Review:

Synthesis and Application of Zinc Layered Hydroxide: A Short Review

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Abstract: *Zinc Layered hydroxide (ZLH) is a layered material easily synthesized with a structure identical to brucite-like material. Due to the exchangeable anions in the interlayer compensating for the positive charge of a brucite-type layer, ZLH provides a wide application in many fields. This review focuses on the properties and method of synthesis of ZLH by giving an overview of intercalated guest anion in the interlayer of ZLH. The further discussion involved the application of intercalated guest anion in zinc layered hydroxide layer and its properties as a sensitizer, controlled release biomedical, and agriculture to provide the scientific community for research and development by giving current findings. This brief review also presents the success of anion intercalation for controlled release along with the kinetic model involved, which increases the bioavailability and effectiveness of the nanocomposite on its target. It shows the development of research on ZLH nanocomposites toward the sustainability of human life and the environment. This study implies that it is a source of knowledge for researchers about zinc-layered hydroxide materials involving synthesis methods and their application to produce more beneficial nanomaterials.*

Keywords: *zinc layered hydroxide; synthesis; intercalation; nanocomposite*

■ INTRODUCTION

Layered metal hydroxides (LMHs) are layered materials, including layered hydroxide salts (LHSs, $M_x^{II}(OH)_{2x-my}A_y^{m-}\cdot nH_2O$) and layered double hydroxides (LDHs, $M_{1-x}^{II}M'^{III}_x(OH)_2(A^{m-})_{x/m}\cdot nH_2O$), where typically M^{II} = Mg, Fe, Co, Ni, and Zn, M'^{III} = Al, Cr, Fe, Co, and In, A^{m-} = Cl^-, NO^{3-}, SO_4^{2-}, and CO_3^{2-} [1]. LMH consists of two parts: an inorganic layer, such as positively charged brucite, and exchangeable anions and water molecules in the interlayer, which has attracted attention due to its potential applications. Layered hydroxide salts, also known as layered single metal hydroxides (LSHs), which only consist of one metal on an inorganic layer, have shown a huge opportunity in industrial and environmental research nowadays [2]. Therefore, this article will briefly discuss the properties, method of synthesis, and application of one of the compounds of LSHs, namely zinc layered hydroxide (ZLH). This review aims to give a general overview of ZLH properties due to the variety of intercalated guest anion species between the interlayers of the nanocomposite. The synthesis method used in the intercalation process via guest anions is also listed in this article. This review also compiles and updates the application of the ZLH nanocomposite, focusing on ZLH as a sensitizer and controlled release formulation, along with the kinetic model in biomedical and agricultural applications. To our knowledge, no review articles have been published on the synthesis of ZLH using direct reaction, ion exchange, co-precipitation, and hydrothermal precipitation methods. Therefore, it is hoped that this review will update the current discovery of intercalated guest anion in zinc-layered hydroxide. The positive development of research in this field allows for various applications in the future, which increases progress in related fields.

■ PROPERTIES OF ZINC LAYERED HYDROXIDE

Zinc-layered hydroxide is one of the inorganic layered materials that has a layer structure similar to that of brucite ($Mg(OH)_2$) and correlates to anionic clay [3]. In brucite, Mg is octahedrally coordinated into six hydroxyl groups that share an edge to build infinitely large layers arranged along the basal direction [4]. Modifying the brucite structure may occur through isomorphic substitution of intra-layer cations or anions or interlayer water molecules for part of the hydroxide groups. In the latter case, the charge of the layer was balanced by the additional anion present in the second sphere. The slightly altered formula for these types of compounds called hydroxide salts (LHS) is generally the formula of $M^{2+}(OH)_{2-x}(A^{m-})_{x/m}\cdot nH_2O$ where M^{2+} is the metal cation (e. g. Mg^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}) while A^{m-} is the counterions in the interlayer space. Zinc-layered hydroxide (ZLH) is a layered hydroxide salt with the formula of $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$ [5].

