Layered Double Hydroxides for Regulating Phosphate in Water to Achieve Long-Term Nutritional Management

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ABSTRACT: Hunger and undernourishment are increasing global challenges as the world's population continuously grows. Consequently, boosting productivity must be implemented to reach the global population's food demand and avoid deforestation. The current promising agricultural practice without herbicides and pesticides is fertilizer management, particularly that of phosphorus fertilizers. Layered double hydroxides (LDHs) have recently emerged as favorable materials in phosphate removal, with practical application possibilities in nanofertilizers. This review discusses the fundamental aspects of phosphate removal/recycling mechanisms and highlights the current endeavors on the development of phosphate-selective sorbents using LDH-based materials. Specific emphasis is provided on the progress in designing LDHs as the slow release of phosphate fertilizers reveals their relevance in making agro-practices more ecologically sound. Relevant pioneering efforts have been briefly reviewed, along with a discussion of perspectives on the potential of LDHs as green nanomaterials to improve food productivity with low eco-impacts.
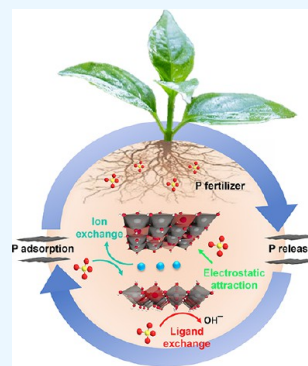
1. INTRODUCTION

The rapid growth of the world's population results in a rising demand for agricultural production.[1,2] It is estimated that more than 690 million people suffered from hunger in 2019,[3,4] and the number of hungry people may have risen to more than 820 million by the end of 2020.[5] Therefore, there is an emerging call for innovation in crop production to avoid food scarcity.[6−8] To avoid deforestation in new agricultural areas, fertilizer management is a practical way to enhance crop productivity.

The agricultural development of worldwide food production depends on soil fertility, i.e., on the presence of essential macronutrients, such as nitrogen, phosphorus, and potassium (NPK fertilizers). Phosphorus (P), mainly used in agriculture (around 80−90%), can facilitate root development, seed development, and plant maturation. However, the tremendously low P availability in soil for nutrient uptake (around 16%), due to the precipitation of PO_4^{3-},[9,10] forces farmers to increase fertilizer usage as a compromise for crop growth and development. However, overfertilization results in phosphate runoff that accumulates in natural water bodies, leading to severe eutrophication and even dead zones (e.g., the U.S. East Coast and the Gulf of Mexico).[11]

Another issue is that approximately two-thirds of the worldwide P resources come from phosphate rock deposits and sedimentary deposits, which are primarily located in just six countries. Besides, the irregularly distributed geographic concentration of P mineral causes political and economic risks for countries that require imports of fertilizer P for food production and is especially severe for low-income countries.

Hence, appropriate phosphate fertilizer management that can recover and reuse the lost P is an obvious way to avoid the loss of nutrients to the environment and reduce the contamination of soils and water.[12,13]

Various conventional techniques have been proposed for the uptake and release of phosphates, including adsorption, sedimentation, filtration, ion exchange, bacteria, algae, or plants.[14] Adsorption, in particular, is considered a highly efficient technique, allowing recovery of adsorbed phosphate from the adsorbates via a slow-release fertilizer (SRF) manner in crop production.[15] Typically, SRFs can restrict nutrient loss, thereby increasing nutrient use efficiency and promoting optimal plant growth.[16] Recently, several types of SRFs have been investigated. Zeolites, for example, exhibit high porosity and cation exchange capacity and have been widely used in soil for prolonged action fertilizer in agriculture.[17] However, their nutrient-limited nature can only allow zeolite to be used as cationic carriers (NH_4^+ or K^+),[18] requiring further surfactant-modified methods to improve phosphate adsorption performance,[19] leading to high cost and ecological issues.[19,20] Carbon-based materials are commonly adopted as fertilizer carriers due to their large specific surface area, high stability, and pore-rich structure; they can serve as SRFs, preventing the loss of
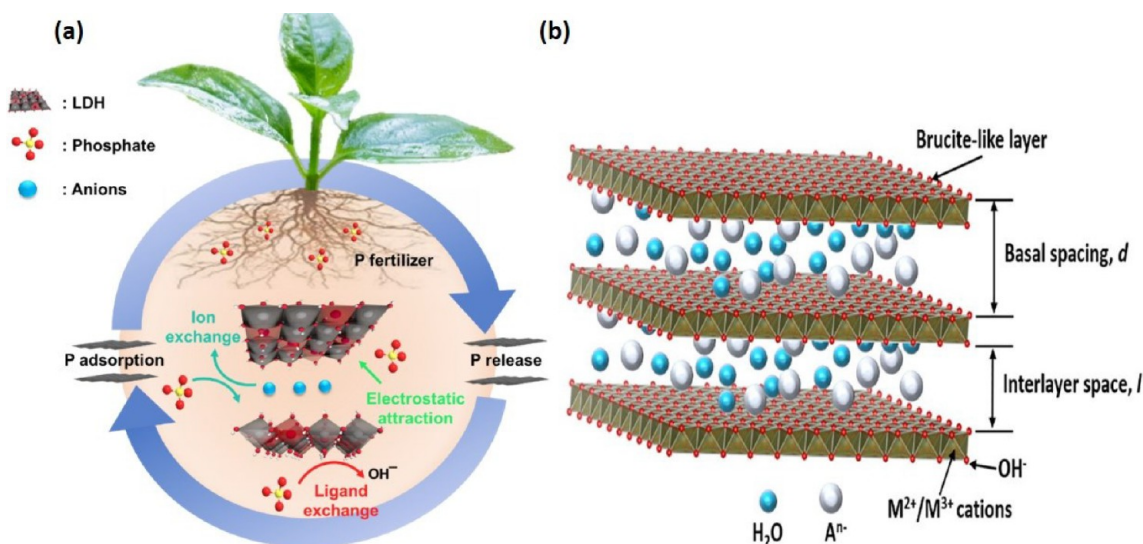
Figure 1. Schematic presentation of layered double hydroxides (LDHs) as favorable nanofertilizers. (a) Versatile phosphate removal/release by LDHs for long-term P fertilizers. (b) Schematic representation of the classical LDHs structure. (Panel b was reprinted with permission from ref 31. Copyright 2022 Elsevier.)

