

Review: Synthesis, Characterization and Studies on Controlled Release Properties of Layered Compound

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Layered inorganic structure such as Layered Double Hydroxide (LDH), zinc layered hydroxide (ZLH) and graphene, in nano-size, have been used widely in the nanotechnology areas as a new and promising problem solving materials. The ability of these inorganic layered compounds that able to encapsulate the organic anions were known to provide greatest benefits; were explained more details in this paper. Intercalations of anion into the interlayer spaces of layered inorganic structure such as anion-exchange, co-precipitation, hydrothermal method and reconstruction with 'memory effect' were also explained. The characterization of intercalated layered nanocomposites such as Fourier Transforms Infrared (FTIR) spectroscopy, PowderX-ray Diffraction (PXRD) analysis, Thermogravimetric analysis, surface analysis was used to explain the successful of anion intercalated in between the interlayer spaces of layered inorganic structures. The application of these hybrids that have been widely used such as controlled release properties in pharmaceutical area, antimicrobial studies, dyeing agent, enhancing UV Sunscreen protection, herbicides and water treatment process were also described in details.

Keywords: layered double hydroxide; zinc layered hydroxide; graphene

I. INTRODUCTION

Nanotechnology is a great human invention which has been used in various economic sectors. Nanotechnology is a branch of nanomaterial or nanostructure which are types of materials with sizes ranging from 1 nm to 100 nm in one or more external dimension (Kuthati *et al.*, 2015). There are a lot of nanomaterials that have been invented by researchers, such as graphene, layered double-hydroxide and zinc layered hydroxide.

phase are in nanoscale range (Kickelbick, 2007). Meanwhile, according to Komarneni (1992), nanocomposites could be divided into five major families according to their structure, function, physical and chemical differentials, and also method of preparation as shown in Table 1. Meanwhile, according to Henrique *et al.* (2009), nanocomposites could also be classified into three types, i.e. - metal, ceramic and polymer as shown in Table 2.

II. NANOCOMPOSITES

A nanocomposite is one of the branch studies in nanotechnology areas. Nanocomposite is a type of hybrid material that contains multiple phases at least one of the

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Table 1. Families of nanocomposites (Komarneni, 1992)

Nanocomposite Family	Details	Types
I Sol-gel	Made at lower temperatures where precursor cause the formation of the homogenous single-crystalline phase ceramics or multiphase crystalline ceramics at high heating temperature.	<ul style="list-style-type: none"> - Compositionally different nanocomposites - Structurally different nanocomposites - Both compositional and structural nanocomposites - Nanocomposite gels with precipitate phases - Nanocomposites of xerogels with metal phases - Nanocomposites of inorganic gels and organic molecules
II Intercalation-type	Made at low temperatures and produces useful materials when heated up to average temperature.	<ul style="list-style-type: none"> - Pillared clay - Metal intercalated clay - Clay-organic nanocomposites
III Entrapment-type	Made from three-dimensional linked network structure such as zeolites and can be prepared at low temperatures.	<ul style="list-style-type: none"> - Zeolite- inorganic nanocomposites - Zeolite organic nanocomposites
IV Electroceramic	Made from mixing nanophase of ferroelectric, dielectric, superconducting and ferric materials in a polymer matrix at very low temperatures.	<ul style="list-style-type: none"> - Magnetic - Ferroelectric - Superconducting ferroelectric - Dielectric - Conducting, semiconducting and insulating type materials
V Structural pyramid	Can be produced through conventional ceramic processing at a very high temperature.	<ul style="list-style-type: none"> - Glass ceramic

Table 2. Types of nanocomposites (Henrique et al., 2009).

	Type	Examples
I	Metal	FeCr/Al ₂ O ₃ , Ni/Al ₂ O ₃ , Co/Cr, Fe/MgO, Al/CNT, Mg/CNT
II	Ceramic	Al ₂ O ₃ /SiO ₂ , SiO ₂ /Ni, Al ₂ O ₃ /TiO ₂ , Al ₂ O ₃ /SiC, Al ₂ O ₃ /CNT
III	Polymer	Thermoplastic, thermosets polymer/layered silicates, polyester/TiO ₂ , polymer/CNT, polymer/layered double hydroxides

A. Layered Metal Hydroxide

Layered metal hydroxides can be divided into three types which are layered double hydroxide (LDH); layered hydroxide salts (LHS) and hydroxyl double salts (HDS). Hydroxyl double salts contain two types of divalent metallic cation with the chemical formula of $[(M^{2+}_{1-x}M^{2+}_{1+x})(OH)_{3(1-y)}]A^{n-}_{(1+3y)/m}.nH_2O$ (Ahmad *et al.*, 2016).