The basic structure of ZLH consists of a brucite type where one-quarter of the octahedrally coordinated zinc ion sites is empty. The Zn atoms tetrahedral bonded to the layer through OH groups, forming the base of a tetrahedron. Besides, the coordinated water molecules were located at the apex of the tetrahedrons, and the nitrate groups occupied the interlayer space of ZLH [5]. The nitrate anions are surrounded by water molecules, which are not directly bonded to zinc atoms [6]. Nitrate, sulfate, phosphate, and chloride anions are also used to synthesize ZLH [7]. The lamellar structure is positively charged; therefore, the counter anions and water molecules were intercalated in the lamellar space to neutralize the layer charge [8-9].

In contrast to LDH, hydroxide ions are removed from the structure instead of metal replacement and replaced by water molecules or other types of oxoanions, generating materials with anionic exchange capacity [10]. Besides that, the water molecules may also be incorporated into the interlayer region, culminating in enhanced stability [11]. The oxoanions are positioned in the second coordination sphere of the metal to stabilize the electrostatic charge or by the direct substitution by another single-charged anion [4,12-14]. Some active agents are occasionally charged with neutral and poorly soluble pesticides that are difficult to intercalate in the ZLH interlayer. Most literature focuses exclusively on anionic pesticides. For charge-neutral and poorly water-soluble pesticides, their intercalation usually depends on anionic surfactants in the gallery, which form a hydrophobic region [15-19]. The interlayer space of ZLH can adsorb targets such as pesticide molecules due to its hydrophobicity and accessibility.

Liu et al. [20] developed a new method for solubilizing chlorpyrifos (CPF) into the interlayer of zinc hydroxide nitrate (ZHN) intercalated with dodecyl benzene sulfonate (DBS). ZHN is modified with DBS to form a hydrophobic region in the ZHN–DBS gallery [20-21]. Liu et al. [20] also suggest that DBS is a tilt monolayer in the gallery when three oxygen atoms in the SO_3 group approach the ZHN layer. According to Demel et al. [22], the mechanism of synthesis of layered zinc hydroxide-dodecyl sulfate (LZH-DS) was described by an extra- and intra- lamellar space template model. The sodium dodecyl sulfate (SDS) bilayer is an extra-lamellar template in which electrostatic interactions occur between zinc atoms and sulfate groups. The insertion of alcohols that act as active agents into the layered sulfate arrangement was assisted by two possible interactions, and one of them is a hydrophobic interaction between the dodecyl chain of SDS and the alkyl chain of the alcohol. The other interaction is an ion-dipole interaction between the hydroxyl group of the alcohol and the sulfate group of SDS. Both interactions contribute to the stability and packed layered dodecyl sulfate arrangement. Therefore, it can conclude that long alkyl chain alcohols have enlarged the extra-lamellar templates. Meanwhile, short alkyl chain alcohols, such as ethanol and 1-propanol, are not successfully intercalated into the layered dodecyl sulfate arrangement. The small size and low stability of ethanol or 1-propanol with an extra-lamellar template will result in ethanol or 1-propanol being outside the extra-lamellar template resulting in encroachment of the adjoining extra-lamellar template.

The interaction of cationic and anionic surfactants will form neutral micelles that permit the anion to be intercalated in the interlayer of ZLH. Since there is an increased distance between the interlayers of the starting material, this method offers particular promise for incorporating large anions [23-25].

SYNTHESIS METHODS OF ZINC LAYERED HYDROXIDE

There are various synthesis methods have been used to synthesize ZLH nanocomposite, which an ion-exchange method [26-28], co-precipitation method [4,18-20], hydrothermal precipitation methods [12,29-30], and direct reaction method [31-33]. Above all, the direct reaction method is often chosen in preparing ZLH nanocomposites because various anions can be directly intercalated alternately between the hydroxylated sheets and increase the quantity of the synthesized material [26,31-34]. The ion exchange process is not involved in this method. The intercalation process of anions into ZLH only involves the direct incorporation of ZnO, which is used as a starting material [35-37]. The advantage of this method is that it is simpler, more environmentally friendly, and more economical because it involves fewer steps and fewer chemicals compared to other synthesis methods of ZLH [3]. The dissociation-deposition mechanism was used in the direct reaction method [35], which is composed of three stages, as shown in Eq. (1-3) [3,35,38-39]:

