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Layered double hydroxides: A brief review from fundamentals to applicationas evolving biomaterials

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ABSTRACT

Layered double hydroxides (LDH) which are one type of layered materials and are also known as anionic clays, are promising layered materials due to some of their interesting properties, such as ease of synthesis, unique structure, uniform distribution of different metal cations in the brucite layer, surface hydroxyl groups, flexible tunability, intercalated anions with interlayer spaces, swelling properties, oxo-bridged linkage, and high chemical and thermal stability, ability to intercalate different type of anions (inorganic, organic, biomolecules, and even genes), delivery of intercalated anions in a sustained manner and also high biocompatibility. Considering the previous work on LDH as novel biomaterials, research on this particular materials has become one of the most interesting topic of today's research. LDH has become an important class of layered materials having prospects in the field of biomaterials, wherein great attention has been paid to the biocompatibility nature, exchange of the existing anion with the target anion, holding of guest species in between the interlayer space and its controlled release of the anion in a particular medium. This article, after deliberating the recent significant evolution in the structure and different methods of synthesis of different LDH materials and its applications in various extents especially its biological applications through their structural and functional properties, considers many typical examples. In particular, recent progress on the emerging strategies of LDH to improve their antimicrobial activity is also presented.

1. Introduction

Synthetic inorganic materials with well-arranged voids and surfaces exhibit advantageous properties towards the solution of today's environmental and industrial problems and for the design of innovative composites for different front-line applications. Among several classes of lamellar solids, so-called layered double hydroxides (LDH), also known very often as hydrotalcite-like systems or anionic clays, have deserved a lot of attention since they qualitatively resemble the conventional intercalation compounds (Cavani et al., 1991;Evans and Slade, 2006; Khan and O'Hare, 2002; Rives, 2001). One of the advantages of LDH among layered materials is the great number of possible compositions and metal-anion combinations that can be synthesized. Apart from that, has peculiar characteristics like good biocompatibility, high chemical stability, pH dependent solubility, etc. (Kuthati et al., 2015).The original discovered LDH was the mineral Hydrotalcite $[Mg_6Al_2(OH)_{16}](CO_3)\cdot 4(H_2O)$ (Gaines et al., 1997). The name was given as hydrotalcite because of its water content (hydro) and also its resemblance to talc (talcite). It occurs usually in nature and also can be synthesized easily, if necessary with other metal ions isomorphously substituted. The structure of most of LDH are similar to that of mineral hydrotalcite (HT) which is a natural magnesium–aluminum hydroxyl carbonate ($Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$).

The structure and properties LDH were first demonstrated by Allmann (1968) and Taylor (1969) through powder X-ray diffraction. The general formula of LDH is $[MII_{1-x}MIII_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$,where M(II) and M(III) are divalent and trivalent metal cations, respectively, and A^{n-} is an n-valent anion. These compounds have layered crystal structure with wide variations depending upon the nature of cations and M(II)/M(III) molar ratios, as well as in the type of anions (Birgul and Ahmet, 2012). The range $0.2 \leq x \leq 0.33$ is generally acknowledged to be suitable for the synthesis of LDH compounds i.e. the ratio of M^{2+}/M^{3+} is in between 2:1 to 4:1. At $x > 0.33$ the increased number of neighbouring M^{3+} containing octahedra leads to the formation of $M(OH)_3$ and, analogously, values of $x < 0.2$ leads to a high density of M^{2+} containing octahedra in the brucite-like sheets resulting in the precipitation of $M(OH)_2$. However, these limits of the value of x must be regarded as the maximum interval, which can be

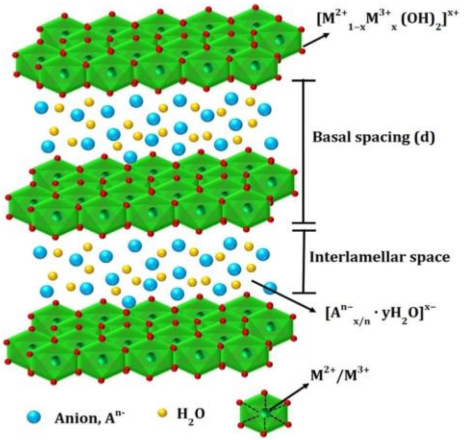

Fig. 1. Structure of layered double hydroxide.

narrower depending on the composition of the LDH. These compounds consist of positively charged brucite-type octahedral sheets, alternating with interlayers containing carbonate anions in the natural mineral or other exchangeable anions in the synthetic HT-like analogues, along with water molecules (given in Fig. 1).

Regarding the anions, their size/charge ratio is important i.e. a large-sized anion with low charge is unable to balance homogeneously in between the positively charged layers. There should be a host-guest relationship in between the host inorganic layer and the dimensions of guest species in the interlayer. For non-spherical anions, and very especially when the anions contain long chains (e.g., carboxylates or sulfonates with long alkyl chains), several arrangements in the interlayer are possible, namely, a monolayer parallel to the layers, a parallel bilayer or tilted monolayers or bilayers. Compositional multiplicity in the layers and in the interlayer anions leads to a functional diversity which allows LDH to be used for variety of applications.

Significant progress has been made in the synthesis of LDH with new compositions and morphologies over the last decade allowing improved applications in many areas (Birgul et al., 2012). Layered double hydroxides (LDH), due to their interesting properties in anion exchangeability, compositional flexibility, and biocompatibility, have attracted great attentions in various technologically significant fields such as catalysis (Shi and He, 2011), separation (Chen et al., 2011; You et al., 2001b), biomedicine (Choy et al., 2004, Costantino et al., 2013; Gu et al., 2010; Gunawan and Xu, 2009; Oh et al., 2009; Wang et al., 2012) drug storage–delivery agents (Li and Duan, 2006; Wang et al., 2012), environmental applications (Mohapatra and Parida, 2016).

Here Fig. 2 reveals different area of applications of LDH. The recent curiosity in LDH is founded on several properties: These are basic materials and the mixed oxides formed after thermal decomposition show even a larger basicity, related to the oxide anions; intercalation of acidic anions provides systems with unique acid–base properties (Rives et al., 2014). They show the so-called memory effect (Chibwe and Jones, 1989), i.e., the ability to recover their original layered structure when mixed oxides (previously prepared by calcination of some LDH at moderate temperatures) are put in contact with solutions containing anions. They also show anion exchange capacity (AEC), usually larger than that shown by cationic clays.

In the last few decades one of the foremost issues which is to be solved by academic or research is contamination by microorganisms.

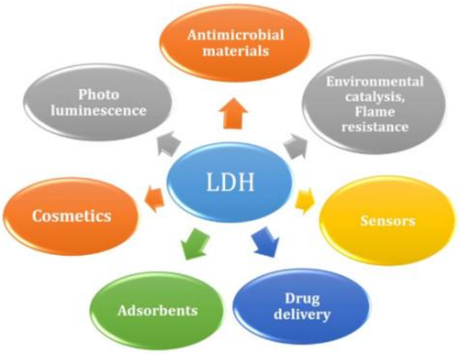

Fig. 2. Different applications of LDH.

Now-a-days infections by pathogenic microorganisms are of serious concern. This problem affects many areas like pharmaceutical fields, healthcare products, food packaging, textile industries, house hold products and many more (Busscher et al., 2010; Chmielewski and Frank, 2003; Park et al., 2001; Patel et al., 2003; Percival et al., 2009; Ranucci and Ferruti, 1991). To overcome from this problem a method was proposed to intercalate the active antimicrobial molecule into an inorganic molecule which is able to hold it, allowing a very slow and controlled release in suitable conditions. Existing surveys show that LDH have high potential as containers for functional agent because of their high biocompatibility, high chemical stability, and controlled release rate (Sokolova and Epple, 2008). However, only a few studies on the application of LDH in active antimicrobial field have been reported (Costantino et al., 2009; Mishra et al., 2013; Ryu et al., 2010) and therefore the rapid growth of use of antimicrobial LDH materials requires a fresh assessment and further research.

This review article presents a concise but detailed information regarding the structure, synthesis methods of different LDH hybrids with various modification strategies and most recent advances in various fields especially in antimicrobial composites which are used for various applications. Moreover, the fundamental strategies that are required to enhance the antimicrobial activity are also discussed.

2. Different synthesis routes of layered double hydroxides(LDH)

In the past few years, several studies related to synthesis of LDH have been reported. There are some simple as well as expensive procedures to synthesize LDH for different applications which are discussed (He et al., 2006; Khan and O'Hare, 2002; Rives, 2001). Among the many proposed ways to prepare these lamellar solids (Forano et al., 2013; He et al., 2006; Kanezaki, 2004; Vaccari, 2001), the main routes which are most frequently followed are:

- Co-precipitation route (direct method)
- Ion-exchange route (indirect method)
- Reconstruction/Rehydration route (memory-effect method).