essential nutrients like phosphorus, potassium, and nitrogen in fertilizers and promoting optimal crop growth and efficiency.[21] However, existing options still have limitations, such as poor adsorption capacity, low adsorption rate, and poor selectivity. Therefore, it is necessary to develop new SRF materials that can support sustainable agriculture and reduce nutrient pollution.

To overcome these limitations, multiple works have been reported for designing new materials to remove and recover phosphorus nutrients from water by modifying their physicochemical properties.[22] Particularly, layered double hydroxides (LDHs), lamellar inorganic materials containing tunable brucite-like structures, have attracted great attention as green and sustainable materials for applications in removing environmental substances.[23−26] Furthermore, their tunable pollutants adsorption capability allows use of LDHs as potential nanofertilizers for agriculture with various unique properties, such as high surface area, robust structure, flexible selection of metal cations, pH-dependence, higher chemical stability, lower production costs, and biocompatibility and environmental compatibility.[27−30] Therefore, this review aims to summarize and discuss the literature about LDHs for regulating phosphate in water and their potential as long-term fertilizers for zero hunger (Figure 1a).

This review's main points are divided into the following aspects: we briefly introduce LDHs and then discuss different LDH synthesis methods. The versatile phosphate adsorption/ release mechanisms will be presented thereafter as well as a summary of the state of the art using LDHs for phosphate removal/recycling. In addition, the LDH-based composites are also investigated, which may guide researchers in choosing appropriate strategies to modify the physicochemical properties of LDHs for realizing high-performance phosphate recovery. Though many open questions and challenges still require further investigations into phosphate's role in long-term nutritional usage, we hope to trigger more interest in the agricultural chemistry field. This work can pave the way for a more detailed exploration of developing new technologies to reduce P losses and ensure the release of nutrients synchronizes with plant demand.

2. INTRODUCTION OF LDHS

LDH, a two-dimensional nanostructured material with multifunctional properties, is widely considered a promising adsorbent for recovering phosphate from wastewater due to its following characteristics: LDHs provide numerous and stable active sites for uptake of phosphate with higher efficiency, flexible tunability of composition for improving targeted pollutant selectivity, higher regeneration ability, and higher exchangeability of interlayer anions, allowing LDHs to recover and reuse phosphate in wastewater with long-term workability. Hence, LDHs with tunable anion exchangeability and affinity have considerable potential for being developed as slow-release and controlled-release phosphate nanofertilizers in agriculture.[32−35]

2.1. Structural Properties. LDHs are composed of brucite-like stacking layers with positive surface charges and interlayer anions. Each stacking layer is formed by octahedral mixed-metal hydroxide complexes, where metal cations are in the center surrounded by hydroxide ions at six symmetrical vertices.[36,37] The divalent metal ions replaced by trivalent ions result in positively charged layers, which are neutralized and separated by the intercalated water molecules and guest anions.[38,39] Water molecules surrounding the intercalated anions provide weak hydrogen bonds to maintain the layered structure, as shown in Figure 1b. The general formula of LDHs is