Stage 1: The process on the surface of solid particles: hydrolysis of ZnO in water to form $Zn(OH)_2$.

$$ZnO + H_2O \rightleftharpoons Zn(OH)_2 \quad (1)$$

Stage 2: Dissociation of $Zn(OH)_2$ layer to form Zn^{2+} ions and OH ions. $Zn(OH)_2$ layer dissolves more easily than ZnO in acid.

$$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH \quad (2)$$

Stage 3: Formation of nanocomposites resulting from the reaction of Zn^{2+} ions with hydroxyl, H_2O, and guest anions (X^-).

$$Zn^{2+} + 2OH^- + X^- + H_2O \rightleftharpoons Zn^{2+}(OH)_{2-x}(X^-)_x \cdot nH_2O \quad (3)$$

The co-precipitation method involves slowly adding a cationic salt solution in a known molar ratio to an aqueous solution, followed by the simultaneous acquisition of an alkaline solution. The pH value is controlled to produce a mixed hydroxide precipitate. In contrast, ion exchange is a method that is applied for the intercalation of ZLHs with anions of different natures. Diffusion of anions into the interlayer is the rate-determining step in the reaction; therefore, the exchange reaction is performed by alternating stirring the ZLH precursor in an excess solution. Ultrasound methods are encouraged to speed up the exchange reaction [28,38,40-42]. Based on Hashim et al. [33], ZLH nanocomposite prepared by the co-precipitation method showed less thermal stability and crystallinity than ZLH nanocomposite synthesis using the ion exchange method.

Meanwhile, the BET analysis found that the co-precipitation method produced a higher surface area nanocomposite than the ion exchange method. The ion exchange method is useful when the co-precipitation method is inapplicable due to unstable metal cations or anions in an alkaline solution or when intercalated with a bigger size anion [43]. Hydrothermal and microwave treatments are another method used to synthesize ZLH nanocomposite. This method has been used to improve the crystallinity and other properties of ZLHs [12,29,44-46]. Compared to other methods, the advantage of the hydrothermal synthesis method for ZLH nanocomposite is that it can produce unstable nanomaterials at high temperatures. In this method, ZLH nanocomposites can form in a wide temperature range, from room to very high temperatures. Apart from that, the morphology of the nanocomposite can be controlled by controlling the vapor pressure of the main composition in the reaction [30]. Fig. 1 shows the schematic structure of ZLH nanocomposite synthesis using the four methods discussed above. The list of methods and intercalated anions has been summarized in Table 1.

APPLICATION OF ZINC-LAYERED HYDROXIDE

The potential for ZLH inorganic hybridization has been extensively explored and studied recently. The ability to tune a material's performance involves tailoring the material's physicochemical properties to lead to the application, elaboration, and relating of novel concepts; therefore, it will open the door to new ideas for a new world in materials science. For example, the rapid development of industry has led to increased waste disposal, such as solid waste or wastewater containing heavy metals [66-68]. The ZLH-based material nanocomposites have been reported to contribute to wastewater treatment, especially in removing heavy metals, through their ability to absorb them [66]. It has the advantages of good selectivity, high efficiency, high adsorption capacity, and no secondary pollution, as well as being a low-cost material [69,72]. ZLH nanocomposite material is one of the ultrafine and tiny powders with a diameter below 100 nm. The nanometer scale particle size of the ZLH material will cause changes in the surface characteristics and crystal structure due to quantum effects, surface effects, and interface effects [71,73-75]. This condition causes the particles to become smaller while the particle surface area, surface energy, surface binding energy, and the number of surface atoms