Co-precipitation route (direct method)

A co-precipitation technique is the most frequently applied method for direct synthesis of LDH with a variety of divalent and trivalent cations and different anions ranging from inorganic anions, such as Cl^-, NO_3^-, and CO_3^{2-} to a variety of organic molecules and even large biomolecules can been intercalated (Evans and Slade, 2006; Vaccari, 2001). Also, co-precipitation methods can be applied for the large-scale

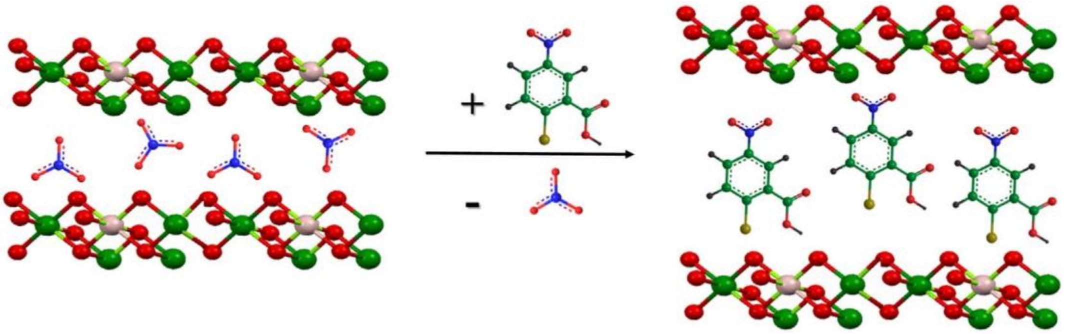

Fig. 3. Schematic representation of ion-exchange technique.

fabrication of the material.

Co precipitation, consisting of the slow addition of a solution containing the target anion to be intercalated into a container containing the solution of divalent and trivalent metal cations in an appropriate ratio and finally increasing the pH by addition of a base or urea hydrolysis that leads to precipitation of the LDH. Thermal treatment i.e. ageing of the solution is often performed after co-precipitation to improve the crystallinity of the sample. The addition of alkali to the mixed metal salts maintains the pH at a selected level, leading to the co-precipitation of the two metallic salts. The mechanism of co-precipitation is ideally based on the condensation of hexa-aqua metal complexes in solution, leading to the formation of brucite-like layers with evenly distributed metallic cations and with solvated interlamellar anions (Mohapatra and Parida, 2016). In case of urea based co-precipitation, the final products provide better crystallinity and better control of the particle size because the hydrolysis of urea proceeds very slowly (Costantino et al., 1998).

Various types of LDH and their composites or hybrids have been synthesized using this method for different purposes, such as, ZneTi LDH having high crystallinity and significant photocatalytic activity where the as synthesized crystals are microspheric in nature and the basal spacing decreases with the incorporation of tetravalent ion i.e. Ti^{4+} into the positive layer (Shao et al., 2011). Similarly, ZneFe LDH have been synthesized by fixing Zn/Fe ratio but varying the intercalated anions such as, CO_3^{2-}, NO^{3-} and Cl^- (Parida and Mohapatra, 2012). The basal spacing of carbonate containing LDH was slightly lower as compared to other two LDH. Also the crystallite size and BET surface area followed the trend of Zn/Fe-Cl > Zn/Fe-NO_3 > Zn/Fe-CO_3. Now-a-days, inorganic-organic hybrid nanocomposites were synthesized by intercalating different organic anions and drug molecules into the interlayer region of positive bilayers by co-precipitation method (Barahuie et al., 2015; Bugatti et al., 2013; Kura et al., 2013; Perera et al., 2015; Rojas et al., 2014; Saifullah et al., 2014a; Wang et al., 2012). The as prepared nano hybrids are having several biological applications. In case of metallic incorporation, co-precipitation method is also a step ahead as compared to other methods. Metallic silver have been incorporated into MgeAl LDH (Chen et al., 2012; Noh et al., 2012) which was confirmed from XRD and TEM analysis. The resulting composites were in nano range as compared to pristine material which was in micron range.

Anion-exchange route (indirect method)

Anion-exchange is also a commonly used method for the synthesis of LDH composites and has been effectively useful for the intercalation of a number of different types of anions (Evans and Slade, 2006; Forano et al., 2013; Barahuie et al., 2015). It is also known as an indirect method, in which the first LDH are prepared by co-precipitation method with host anions, most commonly NO_3^-, CO_3^{2-}, and Cl^- as the exchange is easier than multi charged anions (Rives et al., 2014). In the later stages, anions present in the interlayer region are exchanged with the preferred anions by stirring the LDH precursor in a solution containing an excess of the anion to be intercalated. To avoid carbonate intercalation the whole process of anion-exchange should be carried out under inert atmosphere. The host–guest exchange generally depends on the electrostatic forces between positively charged LDH layers and the exchanging anions (Morel-Desrosiers et al., 2003).

Target anions can be intercalated in two possible ways, as described in the equations:

$$LDH{\cdot}X^{m-} + Y^{n-} \rightarrow LDH{\cdot}(Y^{n-})_{m/n} + X^{m-} \tag{1}$$

or

$$LDH{\cdot}X^{m-} + Y^{n-} + mH^{+} \rightarrow LDH{\cdot}(Y^{n-})_{m/n} + H_mX \tag{2}$$

There exists weak electrostatic interaction with layers, and hence these anions can be easily replaced by anions with higher electrostatic interaction with layers. Fig. 3 shows the schematic representation of ion-exchange method.

The main features associated with anion-exchange reactions of LDH are as follows:

1. The appropriate solvent will favor the anion-exchange process.
2. This process depends on the chemical composition of the brucite type layers.
3. Anion-exchange process will be more favorable at high temperatures.
4. The working pH should be 4.0 or above 4.0 since at lower pH, the hydroxyl layers will break.

Numerous LDH composites have been synthesized via anion-exchange method to get the desired hybrid material out of precursor LDH. This method has been adopted over traditional co-precipitation route because many hybrids are difficult to synthesize by co-precipitation due to large size of anions (Das and Parida, 2007). This method is also useful for different types of drugs to get insert into LDH making the hybrid eligible for biological and pharmaceutical applications (Aisawa et al., 2005; Costantino et al., 2009; Kovanda et al., 2009; Mishra et al., 2017a;Ryu et al., 2010;Saifullah et al., 2014b; Silion Frunza et al., 2009).

Reconstruction route (memory effect method)

In addition to above methods, another method has been established for fabrication of different LDH based composites or hybrids termed as reconstruction or rehydration method. It's an unique property of LDH to get its original structure back after calcination followed by rehydration. Generally LDH can be transferred to the respective metal oxides by calcining it at mild temperature (400–500 °C) and as a consequence, interlayer water molecules, hydroxyl groups of LDH and intercalated anions are completely removed, leaving behind mixed metal oxides (Erickson et al., 2005; Rocha et al., 1999). When these mixed metal oxides immersed in water or any other solution of anions to be

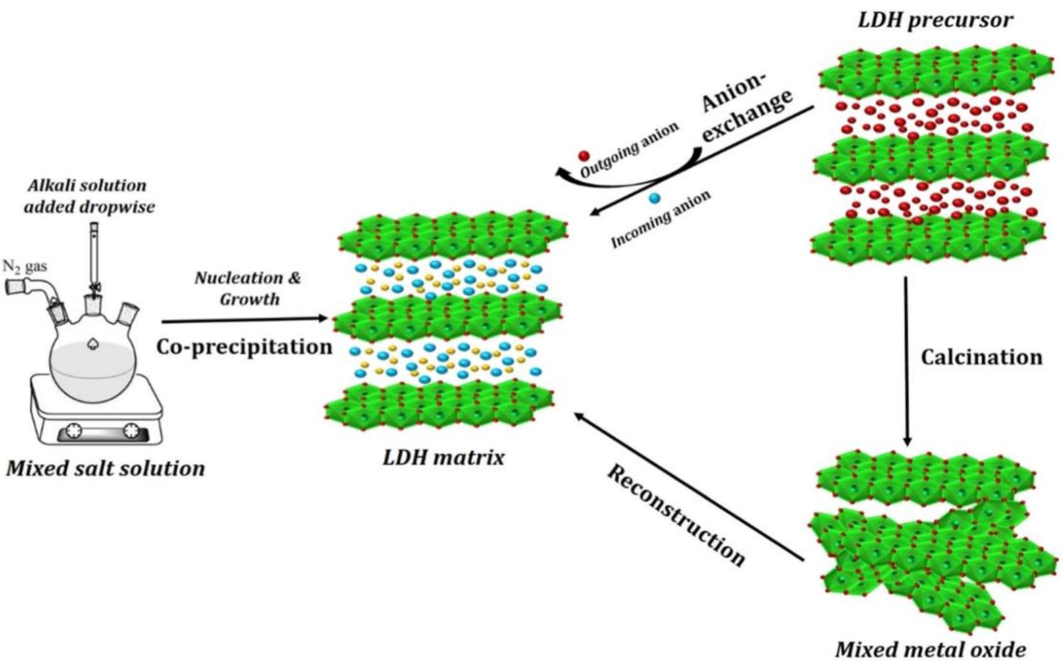

Fig. 4. Schematic representation of three methods of development and modification of LDH.

intercalated, LDH are regenerated back (Rives et al., 2014). This is a very useful method, especially for the intercalation of organic molecules, and many different anions have been successfully incorporated in LDH. The whole process of rehydration should be carried out under an inert nitrogen atmosphere (Evans and Slade, 2006; Rives, 2001).

It should be noted that LDH should be heated within 400 °C–500 °C because heating at higher temperature will affect the reconstruction of LDH because of formation of stable spinels (Evans and Slade, 2006; Rives, 2001). Various composites have been synthesized using this method. For example, Salicylic acid was intercalated into an inorganic host consisting of Zn-Al/Mg-Al layered double hydroxides lamella by reconstruction method (Haraketi et al., 2016). Amino acids like phenylalanine have been successfully intercalated in between ZneAl LDH by calcination-rehydration technique (Aisawa et al., 2004). The uptake of terephthalate anions (TA) from aqueous solutions by Mg-Al-CO_3 layered double hydroxides (LDH) has been reported (Crepaldi et al., 2002). Intercalation of tartarate ion in between the interlayer space of ZneAl LDH by reconstruction process was also carried out successfully (Prevot et al., 1998).

Fig. 4 demonstrates the schematic presentation of the three methods of synthesis in one picture.