$$[M_a^{II}{}_{(1-x)}M_b^{III}{}_x(OH)_2]^{x+}[(A^{n-})_{x/n}] \cdot yH_2O \qquad (1)$$
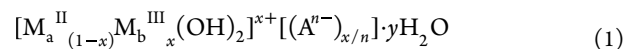
where M_a^{II} is a divalent cation (Mg^{2+}, Fe^{2+}, Zn^{2+}, etc.), M_b^{III} is a trivalent cation (Mn^{3+}, Fe^{3+}, Cr^{3+}, etc.), A^{n-} is the intercalated anion with $n-$ charge (NO_3^-, Cl^-, PO_4^{3-}, etc.), and x is the molar ratio of $M^{3+}:(M^{2+} + M^{3+})$.[40] The metal/ hydroxide complexes share octahedra edges and construct 2D infinite sheets, where the hydroxyl groups can bond to the interlayer anions and water molecules by weak hydrogen bonding, thus allowing LDHs to have high ion exchangeability. These physical and chemical properties imply that LDHs are suitable adsorbents for phosphate removal and recovery from wastewater.[41−43]
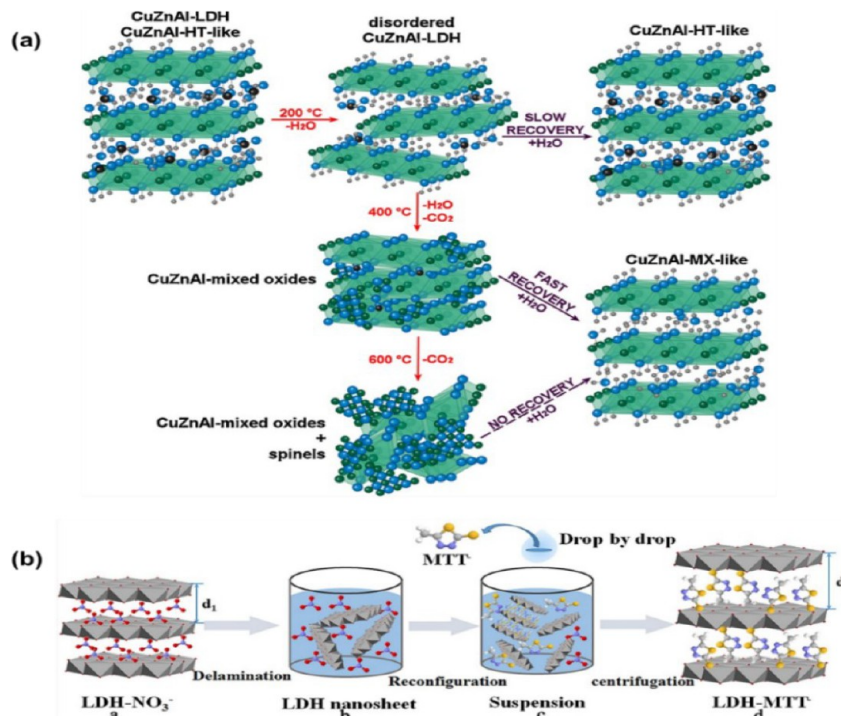
Figure 2. Schematic representation of self-assembly LDH by the reconstruction method. (a) Illustrated "memory effect" induced CuZnAl-LDH structural transformations. (b) Delamination−reconstruction process of LDH-MTT. (Panel a reprinted with permission from ref 65. Copyright 2013 Elsevier. Panel b reprinted with permission from ref 62. Copyright 2018 Elsevier.)

2.2. Synthetic Methods of LDH.

To date, the number of studies discussing the applications of LDH-based materials in phosphate adsorption has increased dramatically. Various synthetic methods can be applied to produce LDHs and directly affect their characteristics, such as morphology, crystallinity, element compositions, surface area, and active sites, thereby changing the phosphate adsorption performance. The aim of the following section is to provide an overview of the common methods for preparing LDHs with versatile properties.

2.2.1. Co-precipitation Method.

Among all of the synthetic methods, co-precipitation is well-established and highly applied in the laboratory due to its simplicity, inexpensiveness, low facility requirement, and high yield.[44] Typically, co-precipitation is conducted by slowly adding the predetermined molar ratio of divalent and trivalent (M^{II} and M^{III}) metal cations into an alkaline solution.[45−47] After the metal precursors are mixed and dissolved in the alkaline solution, homogeneous nucleation generates due to supersaturation, facilitating seed-assisted growth of LDHs.[48] Notably, the type and number of metal precursors and selected anions can be regulated, enabling LDHs to be designed for a particular target. The pH value is also an important factor that affects the LDHs structures and compositions. Li et al. prepared NiAl-LDH at various pH conditions and discussed the transformation mechanism of NiAl-LDH between nitrate and carbonate forms.[49] It was found that when the pH value increased, the Ni/Al molar ratio increased and nitrate hydrotalcite tended to transform to carbonate hydrotalcite. However, the drawback of co-precipitation is that the synthesized LDHs often suffer from low crystallinity, aggregation of the nanoparticles, and broad particle size distribution.

2.2.2. Hydrothermal Process.

The hydrothermal process is another preferred method for preparing LDHs.[50] Typically, the metal precursors are placed into a closed Teflon-lined stainless-steel vessel (autoclave) at a temperature between 80 and 200 °C, ranging from several hours to days under high-pressure conditions.[51] The foremost advantage of the hydrothermal process is that it allows controlling of the LDH layer structure with good crystallinity. For example, Joy et al. prepared Zn_2Al-NO_3-LDH by dissolving 4 mmol of Zn $(NO_3)_2 \cdot 6H_2O$ and 2 mmol of $Al(NO_3)_3 \cdot 9H_2O$ in 100 mL of water with an appropriate amount of NaOH and transferring it into an autoclave at 100 °C for 16 h.[52] However, the hydrothermal process still suffers from several challenges, such as limited reaction volume, incapability to observe the process, and inhomogeneous particle-sized precipitation, which hinder industrial applicability.[53,54]