Layered double hydroxides and layered hydroxide salts were originally derived from the structure of $Mg(OH)_2$ brucite, in the form of octahedrons, with the center is being occupied by the magnesium cation and vertices are occupied by hydroxyl groups. Layered double hydroxide is an inorganic material, that consist of trivalent and divalent metallic cations, with the formula of $[M^{II}_{1-x}M^{III}_x(OH)_2]^{2+}(A^{n-})_{x/n}.mH_2O$, where M^{II} is the metallic divalent cation such as, Zn^{2+} , Mg^{2+} , Ni^{2+} , Fe^{2+} while M^{III} is the metallic trivalent cation which includes Al^{3+} , Cr^{3+} , Mn^{3+} , and A^{n-} is the replaceable inorganic anions (CO_3^{2-} , NO_3^{2-}) or organic anions (Gil *et al.*, 2016). The LDH were obtained when the fraction of divalent cations were replaced isomorphously by trivalent cation and the overall positive charge of the LDH host structure was influenced by increasing charges of the trivalent cation, which were then balanced by interlayer anions (Cho & Lee, 2011).

The properties of LDH could be increased by modifying the surfaces with anionic surfactant, which then causes the nature of LDH to change from hydrophilic to hydrophobic. According to the Zhang *et al.*, (2017b), the surfactants will not only replaces the exchangeable anions present in between LDH but also the outer surface of the LDH host structure in a monolayer form. These new nanocomposites increase the surface for the anionic dyes to be adsorbed not only in between LDH interior surfaces but also at the exterior surfaces. Nonetheless, this organo-LDH absorbance could not be used under low pH values. This happens due to the competition for sites between the hydroxyl group and anionic dyes itself. Besides that, the organo-LDH also could lose its ability to serve as positively charged sites and transform into more negatively charged sites, thus causing the repulsion of the same charge between anionic dyes and surfactant itself.

Furthermore, a recent study was conducted on a new type of LDH which is the flower-like Ni/Al-LDH (talkovite-like clay) (El Hassani *et al.*, 2017). This new feature of LDH has low solubility, which makes it suitable for the adsorption of

the azo dyes in treating water usually found in the dye industry. This new LDH has low stability when used under low pH solution. Under low pH values these new LDH hydrated surface are easily protonated causing it to have more positively charged features, thus allowing electrostatic attraction between the negatively charged azo dyes and the surface of these new talkovite-like clay. These features are interesting in treating the more negatively charged compound under low pH conditions as compared to what is available now. The LDH that has been used up until now could not capture negatively charged anion when being used under low pH values since it is known to be soluble causing less interaction.

Layered hydroxide salts (LHS) can be obtained by two types of modification done on the brucite-like structure, which the hydroxyls substituted with other anion (type I) or octahedral area been replaced by other anion (type II) (Tavares *et al.*, 2017). Furthermore, LHS that are structurally similar to LDH possess the chemical formula of, $M^{2+}(OH)_{2-x}(A^{m-})_{x/m}.nH_2O$, where M^{2+} is the divalent cation mainly Zn^{2+} and A^{n-} are the counter anion or replaceable anions such as CO_3^{2-} , NO_3^{2-} (Megat *et al.*, 2013). LHS were obtained when a fraction of the sites in brucite, $Mg(OH)_2$ were occupied by hydroxyl ions and replaced by water molecules or anions. For example is $Zn_5(OH)_8(NO_3)_2.2H_2O$ (commonly used), which contains zinc atoms that are octahedrally coordinated by hydroxyl anions and tetrahedrally coordinated to three hydroxyl anions and one water molecules where the nitrate being positioned between the exchangeable layers (Jaerger *et al.*, 2014).

B. Mineral Clay

Mineral clays, such as, graphite, zeolites and montmorillonite were also used as host for intercalations of organic anions. Graphite is a type of semimetal that composes stacked hexagonal planes of carbon atoms (Kelly & Halas, 1998) and is made up of multiple layers of graphene, which could be used as a host for guest anions. Graphene is a type of nanostructured sheet with a single-atom-thick size which being arranged in two dimensional structure that contains sp^2 hybridized carbon (Zhang *et al.*, 2017a) that are known to have high specific area, extraordinary electronic conductivity and thermally and chemically stable (Taei *et al.*, 2017). This

make it suitable to act as the host as it able to encapsulate the guest anions. However, the graphite is a natural free-charges metal which is not suitable for interleaving guest anion. Thus, the idea of graphite oxide was formed.

Graphite oxide (GO) is a type of graphite, except that it contains a lot of carboxyl, hydroxyl and epoxy groups at its basal plane. Besides that, GO is known to act as a strong hydrophile, which easily soluble in aqueous solution (Hu *et al.*, 2017). These GO can be prepared using physical and chemical methods:- by first chemically oxidizing the graphite causing it to have carboxyl, hydroxyl and epoxy groups that are responsible in the formation of stable aqueous colloid that obtained through sonication (Ramesha *et al.*, 2011). During first discovery of graphene, method of synthesizing graphene has been upgrading from micromechanical cleavage method, chemical vapour deposition method and exfoliation of graphite (Shams *et al.*, 2015). Exfoliation technique of graphene to graphite was known to have a variety of advantages such as large specific area and ability to absorb organic compound due to the presence of two hydrophobic polyaromatic basal planes (Chuanyu & Yu, 2015). Meanwhile, in industry, natural graphite were treated with sulphuric acid to form exfoliated graphite that is able to absorb abundant amounts of heavy oil suspended on seawater (Toyoda *et al.*, 1998).