Comparing the above three approaches of synthesis, the summaries are as below;

- Anion-exchange route is better for large-sized anions as compared to other two routes.
- Co-precipitation method is more useful taking yield into consideration, as in co-precipitation case, yield of the product will be three times more as compared to other two routes (Nalawade et al., 2009). Another positive opinion regarding co-precipitation is that several synthesis parameters can be controlled independently during the precipitation process (temperature, pH of reaction medium, condition of metallic salts, concentration of alkali solution, anion species, etc.)
- In reconstruction method, the products obtained are poorly crystalized and partial intercalation will be there as compared to other two methods (Moyo et al., 2008).

Apart from the above methods, some other methods, have been established for the fabrication of different LDH and LDH-based composites, such as hydrothermal synthesis, the sol–gel process (Zhang et al., 2013a), etc. In addition, the micro emulsion method (Leroux et al., 2001) is also adopted but only in special cases.

3. Structural description of layered double hydroxide

As it is discussed earlier that layered double hydroxides are made-up of positively charged brucite-type layers of divalent and trivalent metals with exchangeable intercalated anions present in between the layers to compensate the net positive charge.

The structure of layered double hydroxide is similar to that of brucite i.e. $Mg(OH)_2$ where each Mg^{2+} ion is octahedrally surrounded by six hydroxide ions (Paredes et al., 2011) as given in Fig. 4. Each octahedral unit shares their edges to form infinite layers and OeH forms the bond perpendicular to the octahedral layer.

Structure of layers

In case of layered double hydroxide compositional modifications can be made in the brucite structure by the isomorphously substituted bivalent cations (M^{2+}) with trivalent cations (M^{3+}) which results in excess positive charge in the layer and is compensated by charge balancing anions present in interlayer galleries. The general formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{m-})_{x/m}\cdot nH_2O$, where $M^{2+}$is bivalent cation, such as Mg^{2+}, Zn^{2+}, Ni^{2+}, and Ca^{2+}, $M^{3+}$is trivalent cation, i.e., Al^{3+}, Fe^{3+}, and Cr^{3+}, and A is a counter anion with negative charge (m) (Evans and Slade, 2006; Rives, 2001).They have an octahedral structure, in which metal cations are accommodated in the centers of the edge-sharing octahedral; each cation contains six OH^- ions that are pointed towards the corners and form infinite sheets (Evans and Slade, 2006). One of the important structural characteristics of LDH materials is that the M^{2+} and M^{3+}cations are distributed in a uniform manner in the hydroxide layers.

In case of LDH composites,

- There exists columbic attraction between positively charged layers and negatively charged interlayers.
- Hydrogen bonding exists between the OH group of the metal

Table 1
Different advantages and limitations of LDH.

Advantages	Limitations
LDH are Natural clays, but its analogous can be synthesized. It has high anion-exchange capacity and therefore different anions can be intercalated in between the interlamellar space of LDH. It has vast areas of applications i.e. can be used in ceramics, fillers, different add-ons, for fabric modifiers, etc. It has sustained release capacity of the intercalated material under particular conditions. It can be used for environmental remediation i.e. for the removal of harmful contaminants for water through adsorption and intercalation.	There is a limitation during synthesis of LDH i.e. proper LDH will form where divalent/trivalent cation ratio will be within 2:1 to 4:1. Below and beyond this ratio, LDH will not form. Reconstruction i.e. the so called memory effect will feasible when the precursor was calcined within a temperature range of 300–500 °C. Beyond this range, LDH will not come back to its original structure as it will form a stable spinel structure. Most of the LDH are soluble in acidic pH but stable in neutral as well as alkaline pH and therefore its composites will not work in acidic pH.

hydroxides of the brucite type layers and the oxygen atom or any other electronegative atom of the intercalated anions.

All the divalent metal ions ranging from Mg^{2+} to $Zn^{2+}$with an ionic radius in the range 0.65–0.80 Å and all transition metal trivalent ions with an ionic radius in the range 0.62–0.69 Å (with the main exception of Al^{3+}: 0.50 Å) can enter into the LDH hydroxide layers. Higher ionic radii (Ca, Cd and Sc, La) seem to be incompatible with the formation of true brucite-like layers. If the radius of one of the metallic cations becomes too high, the octahedral coordination will be lost by the opening one side of the octahedron on the interlamellar domain leading to additional coordination with one interlamellar water molecule. The symmetry around the metal is lowered from D_{3d} to C_{3v} and such behavior observed in minerals from the hydrocalumite groups.

Interlamellar anions

In case of LDH, the interlayer space contains anions along with water molecules. One of the major characteristic of LDH is that, in most cases, only weak bonding occurs between these interlamellar ions or molecules with the host structure. A great variety of anionic species can either be located between the layers during the formation of the lamellar structure, or by further anionic exchange. A large number of anions including inorganic anions and organic anions as well as large sized bio-molecules as presented below could occupy the interlayer regions of LDH. The amount of the anions in the interlayer spacing is directly related to the charge density of the hydroxide layers which can be controlled by the M^{2+}/M^{3+} ratio whereas their arrangement depends on the interlayer packing related to the layer charge density as well as the anion size and the presence of water molecules; additional parameters such as the preparation route and the synthesis temperature may also influence the interlayer arrangement. These possible anions can be:

- Inorganic anions: F^-, Cl^-, Br^- and I^-, CO_3^{2-}, NO_3^-, ClO_4^-, SO_4^{2-}, $S_2O_3^{2-}$ and CrO_4^{2-}, $NiCl_4^{2-}$, $CoCl_4^{2-}$, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4}$, etc.
- Organic anions: carboxylates, phosphonates, alkyl sulfates, benzoates, etc.
- Anionic complexes: ferro and ferricyanide, $(PdCl_4)^{2-}$, etc.
- Biomolecules: DNA, amino acids, vitamins, peptides, nucleosides, etc.

In relation to the size, charge and layout of these interlamellar species, the basal spacing of the layers are dramatically changed. However, the structure of interlamellar domains is more difficult to characterize than the main layers. The anions orient themselves in such a way that they maximize their interaction with the positively charged hydroxide layers. In pristine LDH, CO_3^{2-}anions lie parallel to the hydroxide layers to ensure intimate interaction between the oxygen atoms and the layer by forming hydrogen bonds. Organic anions always interact via their anionic groups being strongly hydrogen bonded to the surface of hydroxyl groups, while their hydrophobic hydrocarbon chains are pushed far away from the hydrophilic layer surfaces, and adopt the lowest energy conformation (Fernon et al., 1994). The interlayer water and hydronium ions of the layered materials play a key role in enhancing the photo activity with efficient charge separation (Chen et al., 2010). The gallery height of LDH is capable of accommodating much more bulky anions. It has been reported that the intercalation of large anions enhances the photocatalytic activity as compared with the original layered oxides. This is due to the interlayer space that facilitates the reaction between the photo generated charge carriers and the reactant molecules that suppress the charge recombination (Zong and Wang, 2014). It was reported that the OH groups of LDH may enhance the antimicrobial activity. The surface hydroxyl groups are converted into HO% radicals, which are the reactive oxygen species (ROS) responsible for potential damage of bacterial cytoplasmic membrane and DNA (Moaty et al., 2016).

Table 1 provides the summary of comparison regarding the advantages and disadvantages of various LDH.

4. Applications of layered double hydroxides

Compositional variation in the layers and in the interlayer anions leads to a functional diversity that allows LDH to be used for a variety of material science applications such as waste water treatment, ion exchanger, halogen free flame retardant, antacids, stabilizers for polymers, pharmaceuticals and agricultural goods, electro-photoactive materials, catalysts/catalyst precursors, etc.

Ceramics

Attracted by the versatilities of chemical composition and the surface chemical properties of LDH, the preparation and properties of LDH have actively been investigated. The preparation and characterization of different LDH with transition metal cations are the recent trials in the ceramic industry to produce colored ceramics, as current development in the ceramic industry is based on the use of ink-jet ceramic pigments, needing stable suspensions of the pigments. To create colored ceramics, the transition metal salts are used as some key ingredients. They impart varieties of color depending upon their own salt color. Green pigment from a NieAl containing LDH was prepared by two alternative routes, namely, conventional co-precipitation and co-precipitation in the presence of a surfactant in order to control aggregation of the elemental particles through formation of inverse micelles and thus controlling the properties of the final product (Pe'rez-Bernal et al., 2009). $NiAl_2O_4$ spinel obtained by step wise heating of NieAl LDH in the range of 473–1273 K is a suitable candidate for obtaining fine-colored cyan or pale blue nano-pigments for glaze applications or preparation of ceramic pigments (Gabrovska et al., 2015). CoeAl LDH synthesized by co-precipitation method exhibits pink color (Arai and Ogawa, 2009). Co substituted $ZnAl_2O_4$ i.e. $Co_xZn_{1-x}Al_2O_4$ synthesized by polymeric precursor method, exhibits blue color (de Souza et al., 2009). These calcined materials could be usable as ceramic pigments. ZneAl layered double hydroxide is used as white pigment. There are various methods of preparations of Zn aluminate like crystalline nanotube array of Zn aluminate by taking anodized aluminium oxide template (Wang et al., 2005) and by hydrothermal route (Chen et al., 2002; Yang et al., 2004). Apart from being a pigment ceramic zinc aluminate is also found to be showing various properties like elastic, dielectric, thermophysical (Van der Laag et al., 2004) and optical (Sampath and Cordaro, 1998).

