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Layered hydroxide anion exchanger and their applications related to pesticides: a brief review

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Layered double hydroxides and layered hydroxide salts have generated enormous excitement in the inorganic field due to their potential to act as versatile host materials in fabricating novel host–guest layered materials. The ability of the layered hydroxide anion exchanger to be incorporated with a wide range of guest ions enable them to be exploited in various applications related to pesticides. This review sums up the different methods of preparing layered hydroxide anion exchanger, summarises the types of anion intercalated into these layered hydroxide anion exchanger based on their respective systems, and elucidates their potential applications in pesticide-related fields.

Keywords: Layered double hydroxides, Layered hydroxide salts, Hydrotalcite, Nanocomposites, Pesticides

Introduction

A pesticide is a chemical used to control, repel, attract or exterminate pests that are believed to be a threat, such as undesirable plants, insects, fungi, bacteria and viruses. Pesticides can be divided into several major classes, based on targeted pests: fungicides, bactericides, herbicides and insecticides.[1] Each type of pesticide is specifically used to manage different pests. Thus, the scope of application of a pesticide is not only limited to agricultural use, but also other fields including medical and pharmaceutical.

Before the Second World War, the common pesticides used were mainly composed of inorganic materials, including sulphur, lead, copper, arsenic, boron and mercury.[2] The modern chemical age of pesticide were initiated in 1939, with the discovery of insecticidal potential of dichlorodiphenyltrichloroethane.[3] This discovery lead to the development of a variety of other synthetic pesticides, which can be classified according to their chemical compounds, such as organophosphates, organochloride, carbamates, synthetic pyrethroids and inorganic pesticides.[4,5]

Organochloride pesticides are typically large molecules with a huge number of chlorine atoms bonded to their molecules.[6] Organophosphate pesticides are mostly contain a P=S, or thionate bond,[4] the carbamates pesticides contain N-substituted esters of carbamic acid, with general formula $R^1NH–CO–OR^2$ (R^1 and R^2 are aliphatic or aromatic moieties), meanwhile pesticides containing metallic elements or organometallic compound, such as arsenic trioxide, sodium arsenite, mercury sublimate, copper ammonium carbonate and mercury acetate were classified as inorganic pesticide.[4,5] Chlorinated hydrocarbons, for instance, dieldrin, chlordane and aldrin will gradually break down and remain in the environment for a long term, meanwhile organophosphates can only last in the environment in a short period of time.[1] Nevertheless, organophosphates pesticides, including malathion, diazinon and chlorpyrifos are highly toxic to mankind. Carbamate compounds, for example, carbaryl and aldicarb are pesticides that are very toxic to humans, whereas pyrethroids united the high toxicity to insects with low mammalian toxicity and significantly enhanced their insecticidal stability.[1]

Owing to different chemical composition, each class of pesticide may exhibit different physical and chemical properties. There are certain pesticides which may dissociate to form anionic pesticide, such as dicamba and various phenoxyherbicide, meanwhile some pesticide, such as chlorpyrifos remain as neutral charge pesticide, hence lead to different behaviour.[7] The properties and behaviour of inorganic pesticide may also not be similar compared to organic species, especially in terms of kinetics, absorption, distribution and excretion. Hence, their toxicology effect may particularly differ, except for those organic species that immediately metabolised to the inorganic form in the body.[4]

Although the application of pesticides in agriculture increases the productivity of harvested crops,[8] the widespread application of pesticides had a horrendous impact on the environment due to their ability to accumulate in soil and in surface and groundwater.[9] The application of high concentrations of pesticides to crops and unintentional release of pesticide residues via biodegradation, chemical degradation,

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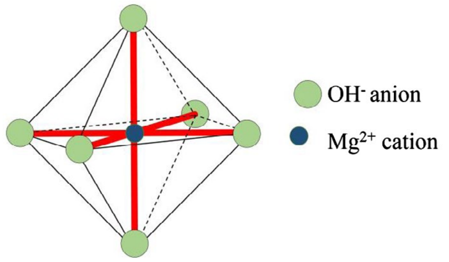
surface runoff and evaporation seems to worsen these polluted environments.[10] Untreated wastewater commonly contains various pesticide residues which are dangerous and toxic to living organisms. Therefore, the continuous use of pesticides may lead to various consequences such as air pollution, water contamination and extinction of endangered species.

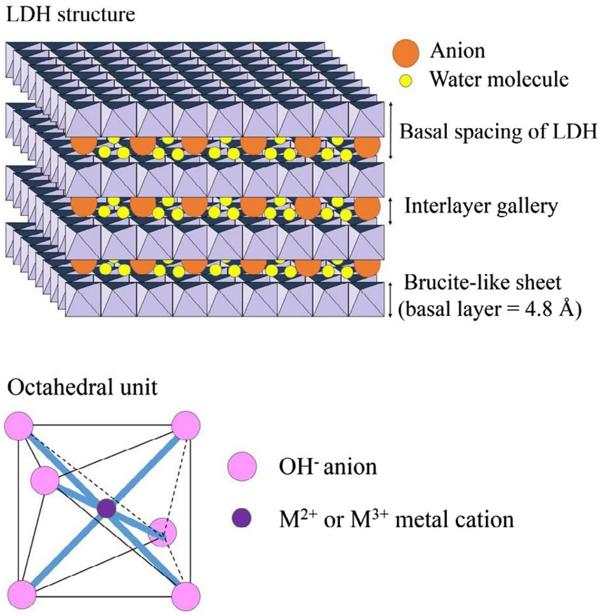
An adsorption properties own by the layered hydroxide anion exchanger; a properties influenced by the number of sites available, porosity and specific surface area of adsorbents can be employed to remove these pollutants from contaminated wastewater.[11] Hence, layered hydroxide anion exchanger, which also exhibit great compatibility with soils and good anion-exchange capacity, were introduced to alleviate the environmental issues which have arisen.[12] The layered hydroxide anion exchanger can be categorised into layered double hydroxides (LDHs) and layered hydroxide salts (LHSs),[13] which are both derived from the mineral brucite ($Mg(OH)_2$).[14]

Previous studies have demonstrated the potential of layered hydroxide anion exchanger to be modified and used as sensors[15] for monitoring environmental pollution levels, or as adsorbents[7,8] and photocatalysts[16] to treat contaminated water. In regard to another field, layered hydroxide anion exchanger has also been reported used in the manufacture of antimicrobial ceramic materials[17] and to enhance the bactericidal performance of drugs.[18]

In this feature article, the use of layered hydroxide anion exchanger in pesticide-related applications is summarised. This review describes the preparation methods of LDHs and LHSs, summarises the types of anion intercalated into layered hydroxide anion exchanger based on their respective systems and elucidates the potential applications of these layered hydroxide anion exchanger in pesticide-related fields.



1 Octahedral unit of brucite, $Mg(OH)_2$



2 Schematic representation of LDH structures

Composition and properties of layered hydroxide anion exchanger

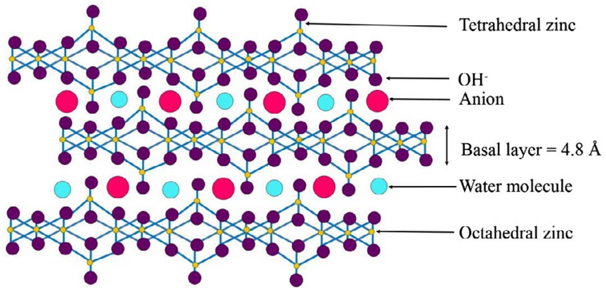
Layered double hydroxides

LDHs, which are also known as hydrotalcite-like systems, are modifications of the brucite-like ($Mg(OH)_2$) structure. The brucite structure are composed of divalent cations, Mg^{2+} bonded octahedrally by OH–, which are located in the vertices (Fig. 1).[14] The brucite-like structure can undergo isomorphic substitution of cations, when the divalent metallic cation in the structure were partially replaced with trivalent metallic cations, thus generates an excess of charges in the layer.[19] The excess positive charges will be counterbalanced by the interlayer anions. This whole compositional changes resulting the formation of LDHs.[14] The LDHs structure was illustrated in Fig. 2. LDHs may consist of two or more different types of metal cation.[20] The exchangeable anions which are introduced between the layers assist in sustaining the net positive charge of the layers.[21] Generally, LDHs also comprise a great amount of water and hydrogen bonded to the hydroxide layers and/or to the interlayer anions.[20] The general chemical formula of LDHs can be stated as $[M^{2+}_{(1-x)} L^{3+}_{x} (OH)_2]^{x+} A^{m-}_{x/m} \cdot nH_20$, where $M^{2+}$and L^{3+} are divalent and trivalent metal cations, respectively, while A is an anion.[22] The ratio of the divalent and trivalent cations can be varied to control the charge density and the anion-exchange capacity of the particular LDH.[23]

LDHs have attracted great attention compared to other layered compounds due to their amazing properties such as high specific surface area, great anion-exchange capability, excellent biomedical properties, chemical inertness, null toxicity and memory effect properties.[24] LDHs, which are basic materials, tend to produce mixed oxides as they undergo thermal decomposition. Incredibly, these mixed oxides will exhibit greater basicity than the original form. On top of that, the intercalation of acidic anions leads to the occurrence of the memory effect, the capability of a compound to regain its previous layered structure, when the mixed oxide is put in a solution containing anions.[25] They are also naturally plentiful, readily manufactured at industrial scale and more economical.[26]

Layered hydroxide salt

LHSs, can be described using the general formula $M^{2+}(OH)_{2-x}(A^{m-})_{x/m} \cdot nH_2O$, where M^{2+} represents metal cations, while A^{m-} represents anions.[19] Their structures also originate from a brucite-like structure; however, unlike LDHs that were formed from metal replacement in brucite structure, LHSs were formed when part of the hydroxide group in the structure is substituted by water molecules and anions.[27] Zinc LHS is one of the example of LHS (Fig. 3). The presence of inert hydroxide layers enables the intercalated anions to be securely preserved from unfavourable conditions. LHSs also exhibit good incorporation with various organic molecules[28] and show low toxicity due to their solubility in weakly acidic biological fluids.[14] All of these unique properties make LHSs worth experimentation in various environmental and industrial research.