Nonetheless, there have been noteworthy studies done by Ramesha *et al.* (2011), using exfoliating graphene oxide (EGO) and reducing graphene oxide (RGO). The EGO is treated with hydrazine nitrate forming a new type of graphene oxide which is the RGO to have more positive features. The hydrazine nitrate causes the EGO to lose its epoxy and hydroxyl groups causing it to be intercalated with more anionic compound such as orange G. The orange G contains more negatively charged sulphonic group causing repulsion and tunable to interact with EGO. Nevertheless, the new features of graphene oxide, which is RGO, causes orange G to be attracted and adsorbed in between the layered graphene host. This new feature of the positively-charged graphene oxide could be used in interleaved the more anionic compounds, which has become the game changer in the field nanomaterial.

Zeolites has been characterized as alkaline aluminosilicate that contains exchangeable cations along with water

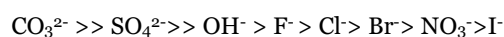
molecules that are coordinated in the structure (Arancibia-Miranda *et al.*, 2016). Besides that, zeolite are known to have smaller pores than mesoporous materials which are the characteristic to achieve efficient release properties (Ainurofiq & Choiri, 2015). Meanwhile, montmorillonite is the most expandable minerals (clay 2:1) that being characterized by its laminar organization, consisting of two tetrahedral layers of silica and a central octahedral layer of aluminium oxide (Arancibia-Miranda *et al.*, 2016).

III. INTERCALATION PROCESS

Intercalation process is the process of inserting the organic anion into the interlayer region of layered salts material forming a hybrid of inorganic-organic composites. Table III shows the method used by others researchers.

A. Anion Exchange Method

Anion exchange is the simplest process for the intercalation to happen. The basis of anion exchange process is the ability of the guest anion to exchange the counter ion that already exists in between the layered host. For an example, FERH (ferulic acid) has taken place between the layered of the synthetic Mg/Al hydrotalcite compound. The Mg/Al-HTic-Cl is prepared by the addition of urea into the Mg/Al-HTic-CO₃. This happens due to the electron affinity of the carbonate which is bigger (2-) compared to chloride that is monovalent anion (1-), causing it to form strong electrostatic bonding with inorganic hosts compared to chloride anions and making the ion exchange process harder. One excellent UV absorber is 5-benzotriazolyl-4-hydroxy-3-sec-butylbenzenesulfonic acid (BZO), which intercalates into the ZnAl-NO₃-LDH using ion exchange method. The divalent anions are more strongly held by the interlayer region of the metal hydroxides compare to the monovalent anions, as shown by sequence below (Carlino, 1997),



A study was conducted on intercalated p-amino benzoic acid (PABA) in the Zn/Ti LDH compound by using anion exchange (Xu *et al.*, 2015). This inorganic compound was new since they are using titanium oxide (TiO₂) and zinc oxide (ZnO) as the precursor for preparation of the layered host.

B. Co-precipitation Method

Co-precipitation method offers advantages like simple and rapid preparation process and method, as it is easy to control the particle size and composition can be made in this method with various possibilities to modify particle surface state and overall homogeneity (Kumar & Sangwan, 2013). This method also does not required ion exchange process which then lead too large quantities of hybrid materials produced through a simple process that lends itself to industrial applications (Choy, 2004). Typically, this method involves by mixing up the divalent and trivalent metal cations at different ratio, commonly 1:2 and 1:4 were being used, as the starting precursors and addition of various concentration of organic anion into the precursor solution which then be treated with alkaline solution and adjusted the pH from 7 to 12 (Asiabi, *et al.*, 2017; Djebbi *et al.*, 2016; Elanchezhiyan & Meenakshi, 2017).

According to Hashim *et al.* (2007), the prepared LDH hosts which are the Zn/Al-LDH was weighed around 2.00 g and mixed with 100 ml of the 4(2,4-dichlorophenoxoy)butyric acid (DPBA) by using concentration between 0.01M to 0.05M that act as the guest anions and aged for 18 hours at 70 °C. Then, the slurry obtained was centrifuged and washed by using deionized water and dried at 70 °C. Insertions of the dexamethasone sodium phosphate into the Mg/Al-LDH were studied by Sahoo *et al.* (2013), using the co-precipitation method. Dexamethone sodium phosphate are known for not being compatible with various drugs and found to be able to reduce restenosis in rats.