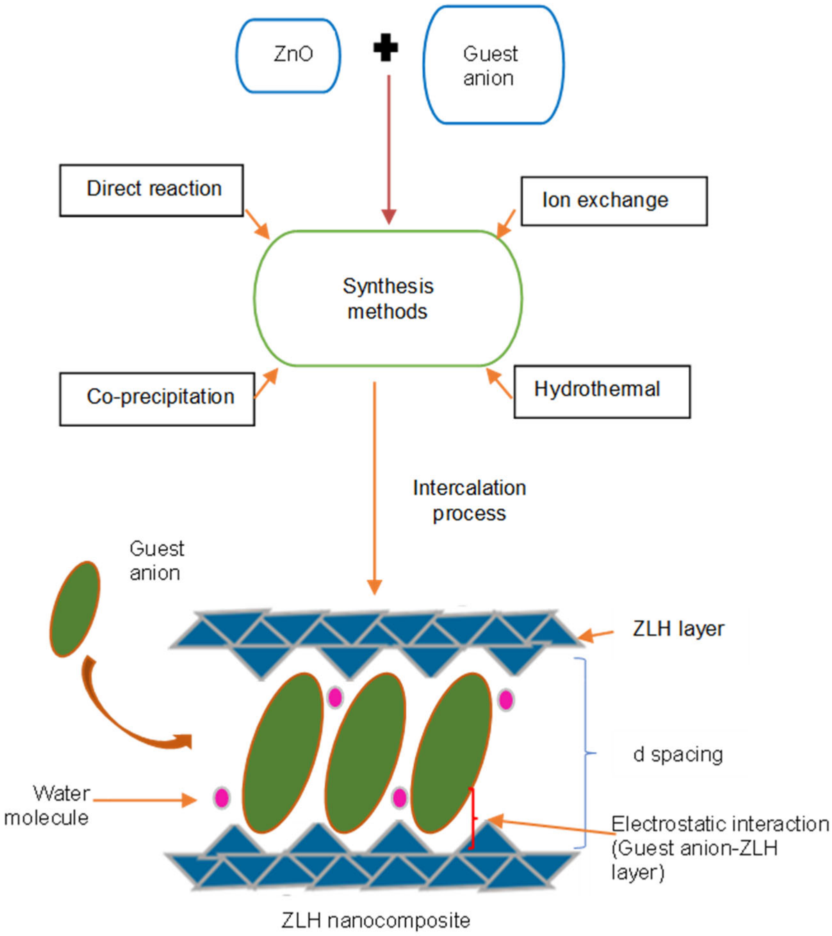

Fig 1. Schematic view ZLH nanocomposite general structure with anions intercalated in the interlayer structure

Table 1. List of methods and intercalated anions that have been intercalated into the interlayer of ZLH

Methods	Guest anions	Ref.
Co-precipitation	Valeric acid	[47]
	Oxalatooxoniobate complex ion	[4]
	3(4-methoxyphenyl) propionic acid	[42]
	Indigo carmine ion	[48]
	Sodium salicylate ion	[20]
	Sodium heptanoate ion	[49]
	Porphyrin ion	[50]
	Methyl orange, orange II ion	[51]
	Aspartic acid	[52]
	Nitrate, phosphate anions	[53]
	Triarylmethane dyes	[18]
	4-aminobenzoic acid	[54]
Direct reaction	Chloroacetic acid	[33]
	3-(4-methoxyphenyl) propionic acid	[32]
	2-(2,4-dichlorophenoxy) butyric acid	[55]
	4-chloro-2-methylphenoxy acetic acid	[56]
	Hippuric acid	[36]
	Cinnamic acid	[3]
	Para-aminosalicylic acid	[57]
	Protocatechuate ion	[38]
	Salicylic acid	[39]
	Cinnamic acid	[58]
	Ferulic acid	[59]
Ion exchange	3-(4-methoxyphenyl)propionic acid	[42]
	Hippuric acid	[36]
	Caffeic acid	[27]
	Ciprofloxacin ion	[60]
	2-(2,4-dichlorophenoxy)butyric acid	[55]
	2-aminobenzoate	[61]
	2-Methyl-4-chlorophenoxyacetic acid	[34]
	Curcumin anion	[62]
	Diclofenac ion	[5]
	Molybdate anion	[63]
	β-glucan ion	[64]
	Amoxicillin trihydrate	[65]
Hydrothermal precipitation	Hexamethylenetetramine	[12]
	2-Methyl-4-chlorophenoxyacetic acid	[34]