3 Schematic representation of zinc LHS structures

Even though numerous studies have focused on LDHs owing to their potential in various fields, until now single-metal hydroxides have rarely been studied.[29] Nevertheless, LHSs are indeed interesting materials worth exploring. Similar to LDHs, LHSs also possess anion-exchange properties which make them capable of being used in various applications related to pesticides, such as in controlled release formulations (CRFs) of pesticides[30] and enhancing the antibacterial activity of bactericides.[31]

Preparation of layered hydroxide anion exchanger

Preparation of LDHs

Countless research papers related to pesticides have reported on the preparation of LDHs containing various species of anion intercalated into the interlayer regions. Until now, these novel intercalated LDHs have been widely exploited as sensors, catalysts, antibacterial agents, and adsorbents, due to their simple preparation methods. Generally, LDHs can be prepared using co-precipitation, ion exchange, rehydration using structural memory effect and the hydrothermal method.[32] This review will concentrate on the preparation of Zn/Al-LDHs and Mg/Al-LDHs as they are the most common LDHs exploited in past decades. The low polarising power exhibited by these LDHs enhances their potential in various applications related to pesticides.[33] Nevertheless, the preparation methods of some less common LDHs, such as Li/Al-LDHs and Mg/Fe-LDHs are also mentioned in this review.

Zn/Al hydrotalcite-like LDHs

The co-precipitation method is the most frequently used method in the synthesis of Zn/Al-LDHs intercalated into pesticides (Table 1). In this one-pot direct synthesis method, an aqueous solution of Zn^{2+} and Al^{3+} containing the anions to be intercalated into the LDHs is used as a precursor. The co-precipitation reaction of Zn/Al-LDHs may be conducted at either low supersaturation or high supersaturation conditions to ensure simultaneous precipitation of both metal cations.[32] However, precipitation at low supersaturation was preferred in many studies, as this condition tends to produce Zn/Al-LDHs with a higher crystallinity, owing to the smaller number of crystallisation nuclei.[26, 27] In this condition, the aqueous solution of metal cations was mixed with the desired intercalated anions in a container. An alkali solution, which acts as precipitation agent, was then added simultaneously to the mixture to maintain a certain pH for the co-precipitation of the metal cations. Thermal treatment was usually performed after the precipitation at either low or high supersaturation to enhance the crystallinity and increase the product obtained.[23] It is essential to vigorously stir the Zn/Al-LDHs synthesised and purge them with nitrogen gas in the synthesis process, so that highly purified LDHs are obtained.[32]

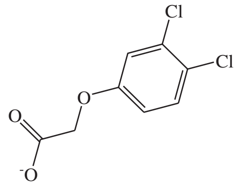
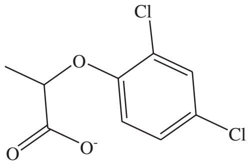
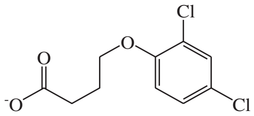
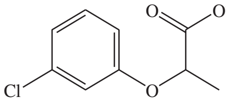
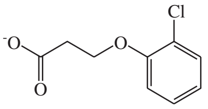
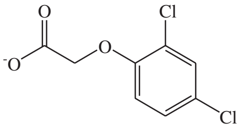
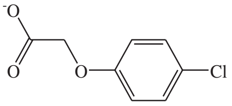
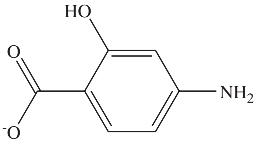
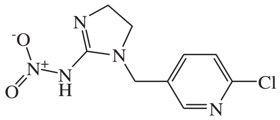
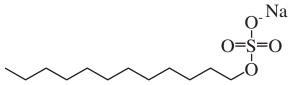
The preparation of Zn/Al-LDH nanocomposites via anion exchange has been widely reported in recent years due to the ready occurrence of ion exchange between the anions in the LDH interlayer gallery and the anions to be intercalated.[28, 29] This method is very convenient for application in certain conditions when co-precipitation is irrelevant, such as in particular cases when the metal cations and anions involved in the reaction are unstable in alkaline solution, or direct reaction between metal cations and guest anions is more desirable.[32] In the preparation of Zn/Al-LDHs via anion exchange, the affinity of anions in the Zn/Al-LDH interlayer gallery is one of the main factors that determines the extent of this method.[32] Affinity for simple monovalent anions is in the order $OH^- > F^- > Cl^- > Br^- > NO_3^-$.[47] The weakest electrostatic interaction, exhibited by NO_3^- in the interlayer of Zn/Al/LDHs, has led to this anion becoming the most favoured initial anion in many studies.[27, 28, 31] Other factors which determine the extent of ion exchange in the preparation of LDHs are the exchange medium, pH value of the reaction solution and the chemical composition of the layers.[32]

All the aforementioned methods can be used to intercalate Zn/Al-LDHs with various pesticides such as herbicides, insecticides and bactericides. Phenoxyherbicide compounds have constituted the most commonly used herbicides in recent years.[48] Even though phenoxyherbicides are classified as only a slightly toxic pesticide, their omnipresent distribution and exposure over a long period could possibly lead to adverse health conditions in living organisms.[49] The intercalation of these anionic pesticides into Zn/Al-LDHs manages to combine optimum bioactivity with allowing application of the minimum amount of pesticide. For instance, 2,4-dichlorophenoxyacetatic acid, which is acknowledged for its toxicity and carcinogenic,[50] has been intercalated into Zn/Al-LDHs 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.[38]

In a study conducted by Hussein et al.,[35] a comparison was made between surface properties and the release behaviour of dichlorprop-Zn/Al-LDH nanocomposites which were prepared using two different preparation methods, namely co-precipitation and ion-exchange methods. The study revealed that different Zn/Al-LDH preparation methods influence the physicochemical properties of the resulting nanocomposites. Nanocomposites prepared using the co-precipitation method exhibited higher crystallinity and greater particle size, but lower loading capacity for the herbicide. The anions in the Zn/Al-LDH interlayer were arranged in an orderly manner during the intercalation process, which led to higher crystallinity. Due to their greater particle size, the nanocomposites tended to release dichlorprop at a lower percentage and slower rate. There have also been several studies which reported the intercalation of Zn/Al-LDHs with anionic 4-amino salicylate bactericides in order to enhance their antibacterial performance.[36, 37] 4-amino salicylate-Zn/Al-LDH nanocomposites were prepared by two different methods, namely co-precipitation and the anion-exchange method.[51] Similar to the result obtained by Hussein et al.,[35] this study also shows that the nanocomposites prepared using co-precipitation method has higher degree of crystallinity compared to ion-exchange method.