Another study done by Cursino *et al.*, (2013) stated that the adsolubilization process of benzophenone into the anionic surfactant that has been intercalated into the LDH. The surfactants, which are dodecylsulphate or dodecylbenzenesulfonate, first, will be intercalated into the LDH using the co-precipitation method with different Zn/Al ratios. It is then followed by the process of the adsolubilization which takes place in three different batches. The purpose of this process is to increase the solubility of the bezophenone and the intercalation of the surfactant causing the affinity of the LDH to allow non-polar and non-ionic species to be intercalated between them.

C. Hydrothermal Method

The host ZnAl:LDH that was prepared by this methods usually was too large to be used for preparations of zinc aluminium MMO nanostructures (Cho & Lee, 2011), causes unacceptable to be used to intercalate a few large anions.

D. Structural Reconstruction 'Memory Effect'

A special characteristic of the anionic clay matrix is the so-called structural 'memory effect', where the layered clay structure can be destroyed by calcination at moderate temperatures (ca. 550°C) to yield low crystalline mixed oxides and then reconstructed by treatment with aqueous solutions containing anionic species (Carja *et al.*, 2009).

The original LDH are being reconstructed from calcined sample being introduced with water containing dissolved anions (Barik *et al.*, 2017). At first, LDH will lose structure when undergoes calcination at specific temperature range which then form highly active composites metal oxide with high thermal stability, large surface area, basic properties, small crystallite size and high stability even under extreme condition against sintering (Benito *et al.*, 2006), which then able to regenerate their structure through rehydration and sorption of anions (Bernardo *et al.*, 2017). This method was reported suitable for incorporation of large anion that are favored using simple method, however, it can also be used for certain type of divalent and trivalent metallic cation which present the amorphous phase that was produced simultaneously (Allou *et al.*, 2017).

E. Sonochemical Method

Sonochemical methods causes the chemical effects of ultrasound to arise from acoustic cavitation, which involves the formation, growth, and implosive collapse of bubbles in liquid which generate transient temperatures up to ~5000 K, pressure of ~1800 MPa and cooling rate in excess of 10¹⁰ K/s that provide a lot of advantages such as rapid reaction rates, controllable reaction conditions and the ability to form high purity nanoparticle (Bozkurt & Derkuş, 2016).

IV. CHARACTERIZATION

A. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was the most commonly used instrument as starting guessing either the intercalation was tending to happen or either way through structural information. The difference and comparison in FTIR spectrum of the host with intercalated compound and sometimes with desire pure anion were also taken into account. Typically, the spectrum for LDH can be found at 3498 cm^{-1} for the O-H stretching vibration of the metal hydroxide layer and interlayer water molecules; 1635 cm^{-1} attribute to the O-H stretching band of water; 1373 cm^{-1} is the stretching vibration of nitrate and 1360 cm^{-1} as for carbonate counter anion and 500 to 1010 cm^{-1} as the M-O, M-O-M. and O-M-O lattice vibrations (Asiabi *et al.*, 2017; Asiabi *et al.*, 2018; El Hassani *et al.*, 2017; Elanchezhyan & Meenakshi, 2017). The band characteristic of starting precursors counter anion may vary according to the M^{2+}/M^{3+} ratio. This can be seen when the band of carbonate was shifted to the low frequencies as the ratios of Zn/Al were increased due to the difference in the atomic mass between zinc and aluminium (Alaâeddine Elhalil *et al.*, 2018). However, as for the LMH type materials, the starting precursors were used to differentiate the structural information of the intercalated LMH materials. For example, the band of ZnO was found at lower wavenumber region between 400 cm^{-1} to 800 cm^{-1} due to the stretching vibration of M-O and M-OH bending vibration (Bashi *et al.*, 2013).

As for the structural information for the intercalated compound, the presence of both characteristics peak of pure anion (C=C group, C=O group, C-H group, C-O group) and typical peak of LDH were observed. According to Cursino *et al.* (2015), the difference between the wavenumber of the asymmetric and symmetric carboxylate band could give information regarding to the carboxylate coordination with the layered materials. Meanwhile, the presence of peaks in intercalated compound that being shifted in position were known due to the interactions between the anion and the host layers (Feng *et al.*, 2006).