2.2.3. Urea Hydrolysis.

Urea hydrolysis has been recognized as a method for producing well-crystallized LDHs. Basically, a slow hydrolysis process occurred when urea is soluble in water, which allows people to control the precipitation rate and makes the dispersed LDH precipitation more homogeneous.[55] Costantino et al. have demonstrated that the urea hydrolysis method is capable of preparing various LDHs with a narrow particle size distribution in a short time since 1998.[56] Afterward, the urea method attracted significant attention to investigate the preparation of LDHs with controllable particle sizes by adjusting synthetic parameters.[57,58] To date, the optimum conditions for urea hydrolysis have been suggested by adopting a urea:metal ion ratio of around 3.3 with 0.5 M urea.[59] Compared with other methods, urea hydrolysis does not produce chemical waste because its conversed products can be employed as the precipitating agent and intercalating anions.[60] More recently, hexamethylenetetramine (HMT), instead of urea, has been reported for homogeneous precipitation of LDHs with high crystallinity.[61]
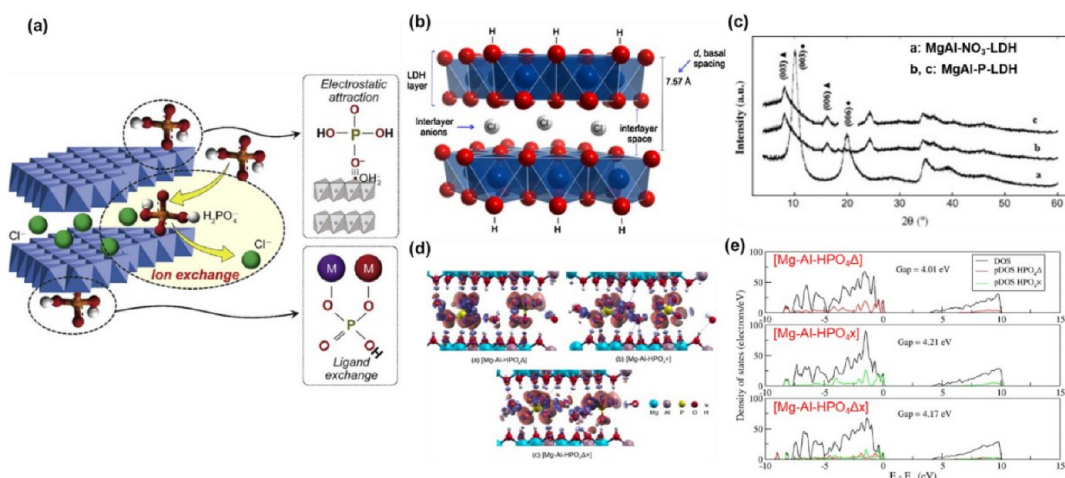
Figure 3. Characterization of phosphate adsorption. (a) Schematic illustration of phosphate adsorption mechanisms includes electrostatic attraction, ion exchange, and ligand exchange. (b) Illustration of d_{003} basal spacing (7.57 Å), LDH layer thickness (4.8 Å), and interlayer space. (c) XRD patterns of before (MgAl-NO$_3$-LDH) and after phosphate adsorption (MgAl-P-LDH). (d) LDH models with different phosphate anion orientations after optimization. The blue region presents the depletion of charge density, and the red region indicates the increasing charge density. (e) Density of states (DOS) and projected density of states (PDOS) for three different models. (Panel a reprinted with the permission from ref 67. Copyright 2019 Elsevier. Panel b reprinted with permission from ref 75. Copyright 2017 Elsevier. Panel c reprinted with permission from ref 77. Copyright 2014 Elsevier. Panels d and e reprinted with permission from ref 12. Copyright 2018 Elsevier.)

2.2.4. Reconstruction Method. Though the anion exchangeability allows us to design various LDHs intercalated with desired anions, how to intercalate macromolecular anions into LDH interlayers remains a challenge. To overcome the limitations of the small interlayer space and integrated hydrogen bonding between LDH layers, synthesizing single-layer LDH nanosheets has aroused extensive attention because they can serve as building blocks to self-assemble with other anions.[62] Recent efforts have been made to produce LDH monolayers, such as electrophoretic or layer-by-layer (LbL) methods.[63,64] Alternatively, the reconstruction method is an efficient approach to producing monolayers or nanosheets of LDHs. The reconstruction method can be thought of as a delamination–reassembly procedure based on the natural "memory effect" of LDHs (illustrated in Figure 2a).[65] Since Adachi-Pagano et al. confirmed the delamination of ZnAl-LDH to reconstruct Zn$_2$Al-[C$_{12}$H$_{25}$SO$_4$·nH$_2$O]-LDH by using butanol as surfactants for the first time in 2000,[66] various works have been reported to produce single-nanosheet LDH for reconstruction method. Liu et al. dispersed ZnAl-NO$_3$-LDH into formamide under ultrasonic and mechanical stir treatments for delamination, followed by drop-wisely introducing 5-methyl-1,3,4-thiadiazole-2-thiol (MTT) to reconstruct LDH-MTT (Figure 2b).[62]

2.3. Phosphate Adsorption Mechanism. Phosphate ions removed by the LDHs from water can mainly derive from the following mechanisms: electrostatic attraction by LDH layers, ion exchange, and ligand exchange with the interlayer anions, as shown in Figure 3a.[67−69] Normally, the electrostatic interaction occurs between the positively charged layer and the negative anions. The high-valence metal cations in LDH layers can also perform as Lewis acid, which has a higher tendency to form complexes with Lewis base of phosphate ions.[70] On the other hand, if the LDHs have weak electrostatic interaction with the interlayer anions, ion exchange will easily occur, resulting in the replacement of interlayer anions by phosphate ions.[71] The charge density of the interlayer anions determines the magnitude of electrostatic interaction with

lamella and the tendency to replace other anions.[72,73] For example, NO$_3^-$ intercalated NiAl-LDH exhibits higher phosphate uptake than the CO$_3^{2-}$ intercalated one, which results from the smaller valence of NO$_3^-$ that can be easily replaced by PO$_4^{3-}$.[74] For the ligand exchange process, phosphate acts as entering ligands and replaces the hydroxyl groups (M-OH) on the LDHs surface, where the metal cation can directly bond to the OH on phosphate.[75,76] The ligand exchange reaction is due to a robust covalent bond formed between the unfulfilled-valence surface of LDH and phosphate ions.