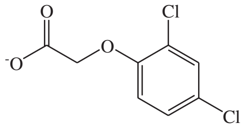
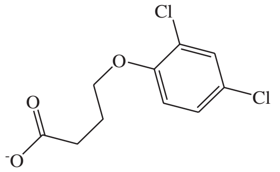
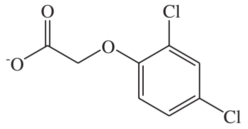
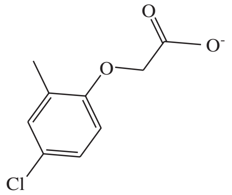
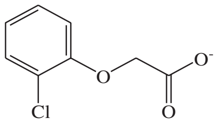
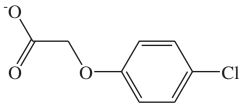
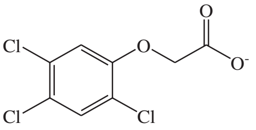
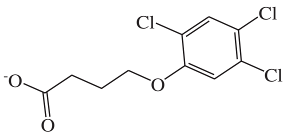
The versatility of Zn/Al-LDHs as host materials is not only limited to anionic guest ions; they are also compatible

Table 1 Preparation methods and pesticide guests intercalated into Zn/Al-LDHs

Preparation method	Structure of intercalated pesticide guests
Co-precipitation[34]	 3,4-Dichlorophenoxyacetate
Co-precipitation and ion exchange[35]	 2-(2,4-Dichlorophenoxy)propionate
Ion exchange[36]	 4-(2,4-Dichlorophenoxy)butyrate  2-(3-Chlorophenoxy)propionate
Ion exchange[37]	 3(2-Chlorophenoxy)propionate
Co-precipitation[38]	 2,4-Dichlorophenoxyacetate  4-Chlorophenoxyacetate
Co-precipitation and ion exchange[39]	 4-Amino salicylate
Co-precipitation and evaporating solvent-enhanced intercalation method[40]	 Imidacloprid (neutrally charged pesticide)  Sodium dodecylsulphate (surfactant)

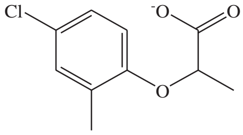
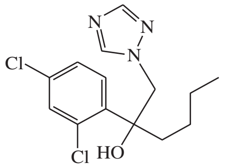
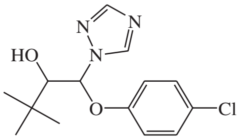
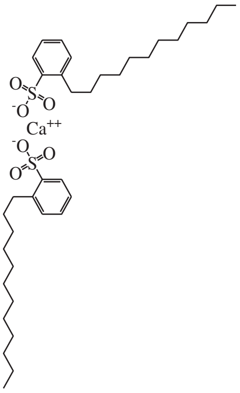
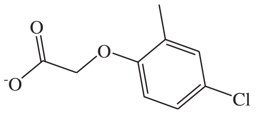
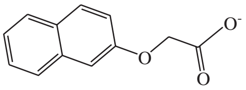
(*continued*)

Table 1 (***continued***)

Preparation method	Structure of intercalated pesticide guests
Co-precipitation[41]	 2,4-Dichlorophenoxyacetate
Direct and indirect method[42]	 4-(2,4-Dichlorophenoxy)butyrate
Co-precipitation[43]	 2,4-Dichlorophenoxyacetate
Co-precipitation[44]	 2-Methyl-4-chlorophenoxyacetate
Co-precipitation[45]	 2-Chlorophenoxyacetate  4-Chlorophenoxyacetate  2,4,5-Trichlorophenoxyacetate
Direct method[46]	 2,4,5-Trichlorophenoxybutyrate

with being incorporated with a neutrally charged guest such as the insecticide imidacloprid.[40] The charge characteristic of a pesticide is one of the major factors that affects its adsorption properties, hence a neutrally charged pesticide may exhibit different behaviour compared to an anionic pesticide.[7] Even though the neutrally charged molecule will not undergo ionisation, it may be momentarily polarised in the presence of an electrical charge. Polarisation is also influenced by the availability of mobile electrons such as π electrons in the benzene ring. Unlike other anionic guest ions that can be simply prepared using conventional methods such as co-precipitation, ion-exchange and reconstruction methods, these neutrally charged and poorly water soluble pesticides frequently require the assistance of surfactants to alter the layered host material. Surfactants can be defined as compounds that are capable of reducing surface tension and modifying energy relationships at interfaces.[52] Surfactants create a hydrophobic region in

Table 2 Preparation methods and pesticide guests intercalated into Mg/Al-LDHs

Preparation method	Structure of intercalated pesticide guests
Co-precipitation[12]	 2-(4-Chloro-o-tolyloxy)propionate
Co-precipitation, ion exchange and reconstruction[18]	 Hexaconazole (neutrally charged pesticide)  Triadimenol (neutrally charged pesticide)  Calcium dodecylbenzenesulfonate (surfactant)
Ion exchange[33]	 (4-Chloro-2-methylphenoxy)acetate
Co-precipitation[53]	 β-Naphthoxyacetate

the gallery of Zn/Al-LDHs, thus making it possible for the desired pesticides to be intercalated into the regions. The list of pesticide guests intercalated into Zn/Al-LDHs is shown in Table 1.

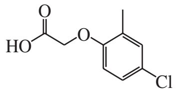
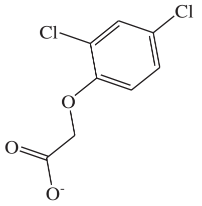
Zn/Al-LDHs have been widely synthesised due to their versatility and easy fabrication, regardless of the methods used. All the methods mentioned above obviously offer their own significant advantages in synthesising Zn/Al-LDHs. However, in order to yield a pure phase of Zn/Al-LDHs with high crystallinity, the preferred method should be chosen wisely. The charge density, affinity and structure of the intercalated anions, the purpose of synthesising the particular Zn/Al-LDH and the stability of the ions involved during the preparation process are some important aspects that should be taken into consideration.

Mg/Al hydrotalcite-like LDHs

Although various methods have been employed in Mg/Al-LDH preparation, the co-precipitation method seems to be the most popular method (Table 2). This simple method uses an aqueous solution of Mg^{2+} and Al^{3+} containing anions to be intercalated into the LDHs as precursors. Various kinds of anion have been intercalated into the Mg/Al-LDHs using co-precipitation, such as 2-(4-chloro-o-tolyloxy) propionate,[12] (4-chloro-2-methylphenoxy)acetate[54] and beta-naphthoxyacetate.[53]

A number of studies have reported preparation of Mg/Al-LDHs via the ion-exchange method.[11, 25] The ion-exchange method comprises two consecutive processes. In the first process, the Mg/Al-LDH precursors usually contain univalent

Table 3 Preparation methods and pesticide guests intercalated into Li/Al-LDHs and Mg/Fe-LDHs

System	Preparation method	Structure of intercalated pesticide guests
Mg/Fe	Ion exchange[33]	 (4-Chloro-2-methylphenoxy)acetate
Li/Al	Ion exchange[57]	 2,4-Dichlorophenoxyacetate

anions with a weak electrostatic force. These univalent anions, such as NO_3^-, Br^-, Cl^- and CO_3^{2-}, are prone to attack by incoming anions and easily exchange during the second process.[32] Some of the incoming guests that have been successfully intercalated into the Mg/Al-LDH interlayer gallery via the ion-exchange method include the anionic herbicide (4-chloro-2-methylphenoxy)acetate and neutrally charged fungicide hexaconazole. There are also several methods that involve the reconstruction of Mg/Al-LDHs during preparation.[18] The calcination process converts the conventional Mg/Al-LDHs into a metal oxide with greater specific surface area, high anion exchange and a flexible interlayer space.[55] However, calcination may also lead to a small loss in crystallinity.[56]

Previous research has demonstrated a number of methods which can be employed in synthesising Mg/Al-LDHs. Although similar anions may be successfully intercalated into the interlayer gallery of Mg/Al-LDHs using different methods, their structure, crystallinity and potential in respective applications may vary. Hence, it is essential to fully understand the method desired, so that wide-ranging and comprehensive findings can be obtained. The list of pesticide guests intercalated into Mg/Al-LDHs is summarised in Table 2.

Other types of LDH

Even though Zn/Al-LDHs and Mg/Al-LDHs are the most widely synthesised LDHs in applications related to pesticides, there are also several previous studies that have reported on the preparation of other types of LDH using the anion-exchange technique, such as Mg/Fe-LDHs[33] and Li/Al-LDHs.[57] The structures of the pesticide guests intercalated into Li/Al-LDHs and Mg/Fe-LDHs are shown in Table 3.

Preparation of LHSs

Zinc-layered hydroxides

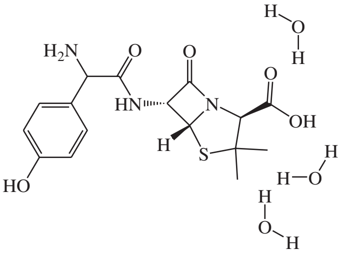
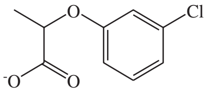
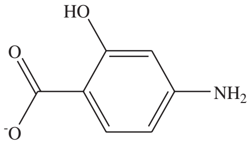
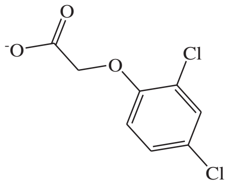
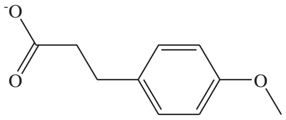
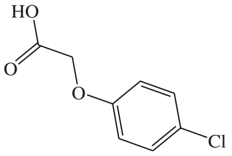
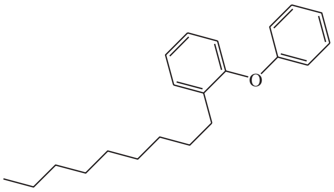
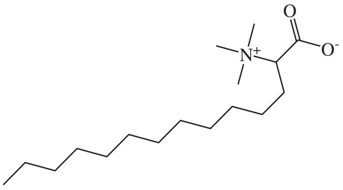
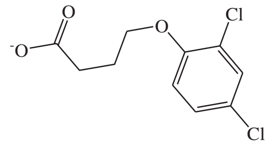
Among LHSs exploited in the past few decades, zinc-layered hydroxides (ZLHs) seem to be renowned in pesticide-related fields. This is owing particularly to their easy preparation and capability for exchanging anions.[58] In these industries, ZLHs may be intercalated with various pesticides, including herbicides, bactericides and insecticides, to enhance their performance. These nanocomposites are mostly prepared by the direct reaction method, as listed in Table 4.