B. Powder X-ray Diffraction (PXRD) Analysis

Intercalation of organic anions can be deduced or investigated from the increment in basal spacing through the PXRD pattern between the host materials and intercalated compound. The increment or expansion of the basal spacing or gallery spaces happen due to the molecular size and geometrical arrangement of anion in between the structure layer (Hwang *et al.*, 2001). Insertion of 4-aminobenzoic acid, 2-mercaptobenzoic acid and 2-aminobenzoic acid into zinc hydroxide nitrate using co-precipitation method causes an increase in basal spacing from 9.74 \AA to 17.2 \AA , 17.72 \AA and 13.2 \AA . The PXRD results show the increase in basal spacing which concluded the presence of the organic anion and absence of the nitrate ions. Besides that, increases of the basal spacing happen due to the size of the anion itself that are larger than the nitrate ions (Demel *et al.*, 2011a). Perioli *et al.*, (2006) experimented p-amino benzoic acid (PABA) into the Mg/Al-HTiC and Zn/Al-HTiC showing that the PXRD pattern increased from 9.0 \AA to 15.9 \AA for the Zn/Al-HTiC-PABA and 9.0 \AA to 15.5 \AA for Mg/Al-HTiC-PABA. Nonetheless, the contamination of the carbonate mainly comes from exposing carbon dioxide in air causing the appearance of peaks at 7.6 \AA in PXRD pattern and 1667 cm^{-1} in FTIR spectra. The PXRD pattern for Mg/Al-HTiC-PABA presents a lot of small peaks, which happens due to impurities or formation of saturated phase. Saturated phase is where the anions are being intercalated in between the host matrix and outside of the host matrix itself. However, different value ratio between the M^{2+}/M^{3+} causes the basal spacing (d) to be varied. This happen when increasing the M^{3+} content causes the increase in charge density of the inorganic brucite like structure which then causes stronger electrostatic attraction between the inorganic layer and organic anions (Jubri *et al.*, 2012).

C. Thermogravimetric Analysis

Thermal analysis was done to study capability of an intercalated compound to withstand high temperature environment. The intercalated compound was known to exhibit two stages of decomposition which are the process of dehydration due to loss of water adsorbed and in-between the intercalated compound and second endothermic reaction event due to the dihydroxylation of the LDH matrix and

exothermic events due to the burning of the organic anions (Marangoni *et al.*, 2009).

Abdul Aziz *et al.*, (2019) stated that there is no maximum temperature appeared in TGA/DTG curve of ZnO indicates that it is a very stable compound, meanwhile, for the intercalated compound shows first two major stages which is the removal the surface and intercalated water molecules. The third weight loss is the organic moiety decomposition from the inorganic interlayer gallery that occur at 450°C with 18.7% decomposition.

The NiZn-layered hydroxide salts – sodium dodecyl sulfate (NZL-SDS) shows three main loss stages where the first stage is the evaporation of surface and structural water with weak and broad endothermic peak at 120°C, second stages at 230°C is due to the melting of SDS accompanying an exothermic reaction which were much higher than SDS and the third stages between 250°C to 500°C happened due to the consequences of the decomposition and combustion of SDS correspond to the strong exothermic peak at 365°C.

D. Surface Analysis

LDH morphology and surface analysis can be observed using FESEM or TEM. ZnO was known to have a granular structure with various shape and sizes ranging from 50 – 600 nm meanwhile, the intercalated compound of ZCA causes the nanoparticles of ZnO to be converted to agglomerates of plate-like particles with non-uniform shapes and sizes (Megat *et al.*, 2013).

Furthermore, porosity and type of the intercalated compound also can be measured through adsorption-desorption isotherms and BJH methods. For example, intercalation of DCPA into Zn/Al-LDH revealed that it is a h3-hysterisis loop according to IUPAC classifications with Type IIb designation due to the aggregates of platy particles or adsorbents containing slit-shaped pores through adsorption-desorption isotherm with pores size of 21 m²/g suggesting it is bimodal, pore size distribution with average sizes pores around 5 to 9.2 nm and total volume of 0.039 cm³/g (Abdul Aziz *et al.*, 2019).

Table 3. Summary of the methods used by others researchers

	Methods	Types of host	Molar ratio	Guest anion	Reference
I	Co-precipitation method Anion exchange Dehydration-rehydration process	Ca-Al-LDH	2:1	Nicotamine adenine dinucleotide (NAD)	(Murath <i>et al.</i> , 2017)
II	Calcination recovery	Zn-Al-LDH	-	p-methycinnamic acid (PMCA)	(Peng <i>et al.</i> , 2015)
III	-	Zeolite (ZLT) Hydrotalcite (HTC)	-	-	(Ainurofiq & Choiri, 2015)
IV	Co-precipitation method	Zn-Al-LDH	2:1	3,5-dimethoxycinnamic acid 3-amino-5-triflouromethylbenzoic acid 3,4-dihydroxycinnamic acid	(Khan <i>et al.</i> , 2011)
V	Co-precipitation method	Zn-Al-LDH	3:1	Polyacrylonitrile (PAN)	(Barik <i>et al.</i> , 2017)
VI	Self-assembly method	Zn-Al-LDH	2,3,4,5	2,4-dichlorophenoxy acetate 4-cholorophenoxyacetate	(Bashi <i>et al.</i> , 2011)
VII	Precipitation and hydrothermally treated under microwave	Ni-Al-LDH Zn-Ni-LDH	2:1 1:1	-	(Benito <i>et al.</i> , 2006)
VIII	Anion exchange	Zinc Basic Salts (ZBS)	-	Caffeic acid/C ₉ HO ₄ (CA)	(Biswick <i>et al.</i> , 2012)
IX	Co-precipitation	Mg-Cu-Al-LDH Mg-Fe-Al-LDH	-	-	(Carja <i>et al.</i> , 2001)
X	Substitution reaction	Kaolinite	-	Dimethylsulfoxide (DMSO)	(Castrillo <i>et al.</i> , 2015)
XI	Co-precipitation	Zinc hydroxide nitrate	-	-	(Demel <i>et al.</i> , 2011b)
XII	Co-precipitation method	Mg-Al-LDH	-	Coated with silver	(Chen <i>et al.</i> , 2012)
XIII	Calcination	Zn-Al-LDH were converted to Zn-Al-LDH MMO	-	-	(Cho & Lee, 2011)
XIV	Ion-exchange	Mg-Al-HTIc Zn-AL-HTIc	-	Ibuprofen, diclofenac, indomethacin, ketoprofen, tiaprofenic acid, ferulic acid, 5-benzoyl-4-hydroxy-2-methoxy-benzenesulphonate acid, p-aminobenzoic acid, 2-phenyl-1H benzimidazole-5-sulfonic acid	(Costantino <i>et al.</i> , 2008)
XV	Co-precipitation	Zn-AL-LDH	2:1 3:1 4:1	Dodecylsulfate and dodecylbenzenesulfonate	(Cursino <i>et al.</i> , 2013)
XVI	Ion-exchange Co-precipitation	Layered zinc hydroxide nitrate (ZHN)	-	2-mercaptobenzoic acid, 2-aminobenzoic acid and 4-aminobenzoic acid	(Demel <i>et al.</i> , 2011a)
XVII	Direct method	Zinc hydroxide nitrate (ZLH)	-	4-(2,4-dichlorophenoxybutyrate) (DPBA)	(Chen <i>et al.</i> , 2013)

