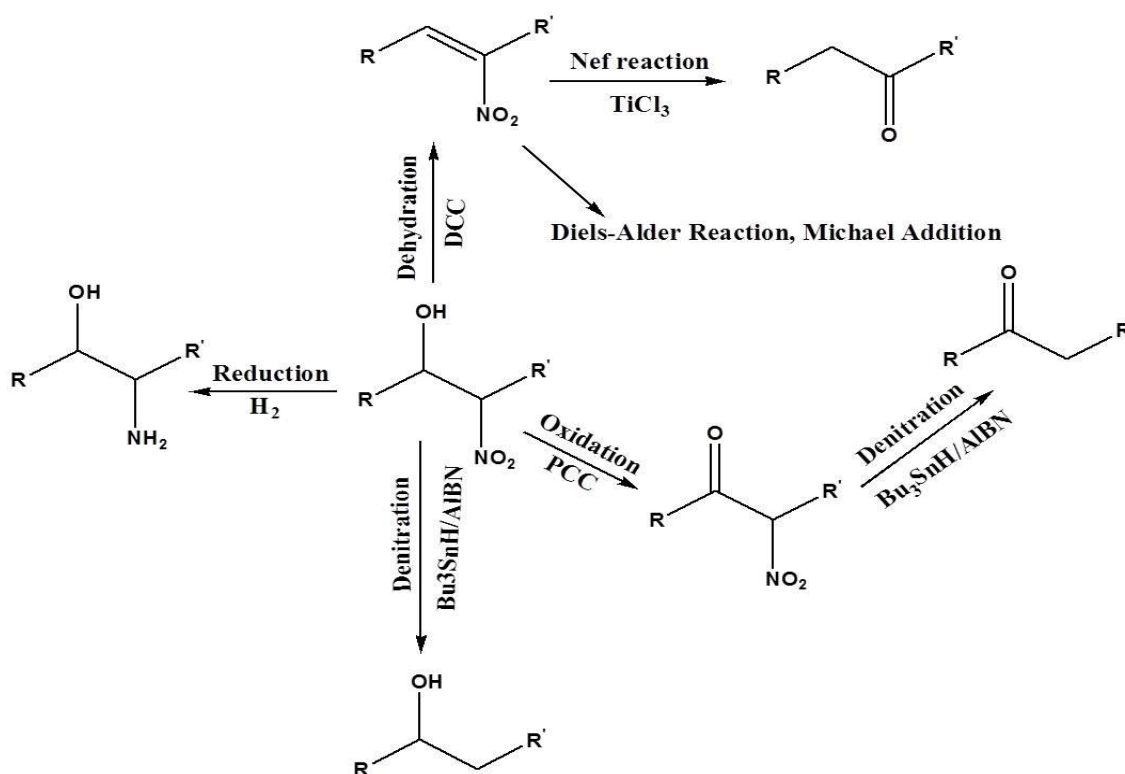


**Figure 1.14.** Schematic diagram for general mechanism of nitro-aldol condensation (Henry) reaction.

The product finds importance in many syntheses including synthesis of various important biological compounds [116,117]. Because of its great importance, it is widely used in bulk and fine chemical industries [118]. The utility of the Henry reaction product, 2-nitro-alkanol or  $\beta$ -nitro-alkanol is schematically shown in Figure 1.15, which includes the formation of various important compounds such as 2-amino alcohol, ketons, amino sugars, and so on [119].

The classical method for the synthesis of 2-nitro-alkanol involves the use of

various bases including alkali metal hydroxides, carbonates, bicarbonates etc. [120,121] and also the use of hazardous solvents which cause environmental problem. The main drawback of the Henry reaction is its tendency to form side products, which include the formation of nitro-alkene by the elimination of water molecule and formation of self-condensation reaction product (Cannizzaro reaction) in case of sterically hindered substrate [118]. Therefore it is very much challenging to develop an economically viable and environmentally safer way for selective synthesis of 2-nitro-alkanol.