increase rapidly, surface atoms lack contiguousness, leading to unsaturated properties. Indirectly, it will stabilize and combine with other atoms [76-77]. It is also supported by the strong adsorption capacity of this material due to the basic structure of nanomaterials that can reach equilibrium quickly. Therefore, ZLH nanocomposites have been used to isolate and enrich ideal materials used to analyze trace elements [70]. Some researchers have conducted studies to evaluate the performance of ZLH in removing heavy metals from wastewater, such as de Oliveira and Wypych [66]. They used zinc hydroxide nitrate layered (ZnHN) to determine the effectiveness of ZnHN on the removal of chromate ions from the solution. The results show that the retention capacity of ZnHN is higher compared to the theoretical value because the presence of CrO_4^{2-} acts to destroy the structure of the material. The chromate removal capacity in the experiment showed a value of 210.1 mg CrO_4^{2-}/g material.

XRD analysis before and after chromate removal of ZnHN shows that the layered material has changed into a new compound, mainly amorphous. The removal of heavy metals from wastewater using ZLH was also done by Jia et al. [70]. Mine wastewater containing Pb^{2+} was treated using nanometer-layered zinc hydroxide, involving several parameters such as pH, temperature, coexisting ions, initial concentration, and time on the performance of the layered material. The results show that the metal ion removal efficiency is higher than 85%, while the concentration of Pb^{2+} in the permeation liquid shows permeation lower than 0.5 mg/L. The pH results show that the pH value influences the adsorption rate, and the temperature has the maximum impact on the adsorption of Pb^{2+} ions. Studies show that the adsorption of nanoparticles is due to nanoparticles that have surface hydroxyl groups. Hydroxyl groups on the surface of nanoparticles allow bonds to be formed with various cations and fulfill the characteristics of ion or organic substance adsorbents. In addition, the large surface area of the nanoparticles also produces unsaturated bonds, which in turn cause the formation of charges on the surface of the nanoparticles. Therefore, ions of different charges are attracted to the surface of the substrate to balance its surface charge [78]. Rhodamine B is one of the water-tracer fluorescent substances widely used as a dye in the textile industry and a substance in the food industry. Studies show that rhodamine B is a carcinogenic substance for humans and animals. Prolonged exposure to this substance can irritate the eyes, skin, and respiratory tract [79-82].

Thao et al. [83] have developed the reaction of zinc hydroxide-layered Ti-doped nanomaterials as a catalyst for decomposing rhodamine B in water under visible light irradiation. The synthesis involves the substitution of Zn^{2+} ions for Ti^{4+} on the ZLH layer to form a heterogeneous catalyst material containing Ti, which gives variation to the solid composition and creates a lot of OH on the hydroxide layer. Zn-based modification as a catalyst material with photocatalytic properties broadens the potential of ZLH to accommodate the difference in cation size and valence for guest anion intercalation in the interlayer domain.

■ SENSITIZERS

Organic sensitizers with strong UV absorption properties have frequently been intercalated into the interlayer of ZLH to convert light energy into excited states [3,23,84]. It is reasonable that the final properties of inorganic-organic functional hybrids depend on the interaction between the host layer, which is an inorganic matrix, and the guest anions that cause interaction and influence the distribution, orientation, the electronic properties of the guest anions [50,85] and control the chemical composition, mesomorphology, and micromorphology of layered material [86]. Much research has been done to study these hybrid materials' spectral, photochemical, and photophysical properties due to the stability and interlayer protection of the inorganic host structure [87-90]. At the same time, the chromophore species has an optical function such as color [91], thermochromicity [92], luminescence [93-94], formation of singlet oxygen [95], nonlinear optical properties, photo-oxidation [96], or UV absorption [97]. This study is important for developing layered materials for energy storage and conversion, photocatalysis, sunscreens, and even devices for sensing or photochemistry. Demel et al. [50] have reported that a solid-state $O_2(1\ \Delta g)$ sensor was developed based on an anionic porphyrin-intercalated layered zinc hydroxide (LZH) hybrid. The newly discovered layered material has an inorganic host layer that provides stability and protection to photo-functional guest species. From the results, both new layered materials, LZH-PdTPPS and LZH-PdTPPC, show strong signals of photo-produced $O_2(1\ \Delta g)$. The obtained $O_2(1\ \Delta g)$ luminescence intensity decays monoexponentially, which gives an effective $O_2(1\ \Delta g)$ lifetime of 30 and 41 μs, respectively, in an oxygen atmosphere for LZH-PdTPPS and LZH-