XVIII	Co-precipitation method	Layered zinc hydroxide (LZH) nitrate		Dodecyl sulfate	(Rives <i>et al.</i> , 2013)
XIX	Urea hydrolysis Hummers/Offeman method	Mg-Al-LDH Graphene oxide	2:1 -	-	(Edenharter <i>et al.</i> , 2016)
XX	Co-precipitation	Mg-Al-LDH	3:1	Fluoride	(Elhalil <i>et al.</i> , 2016)
XXI	Direct method with Separate nucleation and aging step	Zn-Al-LDH	-	2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBA)	(Feng <i>et al.</i> , 2006)
XXII	Co-precipitation method	Ca-Al-LDH	-	Vitamin C (VC)	(Gao <i>et al.</i> , 2014)
XXIII	-	Palygorskite	-	Methyl red, alizarin, Sudan red and Murexide	(Giustetto & Wahyudi, 2010)
XXIV	Co-precipitation	Zinc hydroxide nitrate	-	Adipate, azelate and benzoate	(Guadalupe <i>et al.</i> , 2008)
XXV	Co-precipitation	Zn-AL-LDH	-	Ammonia (reversible reaction without exchange nitrate ions)	(Guadalupe <i>et al.</i> , 2010)
XXVI	Direct method (Self Assembly Method)	Zn-Al-LDH	-	2,4,5-trichlorophenoxy butyric acid (TBA)	(Sarijo <i>et al.</i> , 2015)
XXVII	Co-precipitation Ion exchange	Zn-Al-LDH	3	4-(2,4-dichlorophenoxy)butyric acid (DPBA)	(Hashim <i>et al.</i> , 2007)
XXVIII	Direct Method	Zinc layered hydroxide	-	3-(4-methoxyphenyl) Propionate	(Hashim <i>et al.</i> , 2014)
XXIX	Anion exchange Co-precipitation Method	Zn-Al-LDH	2	4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, 4-hydroxy-3-methoxycinnamic acid, 4,4'-diaminostilbene-2,2'-disulfonic acid, p-aminobenzoic acid, urocanic acid	(He <i>et al.</i> , 2004)
XXX	Self- assembly method	Zn-Al-LDH	4	Pamoate	(Hussien, 2004)
XXXI	Direct Co-precipitation	Zn-Al-LDH Zinc basic salts	-	Citric acid, tocopherol acid succinate, indigo carmine and indole acetic acid	(Hwang <i>et al.</i> , 2001)
XXXII	Co-precipitation	Zinc hydroxide nitrate	-	Dodecyl benzene sulfonate and dodecyl sulfate	(Jaerger <i>et al.</i> , 2014)
XXXIII	Anion-exchange and Calcination	Mg-Al-LDH Mg-Al oxide	2 1.9	Removing boron and fluoride	(Kameda <i>et al.</i> , 2017)
XXXIV	Co-precipitation method	Fe ₃ O ₄	-	-	(Kandpal <i>et al.</i> , 2014)
XXXV	-	Mg-Al-LDH	2,3,4	-	(Kanezaki, 1998)
XXXVI	Co- precipitation Anion exchange	Mg-Al-LDH Zn-Al-LDH	2 -	Acrylate, methacrylate, 2-acrylamido-2methyl-1-propanesulfonate,	(Kovanda <i>et al.</i> , 2009)