2.3.1. Characterization of Phosphate Adsorption by LDHs. Various characterization techniques enable us to understand the phosphate adsorption behavior. The removal of phosphate by LDHs through the anion exchange process can be confirmed by X-ray diffraction (XRD). Novillo et al. discussed the LDH structural variations of MgAl-NO$_3$-LDH after phosphate adsorption.[77] The two characteristic symmetry peaks at 2θ values below 30° are regarded as the basal planes (003) and (006) of layer-structured LDHs. The sharp reflection of the (003) plane corresponds to the basal spacing d_{003}, which is composed of interlayer space and layer thickness (around 4.8 Å for MgAl-LDH),[60] as shown in Figure 3b.[75] After exposure to phosphate solution, the (003) plane shifts toward the lower 2θ value due to the enlargement of basal distance, confirming phosphate's intercalation into the LDH through the ion exchange process (Figure 3c).[77]

Fourier transform infrared spectroscopy (FTIR) analysis is also a useful spectroscopic method for elucidating the interaction of phosphate ions and LDHs. Yang et al. explored the phosphate adsorption mechanism using the CO$_3^{2-}$ intercalated MgA-LDH and ZnAL-LDH.[78] Before phosphate adsorption, the intense peaks observed at 1631 and 3436 cm^{-1} arise from the presence of water molecules. After phosphate adsorption, a new peak that appeared at 1039 cm^{-1}, implying the bending vibrations of adsorbed phosphate (M-P-O), suggests that the surface hydroxyl groups (M−OH) of LDHs could be ligand exchanged by the adsorbed phosphate.

X-ray photoelectron spectroscopy (XPS) can provide more detailed investigations of the chemical interaction between adsorbed phosphate and the LDHs surface. Lai et al. demonstrated thorough investigations of bindings and oxidation states of metal cations of GO/MgMn-CO$_3$-LDH for phosphate adsorption.[79] The ratio of metal carbonate decreased from 16.4 to 7.1% after phosphate adsorption due to the ligand exchange process, replacing CO$_3^{2-}$ with phosphate. Since phosphate is pH-related in solution, it exists differently as H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$ with pK_1 = 2.12, pK_2 = 7.21, and pK_3 = 12.67, respectively.[80] At low pH, it presents as unipositive (H$_2$PO$_4^-$) ions; at pH values ranging from 7 to 10, it primarily exists in the form of HPO$_4^{2-}$, while in the pH region above 13, PO$_4^{3-}$ becomes the dominant species.[81] Feng et al. proposed that pH plays a vital role in determining phosphate adsorption capacities,[68] where the synthesized LDH hydrogels achieved the maximum phosphate adsorption capacity of 19.8 mg/g at pH from 2 to 4. As the pH values increased, the adsorption capacity decreased due to the electrostatic repulsion between the negatively charged LDH surface and phosphate ions. Similarly, at strongly acidic conditions (pH < 2), the phosphate adsorption capacity was limited due to the transformation of H$_2$PO$_4^-$ to H$_3$PO$_4$, thus forming the blockage of ligand exchange between phosphate and LDH surface. Hence, ζ potential analysis provides an efficient approach for optimum phosphate adsorption. When the solution pH is lower than the pHzpc of LDHs, the hydroxyl groups in the layer surface would be protonated to $-$OH$_2^+$ and attract the negatively charged phosphate anions through electrostatic attraction. The shift of pHzpc can also confirm phosphate adsorption, which is attributed to a decrease in charge density in the adsorbent surface.[82]

2.3.2. Theoretical Investigations. Computational calculations such as density functional theory (DFT) are remarkable tools to provide information unobtainable experimentally, assist the characterization of materials, and predict some interesting properties at the molecular level. DFT calculations were performed to investigate the structure of a phosphate-containing LDH: [Mg$_8$Al$_4$(OH$_{24}$)][(HPO$_4$)$_2$·6H$_2$O]Mg-Al with different anion conformations for sustainable phosphate release in agriculture.[12] Three structures with this chemical formula, [Mg-Al-HPO$_4\Delta$], [Mg-Al-HPO$_4\times$], and [Mg-Al-HPO$_4\Delta\times$], were built with two different orientations of phosphate anions in the interlayer region of layered double hydroxides (Figure 3d). Figure 3e shows the calculated electron states of these three structures, where the lowest band gap is 4.01 eV for both phosphate anions that are face- and corner-sharing with an adjacent hydroxide layer, while the LDH with both phosphate anions in edge-sharing with both adjacent hydroxide layers has the highest band gap (4.21 eV). The most stable structure presented the highest band gap, demonstrating the optimization route for LDH-based slow-release phosphate fertilizers. Other efforts are also made to calculate the relative binding energies of the interlayer anions for anion exchange reactions.[83,84] Besides, Lai et al. calculated the adsorption energies of various molecules,[80] including HPO$_4$, SO$_4$, NO$_3$, and Cl, that were 1.42, 1.40, 0.73, and -2.63 eV, respectively, which provide the information of the selectivity of LDH toward phosphate in the presence of competing ions.