As well as using zinc nitrate, the direct reaction method implies the use of ZnO as the precursor in synthesising intercalated ZLHs. This method was employed by dispersing ZnO in deionised water. A solution containing dissolved guest anions to be intercalated was then added to the ZnO heterogeneous solution and aged at 70 °C for 18 h to allow nucleation and particle growth of the nanocomposites. The product obtained was centrifuged, washed using deionised water and dried at 70 °C.[60] There has also been a study which incorporated the addition of HCl during synthesis of ZLHs, so that the dissociated Cl^- could act as a competitor of the organic anion guest, and included the use of nitrogen gas to remove any dissolved carbonate.[58] In several cases, the synthesis methods were conducted at constant pH, adjusted by dropwise addition of NaOH.[23, 54]

Amoxicillin has been reported as intercalated into the interlayer gallery of ZLHs via anion exchange.[59] The ZLHs were initially prepared using a low supersaturation co-precipitation method at pH 7. The ZLHs obtained were centrifuged, washed with deionised water and dried in a vacuum at 50 °C. In order to synthesise amoxicillin-intercalated ZLHs, the amoxicillin was dissolved in deionised water and the pH adjusted to pH 8 under vigorous stirring. The ZLHs prepared earlier were added into the mixture and vigorously stirred by magnetic stirring at room temperature for 24 h. Powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy analysis of the nanocomposite confirmed the success of the intercalation. The basal spacing of 7.17 Å possessed by amoxicillin–ZLH nanocomposites implies that the ZLHs exhibit a monolayer arrangement of amoxicillin anions with an angle of 32°.

A novel method was developed by Liu et al.[62] for synthesising chlorpyrifos (CPF) adsolubilised into layered zinc hydroxide nitrate intercalated with dodecylbenzenesulphonate (DBS). In this method, a co-precipitation method at low supersaturation was initially employed to synthesise DBS-intercalated layered zinc hydroxide nitrate (ZHN–DBS). CPF, which is a neutrally charged poorly water soluble pesticide, was dissolved in alcohol and anionic surfactant sodium DBS, non-ionic surfactant polyoxyethylene(10)nonyl phenyl ether (TX-10) or zwitterionic surfactant dodecyl betaine (DB) was then added to the solution, producing micelles. ZHN–DBS was then added to each of these micelles to synthesise ZHN–DBS–CPF-, ZHN–TX-10–CPF- and ZHN–DB–CPF-intercalated compounds. PXRD analysis demonstrated that these three compounds possessed different basal spacings, hence suggesting the occurrence of different intercalation

Table 4 Preparation methods and pesticide guests intercalated into ZLHs

Preparation method	Structure of intercalated pesticide guests
Ion exchange[59]	 Amoxicillin trihydrate
Direct reaction[30]	 2-(3-Chlorophenoxy)propionate
Direct reaction[31]	 4-Amino salicylate
Direct reaction[58]	 2,4-Dichlorophenoxyacetate
Direct reaction[60]	 3-(4-Methoxyphenyl)propionate
Direct reaction[61]	 4-Chlorophenoxyacetate
Co-precipitation[62]	 Polyoxyethylene (10) nonyl phenylether (surfactant)  Dodecyl betaine (surfactant)
Direct reaction[63]	 4-(2,4-Dichlorophenoxy)butyrate

mechanisms. For instance, the inclusion of CPF into the interlamellae of ZHN–DBS–CPF nanocomposite are successfully achieved via second intercalation of DBS–CPF micelles into the enlarged gallery of ZHN–DBS. For the ZHN–TX-10–CPF nanocomposite, however, the intercalation of CPF into interlayer of the nanocomposite is accomplished by the exchange of TX-10–CPF micelles with the intercalated DBS. The mechanism in these two nanocomposites nonetheless, are completely contrariwise with the ZHN–DB–CPF. For ZHN–DB–CPF nanocomposite, the intercalated DBS is induced and removed due to the strong interaction between DB and DBS anions, and the other DB accompanying CPF enter into the interlamellae gallery of ZHN.

Although LHSs have not been as widely used as LDHs, all these aforementioned studies have proven that LHSs can be easily synthesised using various methods. With similar anion-exchange properties to LDHs, LHSs seem to be a promising layered material, particularly due to (i) the presence of a single metal ion in the O_h sites, (ii) the ability of these compounds to partly exchange the hydroxyl groups for larger anions.[64] This occurrence can be seen in the case of zinc hydroxide nitrate[65] and zinc hydroxide sulphate,[66] as some of the hydroxyl groups are replaced with bigger anions, nitrate and sulphate anions, respectively.

Applications of layered hydroxide anion exchanger related to pesticides

The ability of LHSs and LDHs to be incorporated with a wide range of guest ions enable these layered hydroxide anion exchanger to be exploited in various applications related to pesticides. Countless studies have reported on the potential of LHSs and LDHs in synthesising environmentally friendly pesticides, treating and monitoring wastewater polluted due to excessive use of pesticides and enhancing the antibacterial performance of various bactericides. This section will thoroughly elucidate the aforementioned applications according to their respective systems, so that a detailed review regarding each system can be obtained.

Zn/Al hydrotalcite-like LDHs

Water treatment

The ability of Zn/Al-LDHs to adsorb anionic contaminants comes from their anion-exchange capability that allows exchange of anions from the interlayer with anions found in the polluted water, and their ability to be reconstructed from their calcined structure.[67] Along with a large surface area, the versatility of the interlayer region of Zn/Al-LDHs for incorporation with a wide selection of anionic and polar molecular species is another important quality that enhances their ability to remove pollutants.[23] Zn/Al-LDHs are superior to other conventional anionic exchange resins due to their higher anion-exchange capacity, greater thermal stability and capability to regenerate.[68] Generally, two different mechanisms have been proposed for contaminant removal in water treatment using Zn/Al-LDHs, surface adsorption and anion exchange. 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; meanwhile, interlayer anion exchange is mostly affected by the charge-balancing anions in the interlayer and the layer charge density.[23]

Increasing attention has recently been diverted to investigate the adsorption ability of Zn/Al-LDHs in the removal of oxyanion contaminants such as arsenite and arsenate. Arsenic contamination in water resources may originate from the weathering of naturally occurring arsenic minerals and anthropogenic activities such as the manufacture of pesticides and herbicides.[69] Constant exposure to arsenic over a long period may increase the risk of endocrine, respiratory, gastrointestinal and neurological diseases in humans.[70] Zn/Al-SO_4 LDHs have been successfully developed for the removal of both arsenite and arsenate from simulated soil solutions.[71] Arsenate adsorption kinetics exhibits good agreement with a pseudo-second-order mechanism, while arsenite seems to follow an intraparticle diffusion model. The main mechanism of Zn/Al-SO_4 LDHs over these highly toxic pollutants is mostly exchange on the surface sites of the solid, though some internal exchange may occur as well. The adsorption isotherm for both contaminants can be well described according to the Langmuir isotherm, with maximum adsorption capacities of 34.24 and 47.39 mg/g for arsenite and arsenate, respectively.

Zn/Al–Cl-LDHs have been reported in the removal of the anionic phenoxyherbicide 2,4-dichlorophenoxyacetate, which is often used for weed control in wheat, rice and maize cultivations.[72] 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 phenoxyherbicide 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.

Controlled release formulations

CRFs have attracted great interest in recent years and have been exploited in various fields, including pesticides. Positively charged anionic clays like LDHs and LHSs have been used extensively as controlled released systems in fungicides,[40] insecticides[73] and herbicides.[74] These materials have been used as host materials to demonstrate the controlled release behaviour of active compounds intercalated in them. Due to their relatively low cellular cytotoxicity, high adsorption capacity and particular colloidal properties, they have been widely explored in agrochemical formulations.[75]

The application of CRFs has brought several benefits to pesticide innovation. For instance, CRFs may extend the activity duration of pesticides by supplying a continuous low concentration of pesticide, nevertheless sufficient for long-lasting performance. Slow release of pesticides enables farmers to reduce the repeated use of pesticides, thus resulting in time-efficient and more economical cultivation practices. In addition, CRFs also assist in preventing environmental pollution by minimising the distribution of excess pesticide residues in the environment (via evaporation, degradation or leaching by rain into waterways), which commonly occurred due to simultaneous release of high pesticide concentrations. In fact, CRFs implement the use of solid pesticide formulations instead of conventional liquid pesticides, thus lessening the flammability of the pesticides. CRFs also reduce the high mobility of pesticides in soil, thus lowering mammalian toxicity and phytotoxicity by reducing pesticide residues in the food chain.[76]

Adsorption is one of the mechanisms used by layered hydroxide anion exchanger which helps reduce mobility of the particular material, thus making it suitable for controlling the release of pesticides in the environment. Recent studies have shown that anionic clays like Zn/Al-LDHs can be exploited as materials that support slow release formulations in pesticides.[34] The application of CRFs of pesticides tends to limit the mobility of pesticides through the soil pathway, thus helping to avoid pollution of surface and groundwater.[35] Zn/Al-LDHs have been used as inorganic host materials for CRFs by intercalating them with numerous anionic phenoxyherbicides. The versatility of Zn/Al-LDHs not only allows them to be intercalated with one anion at a time,[26, 45] but it is also possible to simultaneously intercalate these layered hydroxide anion exchanger with several anions.[28, 35] The chlorophenoxyherbicides which have been intercalated into Zn/Al-LDH inorganic interlamellae in recent studies include 3,4-dicholorophenoxyacetate,[34] 2-(3-chlorophenoxy)propionate,[36] 4-(2,4-dichlorophenoxy)butyrate,[28, 42] 2,4-dichlorophenoxy acetate[35, 41] and 2-chlorophenoxyacetates, 4-chlorophenoxyacetates and 2,4,5-trichloro phenoxyacetates.[45]

The loading and release percentage of the herbicide is mainly influenced by the host–guest interaction and molecular size and structure of the intercalated anions.[28, 45] In the controlled released study conducted by Sarijo et al.,[45] Zn/Al-LDHs 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.