Environmental remediation

LDH as adsorbents

Adsorption is a surface property. The candidate material used for adsorption should have high surface area, high porosity and maximum no. of active sites. Layered double hydroxides (LDH) are considered to be the perfect material for adsorption as it has large surface area per unit of mass, large porosity, etc. i.e. it satisfies all the requisite properties of adsorption. It is applied mainly for removal of toxic metals and ions from water and also from the atmosphere through adsorption (Chaara et al., 2010; Yang et al., 2014). Surface adsorption involves the adhesion of the targeted pollutants to the surface of the hydrotalcite, which permits the formation of a molecular or atomic film.

Now-a-days due to increased use of motor vehicles our atmosphere has depreciated because of the toxic gases being released as a consequence of ignition. LDH with different metal compositions have been applied in the adsorption of nitrogen oxides and dusts (Liu et al., 2014; Wang et al., 2009; Zhang et al., 2007, 2010). Removal of toxic material, both organic and inorganic, is very difficult job, which LDH have successfully accomplished.

Moreover, LDH have been successfully applied in the removal of toxic metals in the form of their oxides, such as selenium, arsenic, chromium in wastewater, and radioactive uranium (VI), and have also been utilized for the removal of other heavy metals (Pshinko, 2013; You et al., 2001a).Similarly, cations like Cr (VI) was adsorbed strongly by various calcined and uncalcined LDH of MgeAl, NieAl and ZneCr type LDH Goswamee et al., 1998). Anions like As (V) was adsorbed from water using MgeFe based hydrotalcite (Turk et al., 2009). In another case both arsenite and arsenate have been successfully removed from simulated soil synthesized from Zn/AleSO$_4$LDH (Bagherifam et al., 2014). These materials are also considered as a new variety of material for Sulphur adsorption using DRIFTS study and chemisorption (Toops and Crocker, 2008).

Likewise, LDH have also been successfully utilized in the elimination of many organic compounds from water, such as *N*, *N*-dimethyl aniline, 2-chlorophenol, phenolic compounds, dodecylbenzenesulfonate (Chuang et al., 2008; Kameda et al., 2009). Adsorption of anionic blue dye was successfully carried out by LDH (Marangoni et al., 2009). Also the removal of organophosphate and organophosphonate herbicides was studied from aqueous solution by adsorption through Ni$_2$Al LDH material (Khenifi et al., 2010). The property of organic adsorption is very useful in separation of mixtures of short linear alkanes involving methane, ethane, propane and *n*-butane in pillared layered materials at ambient temperature, $T = 300$ K (Li et al., 2007). In this context comparative adsorption of phenol and 4-nitro phenol on MgeAl calcined LDH as studied by Cheng et al. is also helpful as the adsorption of 4-nitro phenol was 10 h faster than phenol (Chen et al., 2009). Water soluble polymers like polysterene sulfonate (PSS) can also be adsorbed on ZneAl LDH (Moujahid et al., 2003). The adsorption of polymer increases the pore size of the LDH as compared to the pristine material. Pavan et al. investigated that layered double hydroxides are also used in the adsorption of surfactants like sodium dodecyl sulfate on MgeAl LDH (Pavan et al., 1998).

In water-treatment plants, disinfection is a vital procedure, and currently halogens and ozone are employed as disinfectants. However, there are certain issues with respect to these disinfectants, such as the fact that they can form carcinogenic by-products in the presence of organic compounds (Watson et al., 2012). Now-a-days, scientists are looking for alternative disinfectants. One of the important disinfectants is lysozyme (LYZ), which can break down the bacterial cell wall, resulting in bacterial elimination. Therefore by intercalating LYZ into LDH, a novel disinfectant has been developed (LYZ LDH), and its antibacterial capability was evaluated against *Staphylococcus aureus*. The antibacterial activity of LYZ LDH was found to be consistently above 94% in the pH range of 3–9, which was much higher compared to free LYZ. This was due to the double action of LYZ LDH, i.e., adsorption of LDH and antibacterial action of LYZ (Yang et al., 2013). The LYZ LDH formulation is considered to be a green antibacterial agent, as it does not produce any by-product.

Agro industries

The advancement in the agricultural researches generally landed up in high pesticide concentration in the ecosystem. A pesticide is a chemical used to control or repel pests that are believed to be a danger, such as insects, undesirable plants, fungi, bacteria and viruses. Although the use of pesticides in agriculture enhances the productivity of the crops, the extensive application of pesticides had a dreadful impact on the environment due to their capability to accumulate in surface, in soil and in groundwater (Hashim et al., 2016). Untreated wastewater generally contains various pesticides and pesticide residues which are hazardous and poisonous to living organisms. The continuous use of pesticides may lead to various consequences such as air pollution, water contamination and extinction of endangered species. Therefore, advance research now again look forward for use of minimum quantity of pesticides to be used which ultimately protect the soil and ground water. In this context, LDH can act as an efficient material for this purpose due to their relatively low cellular cytotoxicity both for plants and animals, high adsorption capacity and particular colloidal properties. Hence, LDH have been widely explored in agrochemical formulations (Ureña-Amate et al., 2011).

Depending upon the types of applications in agro industries, LDH can be used in two different ways:

I. As adsorbent
II. As anion-exchanger.

LDH as adsorbent. Layered double hydroxides (LDH) as discussed earlier can act as an efficient adsorbent due to its specific surface area, porosity and no. of active sites available. Therefore excess pesticides present in soil and untreated wastewater coming out of lands can be adsorbed by LDH by means of surface adsorption which consequently lowers downstream contamination.

Several works has been carried out for the removal of pesticides by means of adsorption. The ability of MgeAl layered double hydroxides (LDH) and their calcined products to adsorb the water contaminants such as 2,4-dinitrophenol (DNP) and 2-methyl-4,6-dinitrophenol (DNOC) (Chaara et al., 2010). Similarly, Zn/Al–Cl-LDH have been used in the elimination of the anionic phenoxy herbicide 2,4-dichlorophenoxyacetate, which is mostly used as weed controller in wheat, rice and maize cultivations (Legrouri et al., 2005). The study revealed that the removal of these pesticide residues was greatly affected by the amount of Zn/Al–Cl-LDH as the adsorbent, initial concentration of 2,4-dichlorophenoxyacetate, contact time between adsorbents and targeted pesticides and also the anionic exchange capacity of the adsorbents. The adsorption of this anionic phenoxy herbicide mainly occurred on the surface of the adsorbents at low concentration; meanwhile, topotactic exchange between 2,4-dichlorophenoxyacetate and Cl^{-} in the interlayer region predominantly took place at high concentrations.

LDH as anion-exchanger. Also LDH can act as an anion- exchanger host material leading to intercalation of pesticides forming hybrids which can act as pesticides and will release pesticides slowly i.e. in a controlled release manner; therefore lowering the ground water pollution as well as soil and air pollution. So, by this process, only the required amount of pesticides can be supplied for plants, no need to provide in excess. Also the plants will be safe from the harmful effect of surplus amount of pesticide. The use of controlled release formulations may brought numerous benefits, like, it may prolong the activity duration of pesticides by providing a constant low concentration of pesticide, which is enough for long-term performance.

Several literatures have been working on the controlled release study of pesticides, leading to its minimum consumption. A hybrid of herbicide was prepared with anionic herbicide and LDH by three different methods but ultimately giving low herbicide leaching out to the ground water (Cardoso et al., 2006). Compared to the free herbicides, the application of the three LDH-herbicide complexes to soil columns resulted in reduction in the maximum herbicide concentration in leachates and led to the retardation of herbicide leaching through the soil. Trials have been taken to remove pesticide family 2,4-dichlorophenoxyacetate from water by ZneAl LDH (Lakraimi et al., 1999). It has reported that Zn/Al-LDH intercalated to 2,4,5-trichlorophenoxyacetates were the most difficult to release compared to 2-chlorophenoxyacetates and 4-chlorophenoxyacetates, due to their bulkier structure. In fact, the three chlorine atoms bonded to the host create a greater electrostatic force which lowers the percentage release of 2,4,5-trichlorophenoxyacetates (Sarijo et al., 2010). 2,4-dichlorophenoxyacetatic acid, which is acknowledged for its toxicity and carcinogenicity (Bhat et al., 2015) has been intercalated into Zn/Al-LDH using the co-precipitation method to control its release. This approach assists in preventing the release of residues into the environment, hence reducing the risk of soil and water contamination (Bashi et al., 2016). Some work has been done taking the above two postulates si- multaneously into consideration for comparison basis. Hoggan et al. have studied the sorption of pesticide atrazine with pristine LDH and humic acid modified LDH. They found that humic acid modified LDH sorbs more atrazine (Hoggan et al., 2009).

Considering all the facts and studies into consideration, it can be suggested that the intercalation of different pesticides followed by their controlled release will be more beneficial as compared to adsorption of excess unreacted pesticides from soil and groundwater, because as the material (LDH) is capable of producing controlled release mechanism, no need to put excess of pesticides for plants followed by their adsorption.