PdTPPC. The hybrid material shows good potential as an O_2(1 Δg) producer and extends the life of O_2(1 Δg). It shows that the host LZH is a potential material that can be used as an ion porphyrin carrier.

■ CONTROLLED RELEASE FORMULATION IN BIOMEDICAL

A slow-release drug delivery system is one example of applying ZLH materials in biomedicine. Most drugs are difficult to dissolve in water, making delivering the dose to the target area challenging to achieve and less effective. In addition to that, there are unwanted side effects [98-101]. Therefore, the drug delivery system using ZLH material is one of the alternative methods as a drug delivery vector that effectively controls the release rate of drug molecules to maintain drug molecules *in vivo* proportional to time. [57,102-105]. Table 2 shows the biomolecules that have been intercalated into the interlayer of ZLH and the kinetic model of the respective controlled release system.

A kinetic model has been used to explain the process that occurs to study the release behavior of substances in a specific medium. It involves mathematical formulas to determine the quantitative analysis value obtained for the release rate and to explain the process involved easily. The chosen mathematical model will help optimize therapeutic device design by informing the effectiveness of different release models [2,106-109]. Furthermore, the kinetic model output data can be used for several approaches in sustained release or stimulus-responsive systems [109]. Engineers, pharmacists, and researchers are pouring out ideas together to produce new and potentially efficient products in various fields by using controlled-release formulations. Mathematical modeling is helpful in proving the prediction of the kinetic release model before the product is used or implemented on the actual target, which involves the measurement of certain physical parameters, such as drug diffusion coefficients, as well as the use of models that will be selected based on experimental output data [110-111]. Therefore, the mathematical modeling developed needs to be understood by focusing on all the factors that affect the kinetics and has a very important value in optimizing the mathematical formulation used [2,113-114]. The model can be simply a mathematical metaphor for many aspects of reality involved in identifying the set of phenomena governing release kinetics [111,114-116]. UV radiation consists of UV A, B, and C in the electromagnetic spectrum's wavelength range between 200–400 nm. The ozone layer absorbs UV B and UV C radiation, while UV A radiation that reaches the ground will affect human health. Recently, sunscreen formulations made from organic and inorganic compounds have been widely produced to prevent or minimize the effects of being exposed to UV rays [25,117]. Mohsin et al. [3] have intercalated cinnamate acid (CA), which is an efficient UV A and UV B absorber anion, into the interlayer of ZLH. The result shows that

Table 2. List of active agents in the interlayer of ZLH nanocomposite and kinetic model in biomedical applications

Active agent	Kinetic model	Researcher
Cinnamate ion	Pseudo-second order	[3]
Indole-3-acetic acid	Modified Freundlich model	[102]
Hippuric acid	First-order: pH 7.4 Pseudo-second-order: Na_2CO_3 Bhaskar equation: pH 4.8	[36]
Ciprofloxacin ion	Modified Freundlich model	[60]
Ellagic acid	Pseudo-second-order	[35]
4-amino salicylic acid	Pseudo-second-order	[57]
Protocatechuic acid	Pseudo-second-order	[38]
Cetirizine ion	Pseudo-second-order	[103]
Gallic acid	Elovich and Freundlich models	[2]
Ferulic ion	Pseudo-second-order	[59]