The release behaviour of herbicide-intercalated Zn/Al-LDHs was also affected by the preparation method of the nanocomposites. In a study conducted by Hussein et al.,[35] two methods were successfully adopted in the preparation of dichlorprop[2(2,4-dichlorophenoxy)propionate]-intercalated Zn/Al-LDH nanocomposites, co-precipitation and ion exchange. The nanocomposites synthesised using the ion-exchange method were found to exhibit a higher loading percentage of dichlorop herbicide, and were thus capable of releasing a higher percentage of herbicide at a greater rate. Even though the Brunauer–Emmett–Teller surface area of the nanocomposites prepared by the co-precipitation method was approximately 10 times higher than the other method, the kinetic release of these nanocomposites did not demonstrate the expected outcome, due particularly to less accessibility of the surface nanocomposite for the anion exchanged with incoming anions. The nanocomposites synthesised by both methods are governed by a second-order reaction and the release of the dichlorop was related to the dissolution of the nanocomposite and anion exchange between the dichlorop intercalated into the Zn/Al-LDHs and the anion in the aqueous solution.

The release of herbicides intercalated to Zn/Al-LDHs can also be influenced by the type of incoming ions to be exchanged,[43, 44, 46, 52] and their concentration.[35] Different types of aqueous solution that are commonly used in controlled release studies of herbicides are Na_3PO_4, Na_2SO_4, NaCl and Na_2CO_3. When release was studied in different types of aqueous solution, it was proven that the charge density of the incoming anions plays an important role in determining the saturated release of the herbicide from the nanocomposites into the aqueous media.[46]

Bactericides

There have also been several fascinating studies which reported on the effectiveness of Zn/Al-LDHs for inhibiting the growth of bacteria and viruses. Zn/Al-LDHs are outstanding biocompatible inorganic host materials which can be used as antibacterial agents in various applications including ceramic manufacturing,[17] pharmaceutical,[77] biomedical[78] and water treatment industries.[79] Zn/Al hydrotalcite-like LDHs can be exploited to enhance the antibacterial performance and drug delivery efficiency of cephalosporin bactericides such as Cefazolin through controlled release properties.[77] A type of cephalosporin antibiotic, Cefazolin has the chemical formula $C_{14}H_{14}N_8O_4S_3$ and a molecular weight of 454.51 g mol^{-1}. This antibacterial agent has been used to fight against various Gram-positive and Gram-negative bacteria with a wide-ranging antibacterial spectrum. The synthesised nanocomposite was proven to exhibit better stability resulting from the electrostatic interaction between the Cefazolin guest and Zn/Al-LDH host. The release of Cefazolin in the nanocomposite is time dependent, thus indicating the existence of controlled release behaviour of the nanocomposite.

Zn/Al-LDHs have also been modified into potent antibacterial ceramic materials.[17] Silver nanoparticles, known for their antimicrobial properties, were intercalated into the interlamellae structure of Zn/Al-LDHs through a co-precipitation reaction, followed by 4 h aging at 150 °C. The influence of thermal treatment on the antibacterial activity of the composite was also studied by calcining the composite at 800 °C for 2 h. The calcination process combined a $ZnAl_2O_4$ spinel and Ag_2O, as the Zn/Al-LDH was converted to its spinel, while Ag° was converted to its oxide state. The successfully conducted thermal treatment enhanced the antibacterial activity of the composites. Zn/Al-LDHs and their calcined hydrotalcite were deposited with silver nanoparticles, and an antibacterial test was then carried out. The study revealed that the metallic form of silver in Ag-LDH provides resistance against bacterial growth of *E. coli* and *S. aureus*. Although both the composite and calcined products showed good antibacterial performance, calcined Ag-Zn/Al-LDHs were proven to show stronger antibacterial properties compared to Ag-Zn/Al-LDH composites.

Sensors

Due to the widespread use of pesticides, it is crucial to continuously monitor the level of pesticide residues in the environment. Several studies have reported on the potential of Zn/Al-LDHs intercalated with certain herbicides for the determination of various contaminants in wastewater and real samples. A novel pencil-based chemically modified carbon paste electrode was recently fabricated using Zn/Al-LDHs intercalated with 2(3-chlorophenoxy)propionate (Zn/Al-LDH-CPPA) for the determination of cobalt(II).[80] The addition of Zn/Al-LDH–CPPA into the matrix of a carbon paste electrode led to effective catalytic behaviour in the electrochemical response, thus enhancing the sensitivity of the sensor for the determination of cobalt(II). The proposed sensor was proven to show remarkable sensitivity, a low detection limit, wide linear range and non-toxic properties, thus making it reliable for detecting cobalt(II) residues in biological compounds and water samples.

Nano-structured sensors using single-walled carbon nanotube paste electrodes modified with Zn/Al-LDH–3(4-methoxyphenyl)propionate (Zn/Al-LDH–MPP) nanocomposites have been fabricated for the determination of mercury(II).[81] Studies were conducted based on cyclic voltammetry scanning by varying several parameters including the percentage of modifier, scan rate, concentration and pH of the supporting electrolyte. Under optimised conditions, the sensor developed can be used to detect mercury(II) up to nanolevel and can be applied to monitor the mercury(II) level in various samples including vegetables and aquatic life. The combination of single-walled carbon nanotube paste electrodes with Zn/Al-LDH–MPP nanocomposites was proven to enhance the sensitivity and selectivity of the developed sensors for the detection of mercury(II).

Catalysts

Synthetic nano-sized Zn/Al-LDHs have also been developed as an environmentally friendly and effective catalyst used for N-sulfonylation of amines to synthesise sulphonamides.[82] The use of these reusable, solid base catalysts led to the production of quantitative yields under ultrasound irradiation. Nevertheless, high-purity sulphonamide was successfully obtained within a short reaction time.

Mg/Al hydrotalcite-like LDHs

Water treatment

Mg/Al hydrotalcite-like LDHs have been proposed in many studies as adsorbents in treating various water contaminants, including (4-chloro-2-methylphenoxy)acetate,[33] glyphosate,[9] linuron, metamitron and 4-(2,4-dichlorophenoxy)butyrate,[67] 2,4-dichlorophenoxyacetate,[83] thiosulphate,[84] dicamba,[85] nicosulfuron and mecoprop-P,[86] 2,4,5-trichlorophenol,[87] linuron[88] and chlorpyrifos.[89] The specific chemical interaction between adsorbed anions and adsorbents that influences the efficiency of contaminant removal via adsorption not only depends on the structural properties of the targeted anions, but also the structure and properties of the adsorbents as well.[90] Owing to simple preparation and easy anion interlayer exchange, nitrate-containing Mg/Al-LDHs have been extensively exploited as adsorbents for wastewater treatment.[56, 74, 83]

Recent studies have shown that Mg/Al–NO_3-LDHs with higher charge density and basal spacing tend to enhance the anion exchange of interlayer nitrates with the targeted anions.[83] The increased *d*-spacing of Mg/Al–NO_3-LDHs resulting from the increase of layer charge density is associated with the change in orientation of interlayer nitrates in the hydroxide layer of Mg/Al-LDHs.[91] In the study conducted by Chao et al.,[90] the influence of different nitrate orientation in the Mg/Al-LDH structure on the adsorption of 2,4-dichlorophenoxyacetate was investigated. The study showed that Mg/Al-LDHs with different nitrate orientation (parallel and perpendicular orientations) seem to exhibit different adsorption behaviour. Due to the bulky size of 2,4-dichlorophenoxyacetate, the adsorption of 2,4-dichlorophenoxyacetate on Mg/Al-LDH with parallel-oriented nitrate could only occur at the external surface of the adsorbents. For Mg/Al-LDHs with perpendicular-oriented nitrate, however, the larger basal spacing allowed the adsorption of 2,4-dichlorophenoxyacetate via external surface and ion exchange, thus exhibiting greater preferential binding affinity towards targeted anions.