2.4. Phosphate Adsorbability. To effectively examine the phosphate removal system, various models are applied to figure out the actual interaction mechanism between the phosphate

ions and adsorbent. The information on phosphate adsorption isotherms, kinetics, and selectivity is crucial for practical phosphate regulating applications, which will be discussed in detail in the following section.

2.4.1. Adsorption Isotherms. The adsorption isotherms of phosphate removal by LDHs commonly follow two types: (1) Langmuir and (2) Freundlich models.[85,86] The Langmuir isotherm model defines that every active adsorption site homogeneously covers the adsorbent surface and forms a monolayer of adsorption behavior.[87] The Freundlich model describes the adsorption behavior on the heterogeneous surface with uneven active sites and energies. In addition, adsorption capacity increases as the initial adsorbate concentration increases.[14] Azimzadeh et al. prepared MgAl-LDH and their functionalized biochar and hydrochar forms for adsorption isotherms investigations.[88] The results indicated that the Langmuir model could better fit the adsorption data of all of the LDH composites. However, some studies reported that the phosphate adsorption by LDH is in better agreement with the Freundlich model.[89,90] Hence, the Sips model, a combined form of Langmuir and Freundlich models,[91] is proposed to describe the phosphate adsorption system in some works.[92]

2.4.2. Adsorption Kinetics. Four classical kinetic theories are widely applied to modeling phosphate adsorption systems by LDHs:[93] pseudo-first-order, pseudo-second-order, Elovich, and the intraparticle diffusion models,[94,95] which are expressed by the following equations:

pseudo-first-order (PFO) model:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{2}$$

pseudo-second-order (PSO) model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Elovich model:

$$q_t = \frac{1}{b} \ln(abt) = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \tag{4}$$

diffusional model:

$$q_t = k_i t^{1/2} + C_i \tag{5}$$

where q_e and q_t (mg g^{-1}) are the amount of adsorbed phosphate at equilibrium and time t, respectively; k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the rate constants of the PFO and PSO models, respectively; a (mg g^{-1} h^{-1}) is the initial adsorption rate constant of the Elovich model; b (mg g^{-1}) is the desorption rate constant; k_i is the intraparticle diffusion rate constant (mg g^{-1} h$^{-1/2}$); and C_i represents a constant in the intraparticle diffusion equation.[96] Most published works use the PSO model to predict the experimental phosphate adsorption data by LDHs and calculate the adsorption rate constants.[14,67,97−99] For instance, the PSO model can well-fit the phosphate removal by La-CaFe-LDH reported by Yuan et al., indicating a chemisorption process.[100] Interestingly, the Elovich model, an empirical equation considering the contribution of desorption, is reported to be the most suitable for describing the kinetic phosphate adsorption onto Ca$_2$Al-LDH.[101] Novillo et al. elucidated a multistep phosphate adsorption process: (1) the diffusion of phosphate from the aqueous solution to the external surface of LDH, (2) a gradual
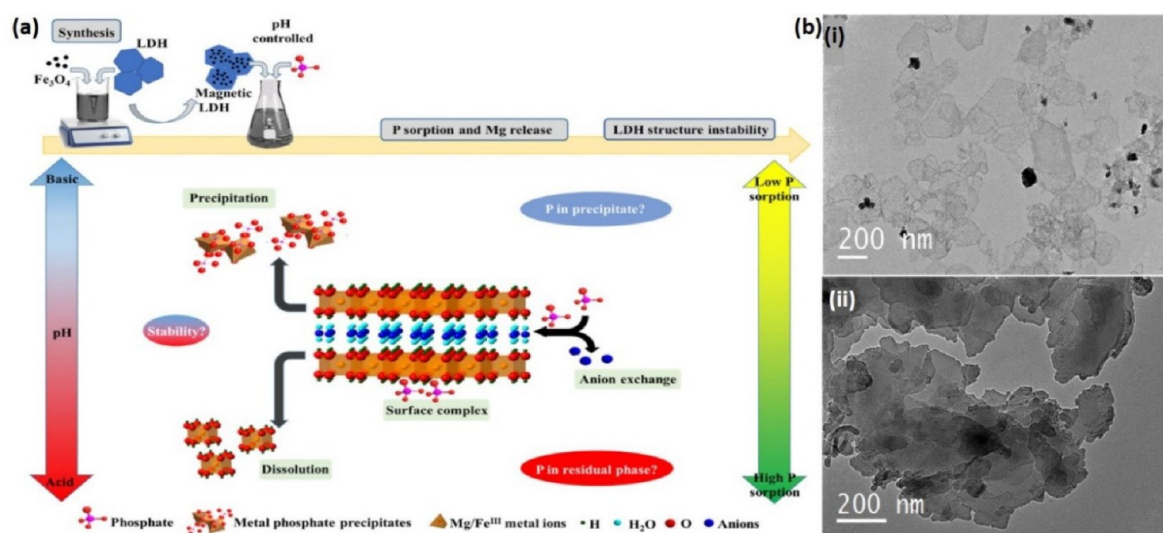
Figure 4. Characterizations of LDH structural stability after phosphate adsorption. (a) Schematic illustration of the phase changes and P sorption processes, and (b) TEM images of (i) MnFe-Cl-LDH and (ii) MnFe-CO$_3$-LDH. (Panel a reprinted with permission from ref 40. Copyright 2020 Elsevier. Panel b reprinted with permission from ref 110. Copyright 2022 Elsevier.)

adsorption stage where the intraparticle diffusion is the rate-limiting process, and (3) the intraparticle diffusion starts to slow down to reach the equilibrium stage.[77] According to the above-mentioned kinetic investigation, phosphate adsorption by LDHs involves multiple mechanisms, which agree with previous studies.