Drug delivery applications

Layered double hydroxides (LDH) are always in the focus of numerous researchers because of their prospective applications in the biomedical field. Composites of layered double hydroxide are now emerging as potential new drug delivery system due to its low toxicity and advanced biocompatibility (Kura et al., 2014). Some studies have shown LDH to have the same or lower toxicity than the corresponding pure drug it carries when tested on normal cell lines (Hussein-Al-Ali et al., 2012a).Application of LDH for the delivery of nonsteroidal anti-inflammatory drugs have been studied (Rives et al., 2013). Many other drugs, such as antidiabetic, cardiovascular, antibiotics, antioxidants, amino acids, and peptides, have been intercalated into the inorganic nanolayers, which were comprehensively reviewed recently (Rives et al., 2014). Nevertheless, the toxicity potential of many drugs was significantly decreased after intercalation in to layered double hydroxides (LDH) as compared to pure drugs. Most body organs, including the brain were accessible by LDH nanocomposite to deliver different types of drug, achievable, especially with those particles whose sizes are < 250 nm (Jin et al., 2013). Similarly, another example is Podophyllotoxin, which is an agent with poor water solubility and low bioavailability. These two negative attributes have limited the success of Podophyllotoxin in cancer treatment (Sugano et al., 2010). However, the anti-cancer

the most important characteristic of the ideal material for drug-delivery systems is biocompatibility with the human body, cells, and tissues.

activity was improved following intercalation into this nanodelivery system. A time-dependent decrease in cervical cancer cells (Hela) viability seen with exposure to 20 μg/mL of paclitaxel (PPT) and its corresponding LDH nanocomposite. The LDH nanocomposite showed higher toxicity (anticancer) effect than pure PPT. This positive outcome is due to better cell penetration of the new delivery system, controlled and sustained release ability, increase stability of the active compound while inside the carrier. The host material (LDH) itself had no significant effect on the cancer cells (Sugano et al., 2010).

Sustained release of drugs

The important factor in drug-delivery systems is their affinity to release the active agents (drugs/biomolecules/genes, etc.) in a constant manner at the target location. The tendency of layered double hydroxides to release the drug in a sustained manner in a particular pH makes them superior from other drug delivery systems. The drug release from LDH can be in a two-phase manner, initially fast followed by a slower release (Liu et al., 2014; Mishra et al., 2017a; Rojas et al., 2012). The ability of these inorganic nanolayers to protect, release in the desired manner, and release at the target site would avoid the physicochemical degradation of the drug, with a reduction in adverse effects and dosing concentration and frequency and in general would improve the bioavailability of the drug (Saifullah and Hussein, 2015). At the same time, There are many parameters, such as pH, mechanisms involved in drug release from LDH, etc. which can affect the release of target materials from the layered structure.

The readily controllable sizes as well as the tendency of cells to invite the LDH particles are playing major role in cellular distribution and uptake. They equally play vital roles in decreasing toxicity and enhancing anti-cancer effects (Saifullah et al., 2013). LDH produces cell responsive by-products (H_2O, Mg^{2+}, Al^{3+}, Zn^{2+}) in physiological conditions (pH = 7.4 or less). These by-products can moderate the acidification affinities of cells after the uptake of nanocomposite (Saifullah et al., 2013). Thus, toxicity due to high acidity will be reduced. Also, recently, a sustained, controlled, slow and pH dependent release of levodopa from ZneAl nanocomposite that lasted 3–6 days was reported (Kura et al., 2013). This slow releasing property of toxic compounds from the interlayer sheet of LDH over time is also a factor in suppressing drug toxicity.

Similarly, Cefazolin, an antibiotic which has potent activity against both gram positive and gram negative organisms, have been intercalated successfully in to Zn-Al-nitrate LDH by ion-exchange method (Ryu et al., 2010). Intercalation was assessed by PXRD, which showed a swelling of the layers from 8.9 Å for the nitrate precursor to 18 Å for the cefazolin-containing solid after exchange. From the gallery height (13.2 Å) and the size of the intercalated drug, these authors concluded formation of a 62°-tilted, intercalated, double layer of drug molecules.

The cefazolin-LDH nano hybrids revealed an enhanced antibacterial activity compared to the cefazolin itself not only due to an improvement of chemical stability of cefazolin molecules but also due to a controlled release property. Likewise, controlled release formulation of anti-carcinogenic drug with Gallate-Zn-Al-Layered LDH was studied (Ghotbi and Bin Hussein, 2010). Here LDH is acting as a perfect storage material of anti-carcinogenic drug with controlled release capacity. Also, Gliclazide have been intercalated on to ZneCr LDH by ion exchange method so as to use it as a matrix to improve the dissolution rate of the poorly water soluble drug (Ambrogi et al., 2009). Gliclazide is a second-generation sulfonylurea compound used in the treatment of type II diabetes mellitus. These results showed that the hybrid nanostructure could represent a promising system to improve drug dissolution rate and to release cations involved in the performance of insulin.

Following the ion exchange method, several antibiotics have been intercalated within MgeAl hydrotalcite, namely, benzoate (BZ), succinate (SU), benzylpenicillin (BP), and ticarcillin (TCC) anions (Wang et al., 2012). Formation of the corresponding drug–LDH systems has been confirmed by PXRD and FT-IR spectroscopy. SU and TCC anions were intercalated in a monolayer arrangement, whereas BZ and BP anions were accommodated in the interlayer region as a bilayer. Release studies indicated that an anion exchange process holds diffusion through the particles being the rate determining step.

Similarly, amoxicillin – a hydrophylic antibiotic of the penicillin group which is generally used to treat many different bacterial infections, has been successfully intercalated in Zn-Al-LDH by rehydration method (Wang et al., 2009). Release studies have been carried out at 37 °C in a phosphate buffer (pH 7.4), comparing the results with those obtained with a physical mixture of 0.05 g amoxicillin and 0.08 g of Zn,Al-CO_3 LDH. Complete dissolution was attained for the physical mixture after 30 min, while with the intercalated sample only 85% of drug was released after 2 h, due to the strong electrostatic interactions between the drug and the layers. These results further confirmed the suitability of these intercalated systems for controlled release of this drug.

pH dependent release of drugs

In vitro release studies are conducted in various solutions simulating different routes of the delivery. In some cases, the release is carried out in phosphate-buffered saline (PBS) of pH 7.4 to check the suitability of the drug-delivery system for intravenous application, as PBS 7.4 simulates blood (Saifullah et al., 2013). The condition of PBS 7.4 is most commonly applied to evaluate the release behavior of any newly designed drug-delivery system. The drug release in PBS 7.4 from LDH has been found to be highly sustained compared to acidic pH conditions (Hussein-Al-Ali et al., 2012b). The in vitro release is also most commonly conducted in PBS 4.8 to mimic the release in lysosomal conditions. Lysosomes are membrane-enclosed organelles present in the cell, and function as the digestive system of the cell. A great deal of in vitro release studies of LDH have revealed that LDH release in PBS at pH 4.8 is sustained, but relatively faster compared to pH 7.4 (Hussein et al., 2011; Saifullah et al., 2013).

The release at pH 7.4 is for the evaluation of the oral route PBS, with pH 6.8 being used to simulate the intestinal environment, and pH 4.8 is used as the simulator for a lysosomal environment. Rives et al. comprehensively reviewed release studies on LDH (Rives et al., 2013, 2014).

The different pattern of drug release from LDH in different conditions is due to diverse release mechanisms. The drug can be released from the interlayer region in two different ways:

I. By ion-exchange mechanism;
II. Weathering mechanisms.

The drug is released by an ion-exchange mechanism under basic or neutral PBS medium, whereas under acidic conditions the drug is released by both ion exchange and by the weathering of inorganic nanolayers (Wang et al., 2005; Xia et al., 2008).

Sustained release drug delivery systems have received considerable attention from the pharmaceutical industries because these systems offer advantages over conventional dosage forms (Tronto et al., 2004). Intercalation of drugs is just like other intercalations. At the time of release, the composite is subjected to different pH conditions so that at the suitable pH, the composite breaks slowly releasing the drug at the required site.

Carnosine and Gallic acid are two antioxidant drugs which were intercalated into Mg/Al LDH by ion exchange and co-precipitation method (Kong et al., 2010). The gradual and biphasic drug release as well as the scavenging action of both the antioxidants on 2,2-diphenyl- 1-picrylhydrazyl (DPPH) radicals were studied. Both the drugs were found to be excellent antioxidants to scavenge DPPH radicals in a long release period. Similarly, anti-tumor drug Podophyllotoxin was also successfully intercalated into LDH and the in vitro cytotoxicity to tumor cells (Qin et al., 2010) was investigated. Likewise, anti-inflammatory drug Fenbufen have been intercalated by co-precipitation on various layered double hydroxides like Mg/Al, Zn/Al, Fe/Al and Li/Al-LDH (Li et al., 2004). Drug release characteristics of the pillared LDH materials were investigated by a dissolution test in a simulated intestinal fluid (buffer at pH 7.8). The results showed that the release was a slow process especially for Mg/Al LDH as compared to other LDH suggesting them to be a very good drug delivery system.

One of the main advantages of supporting drugs in LDHs is that the instability of the drug in physiological media can be avoided. Liposomes present an important drawback for drug delivery, as they are unstable in physiological media, but this can be overcomed by intercalating them in LDH, especially in MgeAl LDH, which are stable under such pH conditions (the ZneAl analogues are stable at more acidic pH). Bégu et al. (2009) have studied the intercalation of lipophilic drug-loaded phospholipid bilayers between the layers of MgeAl LDH, thus obtaining a new class of intercalation compounds affording protection and stabilization of the bilayer and of the drug over a long period of time, and thus can be potentially used for sustained release. The sustained release after subcutaneous application was also studied.