The modification of Mg/Al-LDHs using potential anions and calcination seems to enhance their affinity for targeted contaminants. Zaghouane-Boudiaf et al.[87] proved that Mg/Al-LDHs intercalated with DBS are more effective for the adsorption of organic pollutants of 2,4,5-trichlorophenol from aqueous solution. Adsorption was significantly affected by the pH and temperature of the aqueous solution, as more 2,4,5-trichlorophenol was removed at lower pH and a higher rate of adsorption was observed at higher temperature. In another study conducted by You et al.,[85] calcination of Mg/Al-LDHs was proven to increase the anion-exchange capacity for the adsorption of dicamba. The adsorption process is rapid and mainly influenced by two major factors, electrostatic adsorption and hydrophobic adsorption. The adsorption isotherm was based on the S-type curve, which proposed that the adsorption of dicamba by calcined Mg/Al-LDHs increased with higher concentration of dicamba due to the hydrophobic interaction between dicamba molecules. The study concluded that the calcined Mg/Al-LDHs could be used as alternative adsorbents to treat wastewater contaminated by dicamba and other pollutants with similar properties.

Controlled release formulations

Recent studies on LDHs have shown that Mg/Al-LDHs can be used as support materials for slow release formulations of terbuthylazine, a herbicide widely distributed in agriculture.[54] Mg/Al-LDHs were initially modified with two different types of organic adsorbent, dodecylsulphate and sebacate, to increase their affinity towards terbuthylazine. The study demonstrated that the intercalated Mg/Al-LDH/terbuthylazine complexes slow down the release of the herbicide after application, and are hence relevant for dealing with environmental issues arising such as groundwater pollution and soil contamination.

The release of Mg/Al-LDHs intercalated with the anionic phenoxyherbicide 2-(4-chloro-o-tolyloxy)propionate (Mg/Al-LDH/MCPP) were compared in two mediums, distilled water and soil solution.[12] The release pattern seems to be faster in soil solution than distilled water. Although diffusion occurred during release in both mediums, ion exchange apparently only happened in the soil solution. The intercalated Mg/Al-LDH/MCPP also showed better thermal and acid stability compared to the CO_3^{2-} form of Mg/Al-LDH.

Bactericides

Due to the unique properties of Mg/Al-LDHs, they may act as an ideal sorbent for removing various harmful micro-organisms.[92] In a recent study conducted by Jin et al.,[79] Mg/Al-LDHs were shown to effectively adsorb 99% of the negatively charged bacteria *E. coli* in synthetic groundwater. Mg/Al-LDHs can also be intercalated with various metal nanoparticles and enzymes to enhance their antimicrobial properties. The potential of silver ions to be used as effective antibacterial agents against various types of harmful bacteria has been proven in many studies.[86, 87]

Chen et al.[92] proposed a newly designed nanoporous encapsulation of Mg/Al-LDHs using silver nanoparticle coatings. The silver nanoparticles can be directly regenerated on a Mg/Al-LDH coating, via reduction of silver ions without any reductants. The high-quality antibacterial coating was obtained under hydrothermal conditions using an easily accomplished and superior *in situ* growth method by immersing the substrates in the Mg/Al-LDH medium after the elimination of free electrolytes. The Mg/Al-LDH coating allowed the reduction of silver ions into silver nanoparticles, thus leading to uniform deposition of silver nanoparticles on the Mg/Al-LDH surface. The silver nanoparticle-deposited Mg/Al-LDH nanoporous coating demonstrated excellent antimicrobial properties against *E. coli*, *P. aeruginosa*, *B. subtilis* and *S. aureus*. The proposed method exhibits its own advantages, as the pore size can be simply modified by altering the molar ratio of metal:NaOH during the synthesis of Mg/Al-LDHs. In fact, the developed coating can be applied to various kinds of substrate such as metals, ceramics and glass. Owing to the benefits offered, including low-cost, great antibacterial activity and facile method, the study showed great potential for the fabrication of good quality Mg/Al-LDH films and coatings which can be applied in various clinical and environmental applications.

Antibacterial-intercalated lysozyme–Mg/Al-LDH composites have also been shown to have outstanding bactericidal performance against *S. aureus*.[93] Lysozyme, also known as muramidase, is easily dispersed in water and capable of destroying the cell walls of certain bacteria. This novel nanocomposite merged the antibacterial properties of lysozyme with the adsorption ability of Mg/Al-LDH, thus producing an excellent bactericide without any disinfection by-products. There have also been previous studies that applied the concept of CRF into a water-soluble bactericide to minimise their usage and prevent movement of the bactericides from the target area. Zhenlan et al.[18] encapsulated hexaconazole and tridimenol bactericides into micelles derived from calcium DBS, and intercalated them into Mg/Al hydrotalcite-like LDHs. The nanocomposite positively showed an efficient controlled release system and exhibited a pseudo-second-order model controlled release behaviour.

As well as CRF, the antibacterial properties of Mg/Al-LDHs have also been reported as capable of exploitation for water treatment purposes.[79] Mg/Al-LDHs were prepared and tested for the removal of MS2, φX174 and *E. coli* in synthetic groundwater. Due to the unique structure of Mg/Al-LDHs, they were capable of adsorbing more than 99% of micro-organisms used in the study (measured in pfu/kg, a measure of the quantity of individual infectious particles based on the number of plaque formed per kg), with 5.9×10^6 to 9.1×10^6 pfu/kg and 1.6×10^{10} to 2.6×10^{10} pfu/kg bacterial and viral concentration, respectively. The adsorption density of bacteria in the study was found to lie in the range 1.4×10^{10}–2.1×10^{10} pfu/kg Mg/Al-LDH, whereas for the viruses, the adsorption density was in the range 3.2×10^{13}–5.2×10^{13} cfu/kg Mg/Al-LDH. The study also demonstrated that Mg/Al-LDHs can be applied to inhibit heterotrophic bacterial growth in untreated water, such as river water.

Sensors

Exfoliated Mg/Al-LDHs and carboxymethyl-β-cyclodextrin (CMCD) have been reported as incorporated on glassy carbon electrodes (GCEs) via a facile layer-by-layer (LBL) approach for the detection of acephatemet pesticides.[94] A film was fabricated by alternately depositing Mg/Al-LDH nanosheets and CMCD on a GCE modified with poly o-phenylenediamine film. Cyclodextrins are toroidal cyclic oligosaccharides which comprise six–eight α-D-glucose units, with a hydrophobic inner cavity and hydrophilic exterior. The developed sensor combined the rigid inorganic matrix of Mg/Al-LDHs with the supramolecule and enrichment capability of CMCD, thus producing a simple yet highly sensitive and selective sensor. The LBL deposition method has elicited massive attention in the film fabrication industry due to its simplicity, cost-effectiveness and lack of reliance on the type, size and morphology of the substrate.[95]

Exfoliated Mg/Al-LDH nanosheets have also been incorporated with humic acid for the simultaneous detection of pentachlorophenol and copper ions.[15] Similar to other contaminants, the level of pentachlorophenol residues which are typically found in pesticides must be monitored. Their toxicity and hardly decomposing behaviour makes them a major threat to ecosystems. The sensor developed can nevertheless be used to detect pentachlorophenol and copper ions as low as 0.4 and 2.0 nmol L^{-1}, respectively, which is apparently lower than the guideline limit set by the United States Environmental Protection Agency and the World Health Organization.

Catalysts

Mg/Al hydrotalcite-like LDHs are considered as noteworthy catalysts in synthesising various pesticides due to their reusability, easy separation and non-toxic properties. Mg/Al–CO_3 and Ca/Al–CO_3 hydrotalcites have been reported as being exploited as recyclable solid catalysts in the fabrication of widely used 3,4-dihydropyrimidinones/thione bactericides.[96] In another previous study, Mg/Al-LDHs also acted as catalysts in the fabrication of pyrazole fungicides, via a microwave-assisted regioselective 1,3-dipolar cycloaddition reaction of nitrilimines with enaminone.[97] Environmentally friendly properties, cost-effectiveness, fast preparation, great yield production and greener processes make these hydrotalcite catalysts superior compared to the other catalysts investigated in studies.

As well as synthesising greener pesticides, Mg/Al-LDH catalysts have also been used to treat polluted water caused by the uncontrolled use of pesticides. Mg/Al-LDHs were incorporated with cerium oxide to produce Ce/Mg/Al-LDH catalysts with bifunctional basic/semiconducting characteristics.[56] The photocatalytic properties of the developed catalyst were highly effective in the removal of several carcinogenic contaminants, namely phenol, 4-chlorophenol and 2,4,6-trichlorophenol. Simple, easy fabrication and work at natural pH are the main benefits offered by this catalyst.

Li/Al hydrotalcite-like LDHs

Water treatment

A recent study has demonstrated the potential of Li/Al-LDHs in treating contaminated water caused by arsenate.[98] Their sorption behaviour towards arsenate was investigated and compared with gibbsite, which is the most omnipresent aluminium found in soil. Based on the sorption isotherm obtained in the study, Li/Al-LDHs were found to be outstanding sorbents, apparently better than gibbsite. Even though the specific surface area of gibbsite is greater than Li/Al-LDHs, the sorption maximum of the LDHs was nevertheless six times higher than gibbsite. Sorption studies revealed that the sorption of arsenate not only occurred with Al on the edge of $Al(OH)_3$ layers, but also with Li present in the vacant octahedral sites within the $Al(OH)_3$ sheets acting as permanent sorption sites for arsenate sorption.