**Figure 1.15.** Schematic representation for various applications of Henry reaction product, 2-nitro-alkanol.

With increase demand of green chemical synthesis, chemists are aware of adopting newer catalytic systems with improved reaction conditions to obtain high product yield under mild conditions and minimizing the side reactions. Ballini *et al.* [122] reported the synthesis of  $\beta$ -nitroalcohols using Amberlyst A-21, as the efficient heterogeneous basic catalyst under both solvent and solvent free conditions. They showed that the reactions with both primary and secondary nitroalkanes, exhibited good product yield under solvent free conditions. Again, Devi *et al.* reported that KF loaded NaY zeolite efficiently

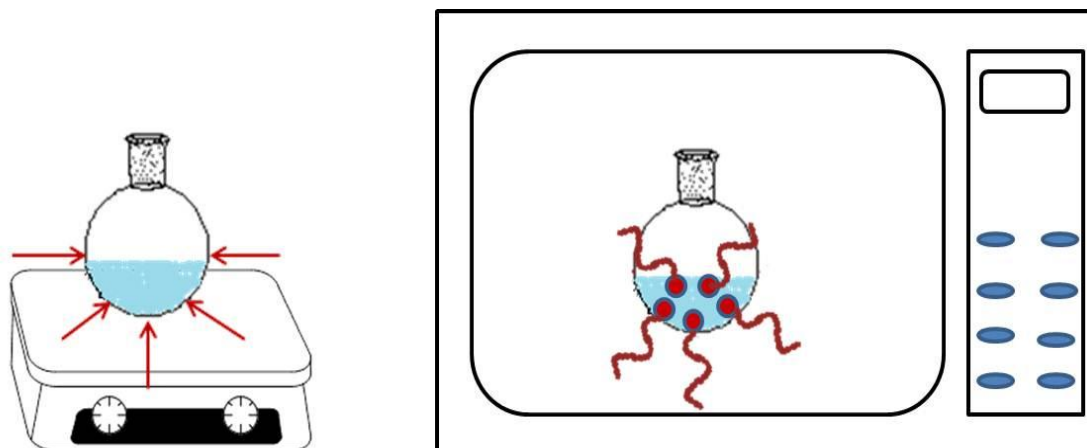
catalysed nitroaldol reaction in MeOH–H<sub>2</sub>O solvent at room temperature with good to moderate yields [116]. In another report, Sutradhar *et al.* [123] demonstrated the synthesis of a new cyclic binuclear Ni(II) complex as a heterogeneous catalyst for nitroaldol (Henry) reaction in water with maximum conversion of ca. 93% and syn:anti selectivity ratio of 76:24.

Although a variety of base catalysts have been studied for this reaction, searching of a better catalyst in order to achieve high yield of the desired product with simultaneous control of the formation of side products is an ongoing research. In the recent years, LDHs as heterogeneous solid base catalysts have drawn significant attention in the field of various organic transformations, owing to various advantages of high surface area, thermal stability, simplicity, cost effectiveness and reusability [124–126]. The thermal treatment of LDHs result in the formation of mixed oxides with unique ability to provide Brønsted basic sites suitable for several important organic reactions replacing homogeneous catalysts. Choudary *et al.* [121] demonstrated the convenient and selective synthesis of  $\beta$ -nitroalkanols by the Henry reaction using activated Mg–Al hydrotalcite in the liquid phase. The activated catalyst displayed efficient catalytic activity with quantitative yields in short reaction times under mild reaction conditions. The efficiency of the solid base catalyst could be related with the Brønsted hydroxy sites present in the modified hydrotalcite. Bulbule *et al.* [127] reported the efficient heterogeneous Henry reaction between aldehydes and nitroalkanes producing *threo*-nitroalkanols in high yields and diastereoselectivity. Again, the exclusive synthesis of 2-nitroalkanols was demonstrated by Choudary *et al.* [128] in excellent yields and 100% selectivity at faster rates using Mg–Al–O–*t*-Bu hydrotalcite in liquid phase under mild reaction conditions. Khan *et al.* [129] reported the use of MgAl-hydrotalcite as a safe and reusable base catalyst in ionic liquid for Henry reactions with significant alteration in the diastereoselectivity in case of nitroethane. The nitroaldol reaction between a variety of aldehydes (aromatic and aliphatic) and simple nitroalkanes (nitromethane and nitroethane) using non-activated Mg:Al hydrotalcite with Mg/Al molar ratio of 2:1 as catalyst was reported by Cwik *et al.* [130]. The non-activated MgAl hydrotalcite showed efficient catalytic activity for the base catalysed reaction. Using nitromethane, 2- nitroalcohols was obtained as product in good

to excellent yields at room temperature. On increasing the reaction temperature upto 100 °C, 1,3-dinitro compounds were obtained and thus opened up a new mechanism using commercially available HT products. Thangaraj *et al.* [131] demonstrated the functionalization of diaminosilane into silicate intercalated hydrotalcite (HT-Si) via a post-synthesis method. The functionalized materials were tested as base catalyst for nitro-aldol condensation of benzaldehyde and nitromethane. The catalyst exhibited efficient catalytic activity for the condensation reaction under solvent-free conditions and the enhanced activity could be attributed to the surface basicity possessed by the diamine-functionalized materials.