2.4.3. Selectivity. Selectivity toward phosphate is an essential concept for treating water with either high or low concentrations of phosphate. The challenge mainly results from the variety of competing ions in natural water or wastewater. Besides, the high hydration energy of PO$_4^{3-}$ (-2773 kJ mol^{-1}), compared with other anions (SO$_4^{2-}$ of -1090 kJ mol^{-1}, HCO$_3^-$ of -368 kJ mol^{-1}, and Cl$^-$ of -347 kJ mol^{-1}), makes it more difficult to move across from liquid phase to other phases.[102,103] Though efforts have been made to compare LDHs anionic exchange selectivity in the following order:[14] NO$_3^-$ < Br$^-$ < Cl$^-$ < F$^-$ < OH$^-$ < SO$_4^{2-}$ < CrO$_4^{2-}$ < HAsO$_4^{2-}$ < HPO$_4^{2-}$ < CO$_3^{2-}$. Zhao et al. systematically investigated molecular dynamics (MD) simulations and DFT methods to study the ton exchange reaction.[83] The acid-based property is proposed for selective phosphate adsorption through the H-bonds.[104] This property allows phosphate to undergo protonation (HPO$_4^{2-}$ and H$_2$PO$_4^-$) as a function of solution pH. HPO$_4^{2-}$ and H$_2$PO$_4^-$ can serve as both H-bond donors and acceptors, forming H-bonds with target sorbents at adjusted pH values.[104,105] The brucite of the structure LDH layers possesses abundant hydroxide groups that can be replaced by phosphate, leading to a covalent chemical bond between the ligand and metal atoms. Some anions such as chloride, nitrate, and carbonate generally form bonding to a single metal atom (outer-sphere complex), while phosphate can attach through one or two metal atoms with one or two oxygen bonds.[106] The stronger interaction offers LDHs a more significant driving force for selective phosphate adsorption.[107]

2.4.4. Influence of Metal Ions Composition. Due to the flexible and controllable design of the composition of metal ions on the laminates in the LDH structure, different divalent and trivalent metal ions would result in a wide range of LDH materials with varying performances of phosphate adsorption. For example, Ashekuzzaman et al. demonstrated the influence

of Ca- and Mg-based LDHs (trivalent, Al^{3+} and Fe^{3+}; interlayer anion, NO$_3^-$ and Cl$^-$) for removing phosphate from water.[97] The Ca-based LDHs showed 85−99% P removal, whereas Mg-based LDHs only exhibited <50% P removal under the same operating conditions. However, the removal mechanism by calcium-phosphate precipitation made Ca-based LDHs in-applicable for regeneration and reuse due to the loss of layered structure. In a recent study by Cao et al., La^{3+} was used as a trivalent ion to synthesize five different LDHs by manipulating the M^{2+} ions (Ca, Mg, Co, Ni, and Cu) to investigate phosphate adsorption systematically.[108] CaLa-LDH showed the highest phosphate adsorption capacity of 194.04 mg of P/g compared to the other four LDHs (94.19, 28.85, 21.00, and 19.57 mg of P/g for CoLa-LDH, MgLa-LDH, CuLa-LDH, and NiLa-LDH, respectively). According to the XPS spectra, CaLa-LDH exhibited an apparent M-OH bonding decrease as well as the conversion of Ca-C to Ca-P bonding, which indicated effective phosphate adsorption involving inner-sphere complexation, ion exchange, and chemical adsorption.