Controlled release formulations

Although Li/Al-LDHs have been exploited rarely compared to the other types of LDH mentioned, this type of LDH has its own uniqueness. Unlike the other types of LDH that are often made up of +2 and +3 cations, Li/Al-LDHs are the only type of LDH that contain +1 and +3 metal ions in their structure.[99]

2,4-Dichlorophenoxyacetic acid has been intercalated into the interlayer region of the rhombohedral polymorph of $[LiAl_2(OH)_6]Cl\cdot xH_2O$ ([rhom-Li–Al]LDH) via the anion-exchange method.[57] The controlled release behaviour of these pesticides was studied in phosphate buffer solution, rainwater and deionised water. The study demonstrated that

2,4-dichlorophenoxyacetate was released in the deionised water as a Li^+/2,4-dichlorophenoxyacetate ion pair, thus producing $Al(OH)_3$ and the solvated ions. Nevertheless, anion exchange seemingly occurred between the fabricated composite and the other two solutions.

Ni/Al hydrotalcite-like LDHs

Water treatment

Direct contamination of water due to the widespread use of pesticides containing glyphosate and glufosinate may disturb the stability of aquatic ecosystems,[100] whereas continuous exposure to these herbicide pollutants may lead to neurotoxicity[101] and damage to human erythrocytes.[102] The use of Ni_2/Al-LDHs as potential adsorbents in removing glyphosate and glufosinate from polluted water was proposed by Khenifi et al.[103] Their study showed that the adsorbents developed effectively removed the targeted pollutant via two different adsorption paths, external surface adsorption and interlayer anion exchange. The rate of diffusion of glufosinate was, however, lower compared to glyphosate due to its greater solubility in water.

Sensors

Owing to good electroactive properties and suitable structural and textural properties for the electrocatalytic detection of negatively charged pesticides, Ni/Al-LDHs are considered as an excellent material to be exploited as sensors for the determination of these pollutants.[104] The study proposed an amperometric sensor for the simultaneous detection of glyphosate and glufosinate using incorporated Ni/Al-LDH films. The oxidation of the amine group in the structure of glyphosate and glufosinate by Ni(III) centres enables the determination of these pesticides with a detection limit of 1 and 5 μmol L^{-1}, respectively.

Ni/Al-LDHs have also been intercalated with nanoparticle platinum (NanoPt) for the determination of the organophosphate pesticide methyl parathion.[105] Thin Ni/Al-LDH films were electrodeposited onto the surface of GCE, and the exchange of $PtCl_6^{2-}$ was carried out successively. The electrochemical reduction of $PtCl_6^{2-}$ was then conducted via cyclic voltammetry scanning, thus enabling the incorporation of platinum nanoparticles and Ni/Al-LDHs on the GCE surface. The developed sensor managed to capture methyl parathion from the solution and preconcentrate the pesticide onto the surface of the Ni/Al-LDH/NanoPt electrode via stripping voltammetric analysis. The sensor combines the versatility of LDHs and the excellent properties of NanoPt, including high surface area and good catalytic properties. Rapid determination, sensitivity, selectivity and easy fabrication make this Ni/Al-LDH/NanoPt sensor relevant for the determination of methyl parathion in real samples.

Cu/Fe hydrotalcite-like LDHs

Water treatment

Cu/Fe-LDHs are another type of LDH which have been reported for use as adsorbents in the removal of the commonly used herbicide 2,4-dichlorophenoxyacetic acid.[106] Results showed that the adsorption of pesticide decreased with increases of temperature, thus revealing their exothermic behaviour. The pH also affected the adsorption process, as the pH of the solution determines the distribution of the active sites on the Cu/Fe-LDH surface. The adsorption of 2,4-dichlorophenoxyacetic acid obeyed a pseudo-second-order kinetic model, whereas the adsorption isotherm seemed to show good agreement with the Langmuir and Freundlich equations.

Zn/Al/Zr hydrotalcite-like LDHs

Water treatment

Recent studies have also reported on the removal of 2,4-dichlorophenoxyacetic acid using calcined Zn/Al/Zr hydrotalcite-like LDHs.[107] Incorporation of the optimum amount of Zr^{4+} ions into the Zn/Al-LDH formed higher positive charge LDHs, thus successfully enhancing their adsorption capacity. It is also possible that the Zr^{4+} ions fill the interstitial space in the LDH, thus reducing their surface potential and lowering the energy required for the adsorption of 2,4-dichlorophenoxiacetic acid. The capability of Zn/Al/Zr-LDHs to adsorb 2,4-dichlorophenoxiacetic acid up to 98% makes these LDHs practical and relevant to be used for water treatment.

Zn/Al/Fe hydrotalcite-like LDHs

Water treatment

As well as using LDHs as absorbents, they can also be used as photocatalysts in order to treat contaminated wastewater. Photocatalytic technology implies the use of a semiconductor catalyst to produce a very reactive hydroxyl radical which leads to the degradation of contaminants.[108] Owing to great photocatalytic semiconductor properties and outstanding adsorptive capabilities, Zn/Al/Fe-LDHs were selected to act as the photocatalyst in the photodegradation of 2,4-dichlorophenoxyacetic acid.[109] The 2,4-dichlorophenoxyacetic acid was totally saturated in the Zn/Al/Fe-LDHs before being destroyed via a photocatalytic process, therefore leaving the wastewater free from 2,4-dichlorophenoxyacetic acid contamination.

Mg/Zn/Al hydrotalcite-like LDHs

Water treatment

Mg/Zn/Al-LDHs have also been reported for use as adsorbents and photocatalytic catalysts for the removal of pollutants in water.[16] Not only reliable for removing the anionic pollutant 2,4-dichlorophenoxyacetic acid, this photocatalytic catalyst can also be used to degrade very stable compounds such as phenol. Mg/Zn/Al-LDHs were prepared by introducing a small amount of zinc into Mg/Al-LDHs via co-precipitation methods. The addition of the optimum amount of zinc into the Mg/Al-LDHs improved the band gap energy and adsorption capacity, thus improving its photocatalytic properties. Other benefits offered by Mg/Zn/Al-LDHs may include easy fabrication, good stability, cost-effectiveness and reusability after undergoing thermal treatment.

Cu/Mg/Al, Co/Mg/Al and Fe/Mg/Al hydrotalcite-like LDHs

Catalysts

Kishore and Rodrigues[110] reported on the use of three different types of LDH, Cu/Mg/Al-LDHs, Co/Mg/Al-LDHs and Fe/Mg/Al-LDHs, as potential catalysts for the oxidation of diphenylmethane to benzophenone, a compound used in the manufacture of insecticides. Among the catalysts investigated in this work, Cu/Mg/Al-LDHs seemed to exhibit the highest percentage yield of benzophenone. Using tert-butylhydroperoxide as the oxidative agent and acetonitrile as solvent, Cu/Mg/Al-LDHs are capable of yielding up to 95% of the desired products.

Zinc-layered hydroxides

Controlled release formulations

Among all LHSs, ZLHs have attracted the greatest attention in recent years, due predominantly to their properties which bear resemblance to those of LDHs.[61] Several previous studies have demonstrated the potential of using ZLHs as a host lattice for CRF phenoxyherbicides, including 2(3-chlorophenoxy)propionic acid[30] and 2,4-dichlorophenoxyacetic acid.[58] The intercalation of 2,4-dichlorophenoxyacetic acid into the interlamellae structure of ZLHs was proven to increase the thermal stability of the nanocomposites.[58]

Comparison of the percentage release of 2(3-chlorophenoxy)propionic acid using two different host materials, Zn/Al-LDH and ZLH, have also been reported.[30] Although both materials showed good capability as a host structure for controlled release, 2(3-chlorophenoxy)propionate intercalated into Zn/Al-LDHs exhibited better controlled release behaviour due to its higher crystallinity. The release behaviour of the nanocomposite demonstrated great agreement with pseudo-second-order and parabolic diffusion for chlorop-LDH and chlorop-ZLH nanocomposites, respectively. The parabolic diffusion model is commonly used to explain that release is determined by intraparticle diffusion or surface diffusion. Hence, it can be postulated that surface diffusion or intraparticle diffusion by ion exchange is the rate-determining step in the release process for chlorop-ZLH.

In the fabrication of 4-chlorophenoxy acetate using the direct reaction method with ZnO, the concentration of 4-chlorophenoxy acetate has been acknowledged as a controlling factor for the formation of a pure phase, well-ordered nanocomposite.[61] The fabricated nanocomposite successfully demonstrated controlled release behaviour, governed by a second-order kinetic model. The study revealed that when a higher concentration of aqueous solution was used in the release study, a greater percentage release of 4-chlorophenoxy acetate from the interlamellae was observed. This was because at a higher concentration, more carbonate ions were available to be ion exchanged with the 4-chlorophenoxy acetate in the ZLH interlayer. The release of the herbicide from the nanocomposite was associated with the dissolution of the nanocomposite and anion exchange between the 4-chlorophenoxy acetate intercalated into the ZLH and incoming anions from the aqueous solution.