	Rehydration		-	4-vinylbenzoate,4,4'-azobis(4-cyanopentanoate)	
XXXVII	Co-precipitation	MnO ₂ nanoparticles	-	-	(Kumar & Sangwan, 2013)
XXXVIII	Co-precipitation Anion exchange with solvothermal treatment	Mg-Al-LDH	-	Aliphatic α -dicarboxylic acid	(Lee <i>et al.</i> , 2005)
XXXIX	Ion-exchange	Zn-Al-LDH	-	5-benzotriazolyl-4-hydroxy-3-sec butylbenzeneulfonic acid	(Li <i>et al.</i> , 2006)
XL	Anion-exchange	Zn-Ti-LDH	-	p-aminobenzoic acid (PABA)	(Xu <i>et al.</i> , 2015)
XLI	Co-precipitation	Ni-Zn-LHS	0.5	Dodecyl dimethyl carboxybetaine, dodecyl dimethyl sulfobetaine, N-dodecyl- β -aminopropionate	(Liu <i>et al.</i> , 2015)
XLII	Co-precipitation	Zn-Al-LDH	3	Anthranilate	(Mamat <i>et al.</i> , 2013)
XLIII	Co-precipitation	Zn-Al-LDH	-	Anionic blue dyes	(Marangoni <i>et al.</i> , 2009)
XLIV	Direct method	Zinc layered Hydroxide	-	Cinnamate	(Megat <i>et al.</i> , 2013)
XLV	Co-precipitation method with colloidal sol immobilization method	Mg-Zn-Al to immobilize Au-Pd nanoparticles	-	Orange II from water	(Sobhana <i>et al.</i> , 2016)
XLVI	Co-precipitation method + Hydrothermal method	Layered hydroxyl double salts	-	Thiophene monomers	(Tronto <i>et al.</i> , 2006)
XLVII	Sonochemical method	Zinc nitrate hexahydrate	-	Hexamethylenetetramine	(Pholnak <i>et al.</i> , 2011)

V. RELEASED STUDIES

Nanotechnology has overcome the barrier in medication, since it can encapsulate drugs and control delivery with the highest advantages. Various medicinal drugs have been used to investigate the suitability and enhancement especially on drug release properties when being encapsulated in between the layered matrix. According to Lee *et al.* (2015), the control release properties in nanomedicines were studied because it able to act as the dosage controller of drug in human blood within the therapeutic window. Thus far, commercial drugs available in the industry right now could not serve this purpose. High dosage of drug need to be introduced for the drugs to achieve minimum target of its concentration effectiveness fluctuations. Thus, repetitive

exposure to the drugs would be needed to achieve this objective, which than could cause harmful side effects towards the patients. Under this section, the intercalated drugs release behaviour will be further discussed.

Barahuie *et al.*, (2014) have investigated the intercalation of chlorogenic acid into the Zn/Al-LDH-NO₃ via co-precipitation and ion exchange methods. The release of the chlorogenate in between the LDH host was slower compared to the physical mixture, which then indicated the slow release of the chlorogenate from the LDH matrix. Nevertheless, the effects of pH could disturb the release mechanism of the anions from the LDH interlayer. At pH 4.8, it showed a rapid release during the first 240 minutes for both nanocomposites: this explains the release of the chlorogenate due to partial dissolution of Zn/Al-LDH host. Then a slow

release was observed within 1350 minutes and 1435 minutes indicating the ion exchange process between the buffer solution and the chlorogenate ions in between the LDH layer. Nonetheless, it should be noted that much slower rate of release was observed when using buffer solution at pH 7.4. This observation could deduce that the release of chlorogenate ions from the interlayer host was much more stable when used under pH 7.4 conditions.

Cursino *et al.*, (2010) have studied the sustainable release of antihypertensive drugs that have been intercalated in between layered double hydroxides by using both anion exchange and co-precipitation methods. The release behavior of these intercalated antihypertensive drugs were studied under buffer solution of pH 4.25 and pH 7.45. They stated that the release behavior is fast at pH 4.25 and pH 7.45 at first rate.

This happens because in acidic conditions, the destruction of LDH and drugs caused the burst affect in the first few hours of release. The destruction caused the solution to become more acidic due to the release of hydroxyl from the destruction of the layered double hydroxide, leading to a much faster rate in the release of the hypertensive drugs. Hence, the less acidic the buffer solution used, the less the destruction of nanocomposites, and thus a much slower rate, and higher time to retain it inside the body without any drug concentration fluctuations.

The release properties of methotrexate MTX-Zn/Al-LDH shows that the release was fast in the initial stage which then proceeded with the slow release of the MTX anion from the host layer (Wang *et al.*, 2016). The mechanism of the drug release was understood to be in two ways which are ion exchange process and destruction of LDH layer in the buffer solution. Besides that, the release mechanism could also be controlled by any of these ideas. In learning and understanding the release behaviour of the MTX/LDH hybrids, these three steps were taken into consideration; which are first order equation, Rigter Peppas (R-P) equation and the parabolic diffusion.