the UV–Vis spectrum of the intercalated material has excellent UV A and UV B absorption abilities. The retention of the cinnamate ion in the interlayer of ZLH in selected media shows slow release over an extended period for sunscreen usage. The MTT assay on human dermal 47 fibroblasts (HDF) cells for intercalated compounds shows the cytotoxicity of ZLH-CA to be concentration-dependent overall and less toxic than its precursor, ZnO. Biswick et al. [27] also intercalate an active agent, caffeic acid, into ZLH nanocomposite as sunscreen material. Caffeic acid was chosen due to its high potential as a material for cosmetic applications and its low stability against UV and oxygen irradiation [117-119]. The finding of slow release for caffeic acid-zinc basic salt (CA-ZBS) shows a fast release in the first 20 min, which is due to small amounts of anions adsorbed on the surface of the inorganic matrix and to anions intercalated close to the edges of the crystals, followed by slow release with time. The slow release of the caffeic ion from the inorganic matrix is due to the strong covalent bonding interaction between the carboxylate group of the anions and the matrix cation. This observation is supported by the FTIR spectrum of the CA-ZBS nanocomposite, where the $\Delta\nu$ value for the caffeate anion in sodium caffeate is higher than that of CA-ZBS. A novel nanocomposite with the guest molecule protocatechuic acid that acts as an anticancer agent has been synthesized by Barahuie et al. [38]. The cytotoxicity test of the nanocomposite for all cancer cells showed an increase compared to the free form of the guest anion. *In vitro* tests of this nanocomposite show that it is an effective anticancer agent, suitable for use as a controlled-release formulation of protocatechuic acid, and has good potential as a chemotherapeutic drug for human cancer [120-122]. A pseudo-second-order kinetic model governed the release study of protocatechuic acid from the interlayer of ZLH nanocomposite into the phosphate-buffered saline solution. Similar research was done by Saifullah et al. [123], who found that anti-tuberculosis drugs in zinc hydroxide-4-aminosalicylate (4-ASA-ZLH) nanocomposite gave minimal drug side effects and protected the drug from enzymatic degradation. It also increases the therapeutic efficacy by delivering the drug at the target site. The release rate of 4-amino salicylic acid from nanocomposite depends on pH, and the release mechanism of 4-amino salicylic acid occurs through both the dissolution of ZLH layers and diffusion [124]. Abdul Latip et al. [60] have also used PBS at pH 7.4 as a medium for the controlled release of the ciprofloxacin (CFX) ion. The release study of CFX release data was fitted with the Freundlich model, followed by the parabolic diffusion model. Sustained release of CFX from the interlayer of ZLH increases the antiproliferative effect. It is due to the strong interaction that occurs between ZLH and CFX, which will facilitate cell uptake and protect guest ions from degradation, causing a slow release of CFX and "killing" A549 cells. The unique properties of ZLH have revolutionized it as a nano vehicle in medical science, especially in drug delivery. ZLH, with drug intercalation between the spaces in its layer, has improved chemical and thermal stability, cell targeting, drug solubility, reduced side effects, and increased drug resistance to disease, further increasing the drug's plasma half-life [38]. Overall, layered zinc hydroxide shows effective potential as a nanocarrier for drugs with efficient delivery and improving the therapeutic efficiency of drugs in treating different diseases.

■ CONTROLLED RELEASE FORMULATION IN AGRICULTURE

Special attention has also been focused on controlled-release formulations of pesticides using layered materials in agriculture. There are many new nanocomposites involving pesticides that have been intercalated into interlayer of ZLH such as cetyltrimethylammonium bromide [125], chloroacetic acid [33], valeric acid [47], propoxur [41], isoprocarb [126], thiacloprid [28], 2-methyl-4-chlorophenoxyacetic acid [34], 2-(2,4-dichlorophenoxy) butyric acid [55], and 4-chlorophenoxyacetic acid [127]. The successful intercalation process of pesticides into the interlayer of ZLH was due to positively charged ZLH layers that promote the attraction force between the guest anion pesticides and the host. Most researchers only use one type of guest anion in the intercalation process into the ZLH interlayer. However, Hussein et al. [128] have successfully intercalated two different guest anions simultaneously into the ZLH interlayer, namely 4-(2,4-dichlorophenoxy) butyrate (DPBA) and 2-(3-chlorophenoxy) propionate (CPPA), using direct reaction method. The release study for both anions showed that the release rate depended on the guest anion size and the interaction between the hydroxide layer and CPPA, DPBA anions. This finding indicates that zinc-layered hydroxide is a versatile use material that can simultaneously intercalate more than one guest anion. ZLH, as a controlled release agent, acts as a host and delivery system that protects the active agent from degradation and increases the stability of the chemical while also preventing loss through leaching or evaporation, thereby increasing the duration of activity of the active agent.