The intercalation of layered zinc hydroxide nitrate with the neutrally charged pesticide chlorpyrifos has been conducted using three different types of surfactant, the anionic surfactant sodium DBS, non-ionic surfactant TX-10 or zwitterionic surfactant DB.[62] The release behaviour of chlorpyrifos was studied in buffer solution at pH 5.0 and 6.8, which revealed that the release rate was greatly influenced by the type of micelle and the release medium. The nanocomposite that used the surfactants DBS and TX-10 was governed by pseudo-second-order and parabolic diffusion models, and the release process was determined by a diffusion process such as intraparticle diffusion between the layered zinc hydroxide nitrate layer or surface diffusion. The synthesised nanocomposites could be used as a potential CRF for the pesticides.

Bactericides

Owing to the antibacterial properties of zinc[111] and its potential to enhance delivery of poorly soluble drugs, reduce drug toxicity and improve drug release rate,[59] ZLHs seem be an excellent choice for use in antibacterial drug delivery. ZLHs have been reported to be intercalated with 4-amino salicylic acid (4-ASA), a type of antituberculosis drug used to fight against *Mycobacterium tuberculosis* bacteria.[23, 36] The study revealed that the release of 4-ASA from the nanocomposites is greatly influenced by pH, as the ZLH layers are more stable at pH 7.4 compared to pH 4.8, hence leading to a slower release rate at pH 7.4. The intercalation of 4-ASA into the interlamellae structure of ZLH successfully synthesised a nanocomposite with good controlled release behaviour, easy fabrication and low toxicity.

Amoxicillin trihydrate, a semisynthetic antibiotic, has also been reported to be intercalated into ZLH via the ion-exchange method.[59] The study demonstrated that the nanocomposite exhibits great antibacterial performance against *E. coli*, *S. aureus* and *K. pneumonia* bacteria. The remarkable antibacterial properties of the nanocomposite can be associated with their extremely small particle size, which is 10 times smaller than the previously used amoxicillin. The larger ratio of surface area to volume of the nanocomposites leads to greater antibacterial performance due to higher particle penetration.[112] Amoxicillin is frequently found in human and animal drugs, due to its great antibacterial properties, along with excellent adsorption and penetration into tissues.[113]

Sensors

The potential of ZLHs intercalated with 2(3-chlorophenoxy) propionate herbicides (ZLH–CPPA) as sensors for the determination of copper(II) has recently been reported.[114] The study revealed that the addition of the nanocomposite into the composition of a multi-walled carbon nanotube (MWCNT) paste electrode was proven to enhance the voltammetric response of the sensor, thus improving its sensitivity and selectivity. Under optimum conditions of 2.5% (w/w) ZLH–CPPA/MWCNT, 4×10^{-3} mol L^{-1} CH_3COONa at pH 2.5 as supporting electrolyte, and scan rate 500 mV/s, the sensor developed could be used to detect copper(II) up to nanomolar sensitivity. The reliability of the sensor was proven based on good agreement between the results obtained using the developed sensor and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Conclusion

In this present review, the use of two types of layered hydroxide anion exchanger, LDHs and LHSs, in pesticide-related applications is summarised. LDHs and LHSs have generated great interest in the inorganic field due to their potential to act as versatile host materials in fabricating novel host–guest layered materials. This key feature enables the incorporation of various guests on the respective layered hydroxide anion exchanger, such as anionic herbicides, anionic bactericides and neutrally charged pesticides (Appendix A1). Incorporation combines all the unique features of both layered host and intercalated guest, thus producing novel hybrid layers with outstanding properties that were possibly exploited in many applications, including sensors, adsorbents, CRFs, catalysts and bactericides. Based on this review, it can be seen that each LDH of different metal cation demonstrate distinctive adsorption behaviour. The adsorption behaviour of the LDHs was mainly affected by their pore size, as LDHs with smaller pore size tends to own higher adsorption capacities.[115] Previous study on adsorption using Mg/Al-LDHs, Cu/Al-LDHs and Fe/Al-LDHs shows that altering the metal cation within the hydroxide layer resulting to dissimilar adsorption/desorption loop structure, due to their different pore size and distribution.[116] Pore distribution is associated to the preparation method in synthesising LDHs and type of ions involved in the LDHs composition, meanwhile the pore size in influenced by the method and interconnection of LDH platelets. In this study, each type of LDH exhibit different pore size and shape, as Mg/Al-LDH possess non-uniform shaped mesopores, (2–10 nm), Cu/Al-LDHs have consistent mesopores with small size distribution, meanwhile Fe/Al-LDHs own both micropores (0–2 nm) and mesopores of irregular geometry. These difference pore size and distribution is probably because of the distortion of the metal hydroxide layer that resulting from the differences in atomic size of the metals. Distinctive adsorption behaviour demonstrated by each LDHs of different metal cation, lead to the existence of diverse compatibility between LDH adsorbents and anionic pesticides. Hence, not all type of LDHs can be used as adsorbents for the same anionic pesticides. In conclusion, both LDHs and LHSs are amazing layered hydroxide anion exchangers, with countless unique properties. Therefore, more study should be continuously conducted to exploit these interesting materials, so that their potential in other applications can be explored as well.

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Appendix A1

List of chemicals and their usage

Chemicals	Usage
3,4-Dichlorophenoxyacetate	To control weeds in paddy field, wheat and corn plantations[34]
2-(2,4-Dichlorophenoxy)propionate	To control ‘dicot’ (broad leaved) weeds in ‘monocot’ crops[35]
4-(2,4-Dichlorophenoxy)butyrate	To control weeds in maize, wheat and corn plantations[63]
2,4-Dichlorophenoxyacetate	A highly selective herbicide, affecting broad-leaved weeds and woody vegetation, while being harmless towards cereals[117]
4-Amino salicylic acid	A acteriostatic agent, which is extremely helpful in controlling the growth of bacteria[31]
2-Methyl-4-chlorophenoxyacetate	To control broadleaf weeds, including thistle and dock in cereal crops and pasture[44]
2-Chlorophenoxyacetate	To control weeds in fields, grasslands, lawns and recreation areas[118]
2,4,5-Trichlorophenoxyacetate	To control weeds in fields, grasslands, lawns and recreation areas[118]
(4-Chloro-2-methylphenoxy)acetate	Used for the treatment of grain, corn, sugar, cane and rice[119]
2-(3-Chlorophenoxy)propionate	Herbicides that mimic the action of auxins and plant growth hormones[36]
2-(3-Chlorophenoxy)propionate	Herbicides that mimic the action of auxins and plant growth hormones[36]
2-(4-Chloro-o-tolyloxy)propionate	A selective herbicide, with toxicity mainly against broadleaves[120]
2,4-Dichlorophenoxyacetate	To control weeds in fields, grasslands, lawns and recreation areas[118]
3,4-Dihydropyrimidinones	Widely use as antibacterial, antifungal, antiviral, antioxidative and anti-inflammatory[96]
4-Chlorophenoxyacetate	To control weeds in fields, grasslands, lawns and recreation areas[118]
Amoxicillin trihydrate	Semisynthetic antibiotic used in human and veterinary medicine for the treatment of bacterial infections caused by Gram-negative and Gram-positive micro-organisms, as well as good absorption and penetration into tissues[59]
Carboxymethyl-β-cyclodextrin	Widely utilised in sensing applications[94]
Chlorpyrifos	Sprayed on rice, fruits, vegetables and horticultural plants to control leaf eating and suckling insects[121]
Dicamba	Used as herbicide on many broadleaf weeds and woody plants[122]
Glufosinate	To induces plant, bacterial and fungal toxicity through inhibition of glutamine synthetase[101]
Glyphosate	Post-emergent herbicide that inhibits the growth of plants through interfering with the biosynthetic pathway of the essential aromatic amino acids phenylalanine, tyrosine and tryptophan[100]
Hexaconazole	A type of bactericides that is widely used in agricultural activities[18]
Imidacloprid	Systemic pesticide with physical/chemical properties that allow residues to move into treated plants and then throughout the plant[123]
Linuron	Non-ionic pesticide that is widely used in agriculture and its presence in the environment could have hazardous effects for human health[88]
Mecoprop-P	A selective, systemic, hormone-type phenoxy herbicide, which is applied as post emergence and is used on ornamentals and sports turf, for forest site preparation and on drainage ditch banks for selective control of surface creeping broadleaf weeds[12]
Metamitron	Inhibiting photosynthesis in targeted weed plants in crops of cotton, potato, corn, bean, asparagus, carrot and fruit[67]
Nicosulfuron	To control annual and perennial grass weeds such as barnyardgrass, fall panicum, quackgrass and john-songrass as well as broadleaf weeds[124]
Pyrazole	The pyrazole nucleus is a ubiquitous feature of fertile source of medicinal agents[97]
Triadimenol	A type of bactericides that is widely used in agricultural activities[18]