The profile of LDH nanoparticles loaded with Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), such as Naproxen, Flurbiprofen, Ibuprofen, Diclofenac, Indomethacin, were widely investigated as well. There are three possible conclusions about Fenbufen and Naproxen:

- NSAID-LDH synthesis; Two different methods were employed for LDH synthesis, co-precipitation and reconstruction. It is believed that co-precipitation showed more advantages over reconstruction. The co-precipitation lead to a perfect single layered structure whereas the reconstructed LDH could be “contaminated” by other unwanted anions (layered $MgAleCO_3$ phase existed in MgeAleOH), also the co-precipitation LDHs possessed a larger gallery than the reconstructed LDHs, indicating a relatively higher drug loading efficiency (Ay et al., 2009; Del Arco et al., 2004);
- Improvement of loaded drug “survival” ability; it has been discovered that the drug-loaded LDH could remarkably enhance the drug solubility in either aquatic environment or in gastric fluid environment (Berber et al., 2008). The thermo-gravimetric analysis also showed that drugs appeared to be more stable after the intercalation with LDH nanoparticles. The presence of LDH nanoparticles could not only prevent loaded drugs from unexpected degradation, but most importantly, lead to an enhancement of gastric mucus permeation and protection of gastrointestinal mucus from ulcergenic activity (Perioli et al., 2011a,b);
- Sustained release of drugs; controlled drug release could be achieved in both gastric environment (pH 1–2) and intracellular environment (~pH 7.5). As discussed above, appropriate modification is required for drug release to appear in a liner manner at pH value of 1–2 (Li et al., 2004). However, at a pH value of 7.5, the different mechanism, ion exchange, was the most responsible for the sustained drug release (Perioli et al., 2011b).

Immobilization

Immobilization is the process of imprisonment of a particular species at a particular place and not disturbing it from that place. Various active agents like Amino acids, DNA, Proteins, enzymes, microbes, etc. are acting as immobilized agents. Different applications of immobilization are;

I. *Industrial production:* Industrial production of amino acids, beverages, antibiotics, etc. uses immobilized cells.
II. *Biomedical applications:* Immobilized enzymes are widely used in diagnosis and treatment of many diseases.
III. *Food industry:* Enzymes like pectinases and cellulases immobilized on suitable carriers are successfully used in the production of jams, jellies and syrups from fruits and vegetables.

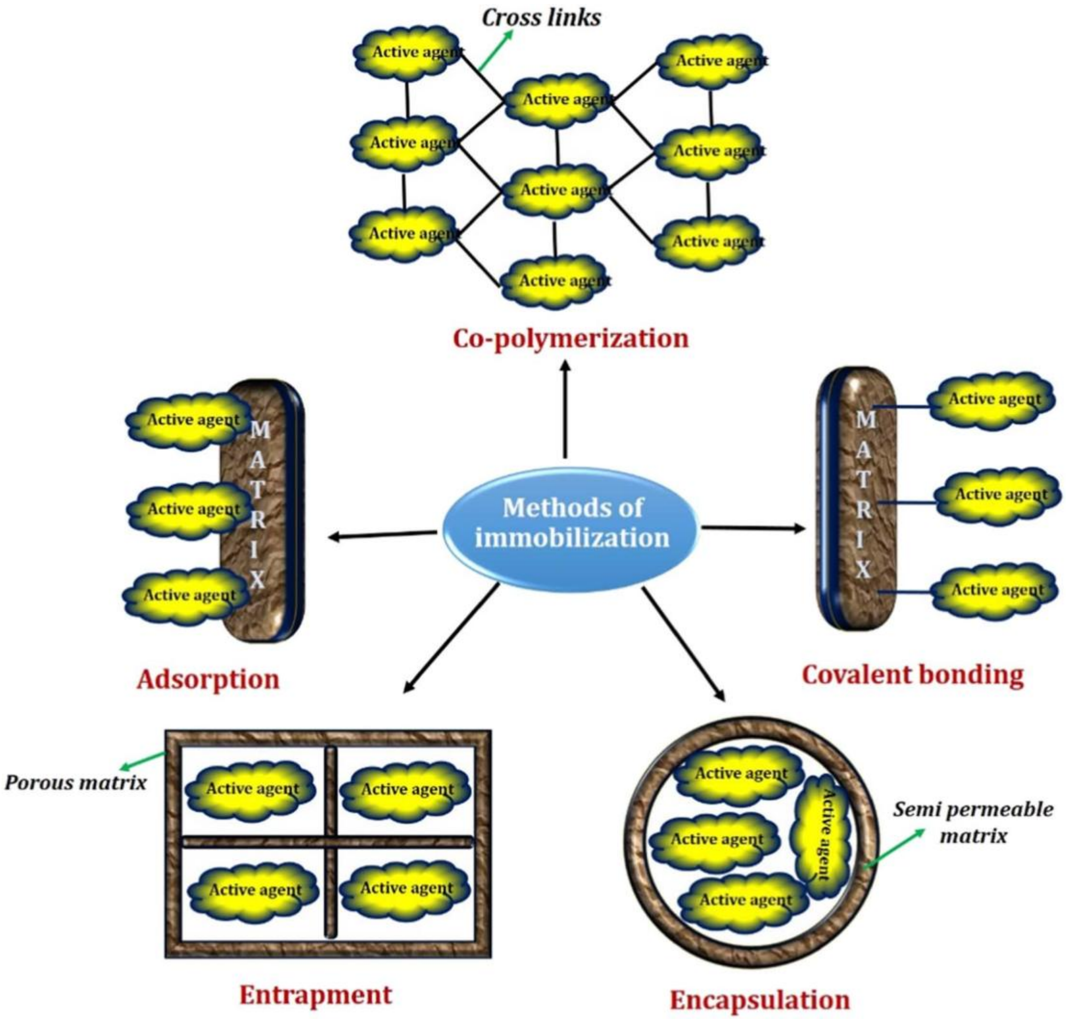

Fig. 5. Schematic representation of different methods of immobilization.

IV. *Research:* Different research activities are in ongoing process for the study of immobilization.

Immobilization can be categorized depending upon the type of matrix and the type of bonds involved such as; Adsorption, Covalent bonding, Entrapment, Copolymerization, Encapsulation, etc. The schematic representation of various methods of immobilization is revealed in Fig. 5.The matrix or support which immobilizes the active agent by holding it permanently or temporarily for a brief period of time should be cheap and easily available. Its reaction with the medium or with the agent to be immobilized should be minimum as possible. Immobilization gives extra stability to the intercalated substance.

Taking all the points into consideration, it can be believed that layered double hydroxides (LDH) can act as the host matrix for numerous immobilization purpose. Immobilization is carried out through ion exchange method i.e. the layered double hydroxide is dispersed in the solution of the suitable intercalating substance (de Freitas Castro et al., 2010). Most of the enzymes and organic species are intercalated through ion exchange method. A second method called "memory effect" is the method of reconstruction of a layered double hydroxide when the calcined LDH (corresponding spinel) is dispersed in the solution of the species to be intercalated (Costantino et al., 2008). Another method is there called co-precipitation where both the salt mixture and the species to be intercalated is co precipitated at $pH \geq 10$.

In all types of intercalation procedure after the species is intercalated, the interlayer space is increased confirming its presence. This can be verified through the XRD patterns through the broadening of the basal plane. For example, the base line broadening of MgeAl LDH from 0.76 nm to 0.84 and 0.86 nm were observed due to ascorbic acid intercalation (Aisawa et al., 2007).

It is also expected that LDH are noble host materials for safe storage of vitamins. It is also observed that the hybrid composite after intercalation exhibit extra stability as illustrated that the cinnamic acid/LDH composite is thermally more stable than the pure cinnamic acid itself (Park et al., 2010). Also the composite shows antibacterial effect and it can be used as green pesticide (Park et al., 2010).

Immobilization of several antimicrobial species was also studied. For example, molecules like 2,4-Dichlorobenzoate (BzDC) and *para*-hydroxybenzoate (*p*-BzOH) when intercalated into ZneAl LDH gives antimicrobial property to the composite with different releasing properties (Bugatti et al., 2011). The presence of the two ions in between the inorganic lamella was confirmed from XRD studies with the shifting of the basal plane towards lower 2θ value as well as increase in the d-value.

Nucleic acids like DNA and RNA are also found to be intercalated in LDH as an example of immobilization so as to give them extra stability. Ladewig et al. have tried to intercalate siRNA in LDH followed by its release and efficient delivery to mammalian cells in vivo (Ladewig et al., 2010). Schematic representation showing immobilization of DNA in between LDH and cellular uptake of the composite followed by its action on the cell are illustrated in Figs. 6 and 7, respectively.

Using the aforesaid aspect of composite formation, trials have been

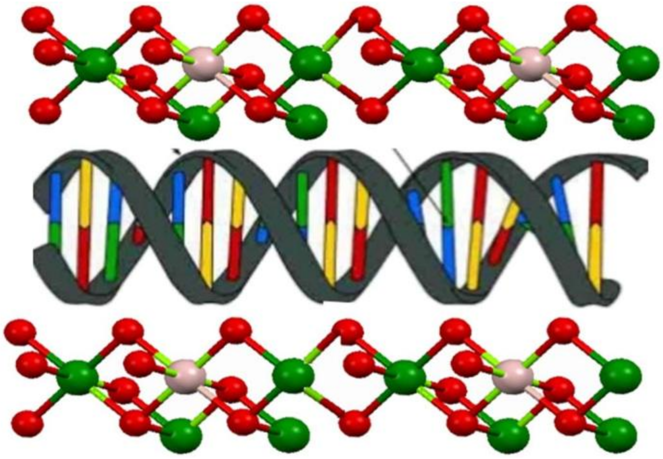

Fig. 6. Schematic image of DNA intercalated LDH.