#### 1.5.2.2 Microwave assisted organic reaction

Microwave (MW) assisted reactions are environmentally benign reactions [132], which have attracted greatest importance in the recent years. These microwave assisted reactions provide simple process that minimizes the environmental harmfulness of classical reactions with enhanced reaction rates at shorter reaction time with greater selectivity of the desired product by reducing the side reactions [133]. Various reactions that are unable to proceed under conventional conditions can be done easily under microwave heating. Figure 1.16 shows the difference between microwave and conventional heating. Microwave heating is homogeneous, selective and rapid or simply it can be said that microwave heating provides internal heating in deeper extend by interaction of microwave energy with the reaction mixture. The phenomenon of microwave heating is based on the ability to transfer microwave energy to heat by a specific reagent or solvent within reaction mixture. The transfer of energy is mainly depended on the dielectric properties of the materials. The polar compounds (high dielectric constants) are microwave active, whereas the less polar compounds are not. In case of conventional heating, it is a process of superficial heating. In conventional heating, the surface of the reaction mixture is comparatively at a higher temperature than the bulk phase and energy can be transferred from the surface to the bulk phase following the convection and conduction mechanism. Moreover, the reaction vessel sometime must be overheated in order to reach the desired temperature.



**Conventional heating**

**Microwave heating**

**Figure 1.16.** Difference between conventional and microwave heating.

The improvement of product yield in short reaction time can be achieved through microwave assisted organic synthesis which make it highly demandable for research as well as industrial applications [134]. Microwave assisted nitroaldol (Henry) reaction has been practiced by many research groups over the years under solvent and solventfree conditions using various catalytic systems. Varma *et al.* [135] studied the solventless Henry reaction of nitroalkanes with arylaldehydes in the presence of ammonium acetate under microwave irradiation for one step synthesis of conjugated nitroalkenes without the isolation of intermediary  $\beta$ -nitro alcohols. Kumar *et al.* [136] reported the rapid addition of nitroalkanes to aromatic aldehydes to give 2-nitroalkanols in moderate to high yields in dry media using activated  $\text{SiO}_2$  under microwave irradiation. Rodríguez *et al.* [137] demonstrated microwave assisted Henry reaction for one-pot synthesis of nitroolefins from aryl aldehydes using ammonium acetate as a catalyst without solvent. They also reported that the yield of the nitroalcohols was improved on use of microwave irradiation as the energy source. Neelakandeswari *et al.* [138] studied the microwave-assisted Henry reaction of nitromethane with a series of aromatic aldehydes using nickel hydroxyapatite nanocomposite (Ni-HAp) as a green catalyst under solvent free condition to afford nitrostyrenes. An environmentally benign way to synthesize  $\beta$ -nitroalcohols in methanol-water solvent with excellent yield and selectivity under microwave irradiation using potassium salt modified NaY zeolite was reported by Devi *et al.* [139]. However, the

study on microwave assisted nitro aldol (Henry) reaction using LDHs and mixed metal oxides derived from them are limited. Herein, we have explored the combined benefits of microwave irradiation with highly basic sites of LDHs and their derived mixed oxides for the reaction under solvent free condition.

## 1.6 Objectives of the research work

Going through the extensive literature survey, the main objectives of the research work are set according to the following points:

- (i) To synthesize various LDHs and LDH derived mixed metal oxides with varying metal compositions via the co-precipitation method and sonochemical method.
- (ii) To characterize the obtained LDHs and LDH derived mixed metal oxides by using various techniques such as XRD, FTIR, TGA, SEM, TEM, N<sub>2</sub>-adsorption desorption method, UV-DRS, Raman etc.
- (iii) To utilize the various ternary and binary LDHs of varying metal compositions synthesized via the co-precipitation method and sonochemical method for adsorptive removal of different organic dye pollutants from aqueous solution.
- (iv) To utilize the Zn-based LDH synthesized via the co-precipitation method for photocatalytic degradation of various organic pollutants such as dyes and phenolic compounds from aqueous solution.
- (v) To utilize the various ternary LDHs derived mixed metal oxides for base catalyzed nitro-aldol condensation reaction.

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