Furthermore, ZLH also prevents active agents from being directly exposed to humans or the environment, which will reduce application and promote a safer environment [47]. To this end, controlled-release formulations encourage the effective use of agrochemical herbicides and produce new products that can be used in the agricultural sector [2,129]. Therefore, it can limit the amount available for unwanted processes and reduce the presence of agricultural chemicals in soil and surface water [32]. The use of mathematical modeling is beneficial in cases where the prediction of release kinetics is controlled before it is realized in a real system [130-131]. It directly collects measurements of important physical parameters, such as diffusion coefficients, and model matching to experimental output data. Therefore, the

Table 3. List of pesticide anions that intercalated into the interlayer of ZLH and its kinetic model

Pesticides	Kinetic models	Researcher
2,4-dichlorophenoxy acetic acid	Pseudo-second-order	[31]
Valeric acid	Pseudo-second-order	[47]
Hexenoic acid	Pseudo-second-order	[135]
Cloprop	Parabolic diffusion	[32]
4-chlorophenoxyacetic acid	Pseudo-second-order	[127]
Chlorpyrifos	pseudo-second-order (ZHN–DBS–CPF) parabolic diffusion (ZHN–TX-10–CPF)	[20]
Cetyltrimethylammonium bromide		[125]
Chloroacetic acid		[33]
3-(4-methoxyphenyl) propionic acid	Pseudo-second-order (phosphate medium) The first order (sulfate and chloride medium)	[32]
(2-(2,4-dichlorophenoxy)butyric acid		[55]
4-(2,4-dichlorophenoxy) butyric acid and 2-(3-chlorophenoxy) propionic acid	Pseudo-second-order	[128]
4-chlorophenoxy acetic acid	Pseudo-second-order	[127]
Nitrate anion Phosphate anion	Pseudo-second-order	[53]
Isoprocarb	The first order (phosphate solution) Pseudo-second order (sulfate and chloride solutions)	[126]
Thiacloprid	First-order kinetics (phosphate solution) Parabolic diffusion kinetics (sodium sulfate and sodium chloride solutions)	[28]
Imidacloprid	Pseudo-second-order	[136]
Bispyribac	Pseudo-second-order (phosphate and sulfate solutions) Parabolic diffusion (chloride solutions)	[137]
Fluazinam	Pseudo-second-order	[138]

mathematical modeling developed needs to be understood to see the factors that influence the kinetics of pesticide release [132-134]. It has important value in optimizing the formulation process. The list of pesticides intercalated into ZLH and its kinetic model are presented in Table 3.

■ CONCLUSION

The zinc layered hydroxide intercalated with anion can be synthesized using four methods such as co-precipitation, direct reaction, ion exchange, and hydrothermal. Each method is chosen due to the difficulty of the intercalation process. Among them, the co-precipitation method was found to be the most popular choice to be used due to the simple and lower cost of synthesizing ZLH nanocomposite. This intercalated nanocomposite has shown great potential as a sensitizer due to the stabilization and protection layer, which gives effective life to the guest anion. While the controlled release formulation of ZLH nanocomposite for biomedical and agriculture enables it to produce material that has better efficacy and is safe for humans and the environment. It can also reduce overall costs by eliminating the time and cost of repeated and redundant applications. Therefore, knowledge and awareness about the application of nanocomposites in agriculture and biomedicine need to be expanded to fully utilize this technology fully, thereby increasing the income of related sectors. This knowledge will indirectly also help researchers diversify ZLH nanocomposite applications in the future.

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■ AUTHOR CONTRIBUTIONS

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