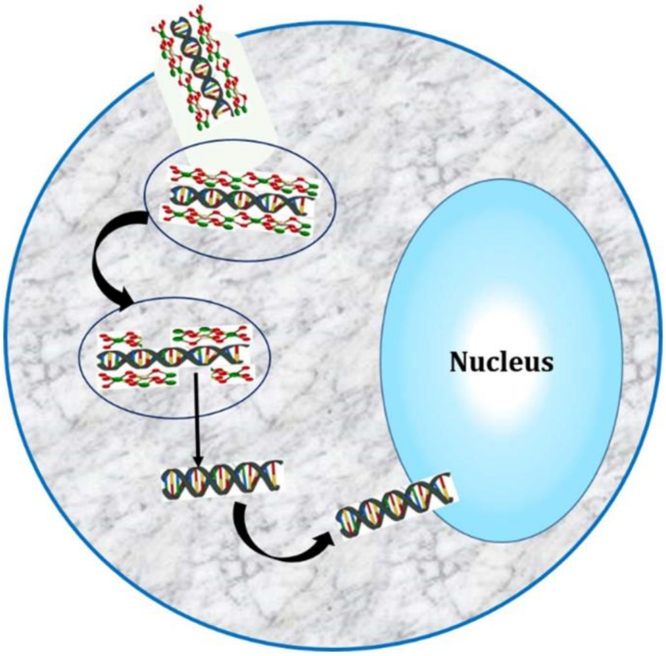

Fig. 7. Schematic image of cellular uptake of DNA intercalated LDH nano hybrid and its action on cells.

taken to immobilize bacteria and viruses in the interlamellar space of layered double hydroxide and resulted in its removal from the drinking water (Jin et al., 2007).

Similarly, LDH also intercalate various amino acids, vitamins, peptides, and nucleosides resulting immobilization of the above bio-molecules. The intercalation behavior of various amino acids for the LDH was also found to be greatly influenced by the feature of the amino acid side-chain, namely, its carbon-chain length, structure and physico-chemical property. In particular, amino acids possessing a hydrophobic or negative-charged side-chain were preferentially intercalated for the LDH (Aisawa et al., 2004). Schematic diagrams of the intercalated amino acids are given in Fig. 8.

The selective interaction of nucleoside monophosphate in LDH opens up the possibilities of using layered host as rapid, cost effective and recyclable materials for the purification and separation of complex biomolecules like nucleosides (Lotsch et al., 2001).

Hydrotalcite like layered double hydroxide could also be used to immobilize enzymes. Immobilization of glucose oxidase in Ni/Al LDH by means of electrochemical method was studied for the preparation of a biosensor (Guadagnini et al., 2010). In the same way immobilization of Iron (II) porphyrins into MgeAl layered double hydroxides has been explored (Halma et al., 2009). Zhu et al. have immobilized acid phosphatase on uncalcined and calcined MgeAl LDH through adsorption process (Zhu et al., 2010). The hydrolytic stability of acid phosphatase was promoted significantly after the immobilization on LDH-CO_3 especially the calcined form. Reusability investigation showed that > 60% of the initial activity was remained after six reuses of immobilized enzyme on Unc-LDH-CO_3 and C-LDH-CO_3. Therefore, immobilization of acid phosphatase on Unc-LDH-CO_3 and C-LDH-CO_3 by direct adsorption is an effective means and would have promising potential for the practical application in agricultural production and environmental remediation.

Another enzyme named lipase from *Candida rugosa* was intercalated into MgeAl LDH and the so formed nanocomposite was used as a biocatalyst for the synthesis of ester (butyl oleate) (Rahman et al., 2004). Ren et al. have immobilized penicillin G amylases into calcined LDH (Ren et al., 2001). The activity of the immobilized enzyme decreased with increased Mg/Al ratio and vice versa. The activity of the enzyme is maximum when the calcination temperature was 450–500 °C. Penicillin G amylases was again immobilized into glutamate pillared LDH (Ren et al., 2002). Here the inorganic nano composite shows 90% of the activity retention even after 10 recycles. Likewise, glucose oxidase enzyme has been encapsulated in the nano porous alumina membrane so as to develop amperometric biosensor (Darder et al., 2006). So, it is well observed that enzymes when immobilized not only give extra stability and protection to the species but also it is applied in different field of researches.

Layered double hydroxides (LDH) as antimicrobial biomaterials

Preparation of biomaterials having antimicrobial properties is another challenging area of research, as in today's world, many of the diseases are caused by microbes. Biomaterials with antimicrobial properties have a variety of applications, such as in medical implants, medical devices, food packaging (Costantino et al., 2009), healthcare and household products (Saifullah and Hussein, 2015). It is well-known that LDH is also identified as functional material i.e. depending upon the nature and function of the intercalated or incorporated species, the LDH composite will behave accordingly. Therefore, if some anti-microbial species would be incorporated or intercalated to LDH, the composite can behave as an antimicrobial material.

Taking this concept into consideration, nano silver has been incorporated into ZneAl LDH and antibacterial activity of the composite was verified (Chen et al., 2012; Carja et al., 2009; Mishra et al., 2013). It was found that the product shows positive antibacterial effect towards both gram positive and gram negative bacteria. Silver nanoparticles (NPs) have been testified for having strong antimicrobial properties, but due to its toxicity level, its application reduces (Saifullah and Hussein, 2015). Marcato et al. synthesized biogenic silver NPs (AgNPbio) with Mg/Al LDH (Marcato et al., 2013) to make silver NPs more biocompatible. They evaluated the biocompatibility of free AgNPbio, LDH, and AgNPbio LDH against a lung fibroblast cell line (V79), and found that AgNPbio caused 50% cell death at a concentration of 45 $\mu mol\cdot L^{-1}$. However, even at a concentration of 45 $\mu mol\cdot L^{-1}$, LDH alone and AgNPbio LDH did not show any toxicity (as shown in Fig. 9). This difference can be attributed to the immobilization of AgNPbio on the LDH surface, as shown in Figure suggesting that LDH can be used as a vehicle for the compatibilization of AgNPbio in medical and cosmetic applications.

In addition, AgNPbio LDH hybrid material was found to retain the antimicrobial effect, and the minimum inhibitory concentration (MIC) of AgNPbio is very less i.e. 6.6 $\mu g\cdot mL^{-1}$ against Gram-positive (*S. aureus*) and 12 $\mu g\cdot mL^{-1}$ against Gram-negative (*E. coli*) bacteria (Marcato et al., 2013). This attractive hybrid material is appropriate to be useful in biomedical devices, cosmetics, and household items.

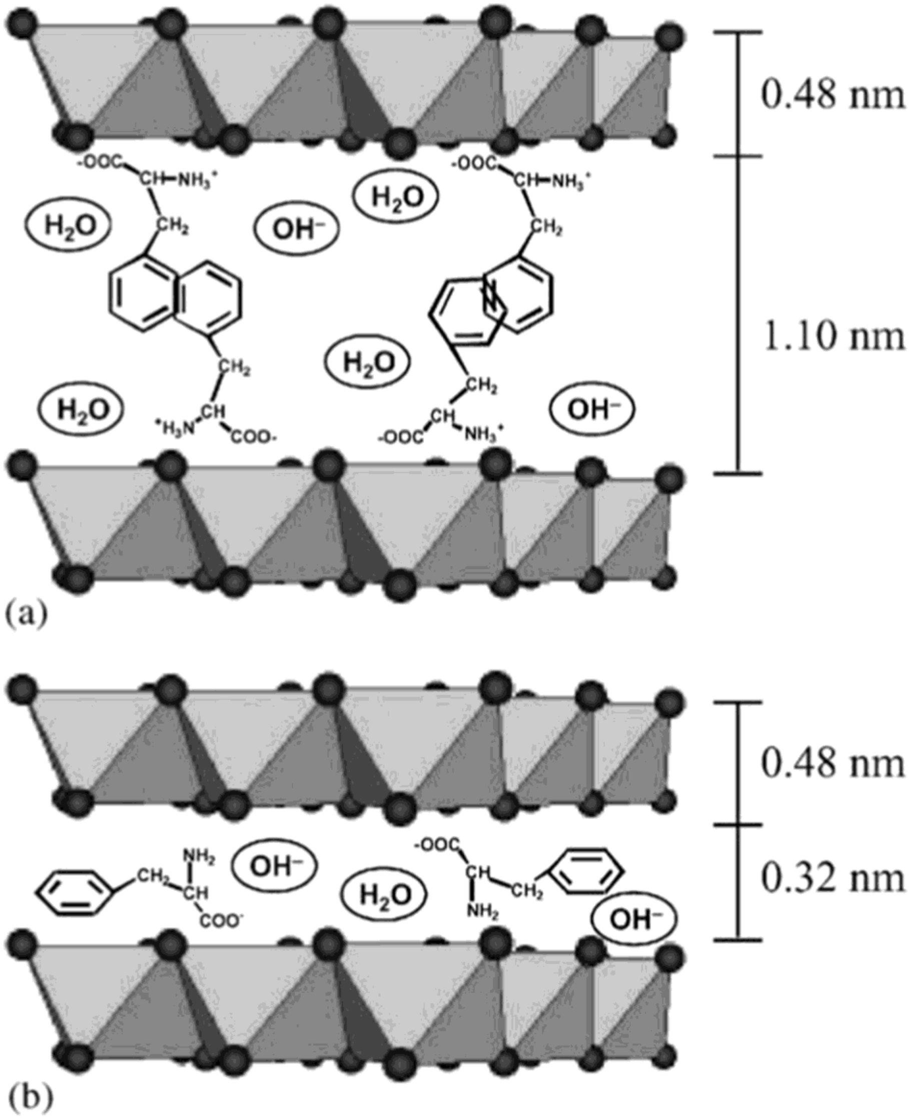

Fig. 8. Spatial orientation of Phe/LDH. (a) pH 7.0 and (b) pH 10.5. Reprinted from Aisawa et al. (2004). Copyright (2004), with permission from Elsevier.