In the first order equation, the release process was described based on the ability to exchange ions and the disaggregation step, i.e., the dissolution rate depended on the composition of the drug being loaded in between the LDH host interlayer regions. The R-P were then being used to

explain drug diffusion and dissolution of LDH layer. These steps were discussed on the value of the n ; when

1. $n < 0.45$ due to drug diffusion control (ion-exchange process)
2. $n > 0.89$ explain the dissolution of LDH, and
3. $0.45 < n < 0.89$ is the combination of drug diffusion and the dissolution of LDH matrix.

Meanwhile, parabolic diffusion stated that the release processes were controlled by the external surface or edge diffusion process.

Kinetic release was also used to study the release behavior of the anions loaded in between LDH host matrix. According to Gao *et al.* (2014), the release kinetic of vitamin C was studied using different kind of kinetic release model. Nonetheless, Avrami-Erofe'ev model were more suitable in explaining the release of vitamin C from the interlayer regions of LDH. These models explained that when the value of n was near to 0 or 1, instantaneous nucleation takes place. Nevertheless, the value of n for the phosphate buffer solution used in their study were 0.9 thus explaining ion exchanging process of the buffer solution and the interlayer anions. The abundant amount and big in sizes of the phosphate anions causes it to moves along the edges of LDH and force the vitamin C to move out of the LDH host matrices. These phenomena are known as the nucleation control, by which the phosphate buffer anions control vitamin C anions.

Ashwanikumar *et al.*, (2014) stated that the release behaviour of the 5-Fu and MTX followed the Peppas model kinetic study when both anions are being intercalated in the nanomicelles interlayer region. Although the release of MTX was much slower compared to 5-Fu, they both showed a slower release rate compared to the naked anion, which then exhibits properties of controlled release and can work as a dual drug delivery system. Table 4 shows other types of kinetic model studies of the LDH-organic anions used by other researcher.

Technically, the release of the organic anions from the LDH matrix is basically being manipulated by the pH of the buffer solutions and the exchangeable ability of the counter anion in between the LDH matrix. The pH of buffer solution that acts as the simulated condition or environment could affect the release mechanism of the anions out from the LDH matrix. Acidic pH solution causes dissolution of LDH matrix, while

alkaline solution affects the release mechanism of anions. Besides that, the ability to exchange ions in and out of LDH matrix depends on the atomic size and charges of the anion.

Table 4 Example of Kinetic Model Studies of the LDH-Organic anions.

Nanocomposites	Name of Model	Equations	References
MTX-Zn/Al-LDH	I First order	$\lg(1-M_0/M_t) = -k_B t^{0.65}$	(Wang et al., 2016)
	Riger-Peppas (R-P)	$M_0/M_t = k_m t^a$	
VC-Ca/Al-LDH	Parabolic diffusion	$(M_0/M_t)/t = k_p t^{-0.5} + b$	(Marto et al., 2016)
	II Avrami-Erofe'ev	$\ln(-\ln(C_t/C_0)) = n \ln(k_d) + n \ln(t-T_0)$	
	Elovich	$1-C_t/C_0 = a \ln(t-t_0) + b$	
	Freundlich	$\ln(1-C_t/C_0) = \ln(k_d) + a \ln(t-t_0)$	
5-FU-PBP-MTX nanomicelles	III Riger-Peppas	$M_0/M_t = k_m t^a$	(Ashwanikumar et al., 2014)
	Parabolic diffusion	$(1-C_t/C_0)/t = k_d(t-t_0)^{-0.5} + a$	

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THP-Zeolite and THP-LDH	IV Zero order	$Q_t = Q_0 + K_0 t$	(Aimurofiq & Choiri, 2015; Dash et al., 2010)
	First order	$\log C = \log C_0 - K_1 t / 2.303$	
	Higuchi	$f_t = Q = A = \sqrt{D(2C-C_x)} C_x t$	
	Hixson-Crowel	$W_0^{1/3} - W_t^{1/3} = kt$	
	Quadratic	$M_t/M_\infty = Kt^n$	
	Peppas-Sahlin	-	
	Weibull	$M = M_0 [1 - e^{-\frac{(t-T)^b}{a}}]$	
Korsmeyer-Peppas	-		

VI. CONCLUSION

In general, the studies of the layered compound have been carried out due to its advantages, such as controlled release purposes, increases thermal stability of the organic anions due to the electrostatic bonding between the positive layered host and the negatively charge anion, and able to use in water treatment plant. A recent study also stated that the ability of layered host to encapsulate the bacteria. Thus, it shows that layered hosts providing a lot of advantages should be studied in other areas, such as biodiesel.

VII. ACKNOWLEDGEMENT

The authors want to thank the Fundamental Research Grant Scheme (FRGS/1/2016/STG01/UITM/02/4) for financial support. The gratitude also applies to Universiti Teknologi MARA (UiTM) and Nuclear Agency Malaysia for facilities that been provided.

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