A similar method was previously implemented for the preparation of hybrid material by fabrication of AgNPs on the surface of LDH (AgNP LDH) (Carja et al., 2009). They have evaluated the antimicrobial effect of AgNPs alone and hybrid AgNP LDH with respect to time, and found that AgNP LDH retained the inhibition zone against the Gram-positive *S. aureus* (American Type Culture Collection [ATCC] 25,923) and the Gram-negative *E. coli* (ATCC 35218).

Similarly, ZneTi LDH nano sheets were developed by Zhao et al. It

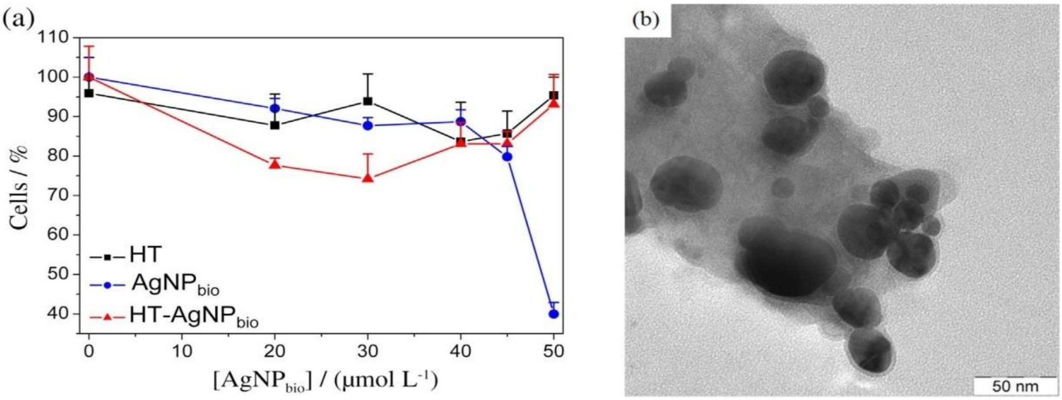

Fig. 9. (a) MTT cytotoxicity assay of LDH, AgNPbioand LDH-AgNPbioon fibroblast V79 cells and (b) TEM image of new hybrid material LDH-AgNPbio. Reprinted from Marcato et al. (2013). Copyright (2013), with permission from SociedadeBrasileira de Química.

was found that photochemical activity and nano size deliberate antimicrobial activity under visible light. The material was found to possess a strong antimicrobial effect against *Saccharomyces cerevisiae* (85% inhibition), *S. aureus* (65% inhibition), and *E. coli* (100% inhibition) (Zhao et al., 2013).Another antimicrobial nanocomposite was designed by combining Zn/Al LDH, waterborne polyurethane, and ZnO NPs. The designed nanocomposite showed strong antimicrobial activity against the Gram-negative *E. coli* and the Gram-positive *S. aureus* (Zhang et al., 2013b).

Layered double hydroxides (LDH) as fashionable antimicrobial formulations

Layered double hydroxides (LDH) have been used for antimicrobial formulations by intercalating different types of antimicrobial agents into them. For instance, antimicrobial drug ciprofloxacin has been intercalated into MgeAl LDH and its in vivo antimicrobial effect has been evaluated in rabbit ears against the bacterium *Pseudomonas aeruginosa*, and the material was found to show excellent antimicrobial effect even after 1 week (Hesse et al., 2013). Hippuric acid has been reported to have antimicrobial and antitumor properties (Hussein et al., 2011). Nano composite formulations were developed by the intercalation of hippuric acid into Zn layered hydroxides (ZnLHs) (Hussein et al., 2011). The antimicrobial study revealed that hippuric acid ZnLHs showed strong activity against *P. aeruginosa*, and most importantly hippuric acid ZnLHs showed better antimicrobial properties against drug-resistant bacteria, namely methicillin-resistant *S. aureus*, as compared to free hippuric acid (Hussein Al Ali et al., 2013).

An antimicrobial film was synthesized by intercalating benzyl penicillin which is an antimicrobial agent into MgeAl LDH, and then that nano hybrid was fabricated with graphene oxide (Wang et al., 2012). Results exhibited that a sustained release mechanism of the antimicrobial agent i.e. benzyl penicillin from the film was established and the film showed strong antimicrobial activity against *Micrococcus lysodeikticus* and sulfate-reducing bacteria (Wang et al., 2012).

Layered double hydroxides (LDH) in bio-sensing

Bio sensing is an emerging technology that has a number of applications in biomedical diagnosis, food sciences, and environmental sciences. Sensors are small devices that can detect chemical or biochemical changes in the medium around them and can convert them into the analytically useful signal. The sensor contains two basic components:

1) A receptor that can recognize the occurrences of events in the analyses of interest and.
2) A transducer that converts the events into measurable signals (Mousty, 2004).

In biosensors, transducers are attached with biological materials (enzymes, affinity ligands, antibody, oligonucleotides, receptors, peptides, etc.), which can serve as a biological recognizer (Yin et al., 2010). The high thermal stability and tendency of inorganic nanolayers to protect immobilized bioactive molecules and their biocompatibility make them ideal material to be applied in bio sensing technology.

The immobilized enzymes and other intercalated substances forming composite with LDH also acts as a sensor in many cases. When enzymes are immobilized their specific reactions are noted. For example - Urease enzyme was immobilized on Zn/Al nano hybrid LDH and used the same for urea biosensor. As urease dissociates urea and the rate is noted as electronic pulse and it gives information about the amount of surrounding urea (Vial et al., 2006). Like that laccase; one versatile enzyme used in oxidation-reduction reactions is hybridized with ZneCr LDH (Mousty et al., 2007). This is a new system for amperometric determination of dissolved oxygen and its application for the detection of anionic toxic substances. It provides a fast and a sensitive response for dissolved oxygen determination between 6×10^{-8} and 4×10^{-6} M and very low detection limits for azide (5.5 nM), fluoride (6.9 nM) and cyanide (6.2 nM).

Tyrosinase was immobilized in MgeAl LDH used for the amperometric detection of *N*-acetyl-ʟ-tyrosine ethyl ester monohydrate (N-Ac-Tyr-OEt) at −0.2 V. This compound was released during an enzymatic reaction catalyzed by transketolase with *N*-acetyl-O-(2*R*, 3*S*, 5-trihydroxy-4-oxopentyl)-ʟ-tyrosine ethyl ester used as donor substrate (Lopez et al., 2010). Alkaline phosphatase (AlP) biosensors were developed based on the immobilization of this enzyme by adsorption or co precipitation methods in different LDH. The synergy between the LDH immobilization matrix and the use of hydroquinone diphosphate (HQDP) as substrate provided a very fast and stable response for the AlP/Mg-Al–LDH biosensors at 0.4 V (Mousty et al., 2008). A new type biosensor involving a two enzyme (HRP and catalase) system was developed. Both enzymes catalyzed the decomposition of H_2O_2, HRP senses its reduction and catalase its breakdown into oxygen and water (Chen et al., 2008). Immobilization of urease within layered double hydroxides (LDH) may lead to urea biosensors for medical diagnostic monitoring (Barhoumi et al., 2006).

Table 2 Summarizes various bio-applications of layered double hydroxides.

Conclusions

Layered double hydroxide is a functional material having all types

Table 2
Bio-applications of layered double hydroxides.

Sample	Type of formulations	Name of the composite	Against the disease	References
1	Antimicrobial formulations	• Ciprofloxacin-LDH	• Chronic otitis media, i.e. disease of the eardrum	Hesse et al., 2013
		Hippuric acid-LDH	Synergistic potentiating actions on tumor cell lines when mixed with other components.	Hussein et al., 2011
2	Antimicrobial biomaterials	Benzylpenicillin-LDH	*Micrococous lysodeikticus* and sulfate-reducing bacteria (SRB).	Saifullah and Hussein, 2015
		• Ag-LDH	• Disease caused by *E.coli* and *S. aureus*	Mishra et al., 2013
		Benzoate-LDH	Disease caused by Bacteria (*E.coli* and *S. aureus*) and fungi (*F. oxysporum*)	Mishra et al., 2017b
		• AgNP-LDH	• Disease caused by *E.coli* and *S. aureus*	Carja et al., 2009
		Zn-Ti LDH	Disease caused by *E.coli* and *S. aureus*	Zhao et al., 2013
		• AgNPbio-LDH	• Disease caused by *E.coli* and *S. aureus*	Marcato et al., 2013
3	Drug delivery	NSAIDs-LDH	Against pain and fever	Rives et al., 2013
		• Podophyllotoxin-LDH	• Against cancer	Sugano et al., 2010
		Levopova-LDH	Against Parkinson's disease	Kura et al., 2013
		• Gallate-LDH	• Against cancer	Ghotbi and Bin Hussein, 2010
		Glaciazide-LDH	• Against type-II diabetes millitus	Ambrogi et al., 2009
		• Amoxicillin-LDH	Against different bacterial infections	Wang et al., 2009

of applications in almost every field starting from ceramics, cosmetics, biotechnology, drug delivery, sensors to environmental remediation. In each field this anionic clay could be proved as the best suited materials. The greatest use of it is because of its interlamellar spacing which is its exclusive characteristics.

There are varieties of materials being studied for biomedical and other applications. However, these layered double hydroxides are unique and very useful in many aspects, such as their easy preparation and proven in vitro and in vivo biocompatibility. Their tendency to intercalate a variety of anions, such as inorganic and organic acids, organic dyes, pharmaceutical drugs, biopolymers and also some biomolecules and being able to be fabricated with other metallic materials like silver and ceramics either by intercalation or by surface interactions, resulting in fabulous material with numerous applications, makes them all the more advantageous. Apart from all the mentioned uses LDH has now found its uses in genetic technologies. In the near future we can hope that LDH will grow more into several more dimensions.

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