2.4.5. LDH Structural Stability. LDH materials belong to a class of inorganic functional layered materials that exhibit a diverse range of anionic layered structures, which is achieved by controlling the structure of the basal layers and the interlayer ions and molecules, as depicted in Figure 1b.[109] Though the adsorption−desorption of P by LDHs has been extensively studied, the practical applications for wastewater treatment suffer from low stability and decreased adsorption capability due to pH variation.[110] Lu et al. prepared MnFe-LDH/magnetic composite as a P adsorbent, with a focus on tuning the stability of LDHs under different pH and P concentration conditions, as shown in Figure 4a.[40] At pH 5, the LDH composite reached a high P adsorption capacity of 80 mg of P/g but with an increased LDH dissolution rate, resulting in the formation of ferrihydrite components confirmed by Mössbauer spectroscopy. At neutral conditions, more than 60% of LDH dissolved within 60 min. In alkaline pH conditions, LDH can maintain stability but its P sorption capacity decreased remarkably. The XRD patterns show a significant decrease in LDH basal (003) and (110) reflections after P adsorption, indicating the dissolution of the LDH phase
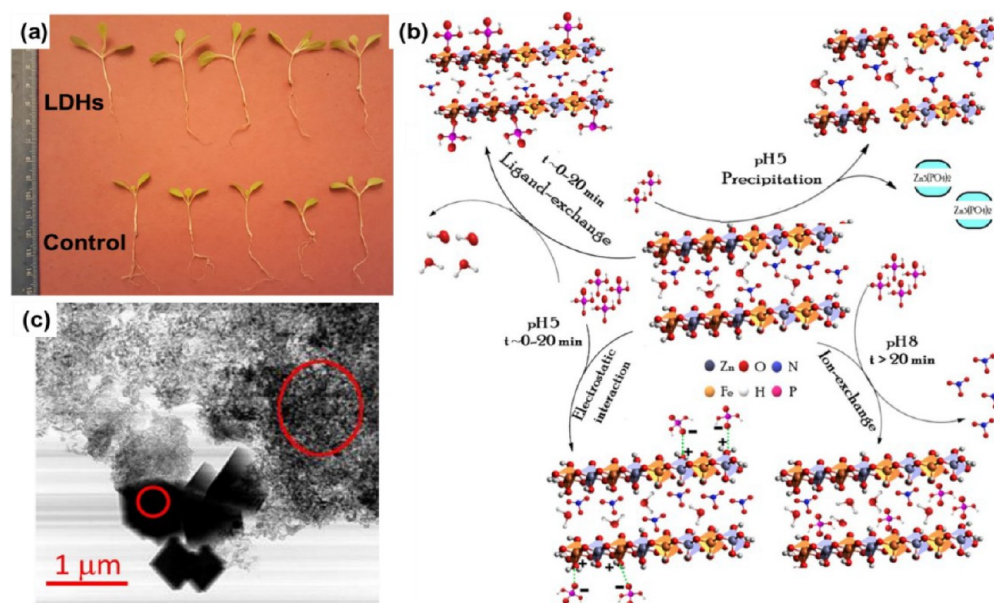
Figure 5. Versatile binary LDHs for phosphate adsorption applications. (a) Comparison of lettuce seedling growth bioassay between control and P-laden MgAl-LDHs/biochar composite. (b) Illustration of the phosphate adsorption process onto ZnFe-LDH in various pH values and reaction times. (c) TEM images of the transformation products obtained after the interaction of CaFe-LDH with a phosphate solution. (Panel a reprinted with permission from ref 117. Copyright 2017 Elsevier. Panel b reprinted with permission from ref 119. Copyright 2020 Elsevier. Panel c reprinted with permission from ref 115. Copyright 2019 Elsevier.)

due to the precipitation of $Mg_3(PO_4)_2$, which is in accordance with other studies in phosphate adsorption by Mg_2Fe-LDH.[111] Though the solubility of LDHs is reported to decrease in the divalent cation order: $Mg^{2+} > Mn^{2+} > Co^{2+} \approx Ni^{2+} > Zn^{2+}$,[112] the interlayer anions and charge density of LDH layers also affect the stability of LDHs.[113] In a recent report by Lu et al., MnFe-LDHs intercalated with Cl and CO_3 were synthesized to study P adsorption and dissolution behavior under neutral conditions.[110] Fast destruction of the LDH structure can be observed in $Mn^{II}Fe^{II}Fe^{III}$-Cl-LDHs with 70% of Mn released and the formation of $MnFe_2O_4$ within 2 h. On the contrary, CO_3^{2-} intercalated LDHs showed much lower Mn dissolution (5.4%). The TEM image of MnFe-Cl-LDH (Figure 4b(i)) exhibits small particles around the LDH plates, which may attribute to the dissolution of Mn and formation of amorphous ferrihydrite. Nevertheless, after oxidation of Mn^{II} to Mn^{IV}, $Mn^{IV}Fe^{III}$-CO_3-LDH shows a large size of LDH plates around 300 nm−400 nm (Figure 4b(ii)). These studies pave the way for controlling the stability of LDHs during P adsorption by designing metal compositions, interlayer anions, pH values, and oxidation of metal in LDH layers.

3. PROGRESS OF LDHS IN PHOSPHATE REMOVAL AND RECYCLING

The primary scope of this section is to provide an introduction to recent advances in achieving selective removal of phosphate from water by LDH-based materials. The following section also discusses a survey of the recently published achievements by diverse LDH composites.

3.1. Typical LDHs. The typical LDHs, combining only two different oxidation states of metal cations, are the most accustomed type of LDH for phosphate removal.[114] The divalent cations control the rate of dissolution of LDHs, and trivalent cations generate the hydroxide precipitates with negligible solubilities.[115,116] For example, Mg containing LDH of $Mg^{II}Fe^{III}$-LDH showed a high surface complexation of 52−

88%, contributing to more anion exchange (0−29%) for phosphate removal.[111] The phosphate removal efficiency can be varied by using different intercalated anions, such as Cl^- and NO_3^-, the molar ratio of M^{II}/M^{III}, and the pH value and exhibits a high phosphate uptake efficiency of 90−98% (12−13 mg of P/g) at a pH of 7.4. They claimed that the intercalated CO_3^{2-} reduces the ion exchange capacity due to a higher affinity for LDHs, which is in agreement with previous literature.[89] Wan et al. prepared MgAl and MgFe (3:1) LDHs to functionalize bamboo biochar for phosphate adsorption.[117] The results validated that biochar containing 40% MgAl-LDH exhibited a higher phosphate adsorption than MgFe-LDH, with >95% phosphate saturation achieved within 1 h, following the pseudo-second-order kinetics model. The inferior phosphate adsorption of MgFe-LDH is primarily due to the lower phosphate affinity and the difficult dispersity of MgFe-LDH.[118] Besides, the bioassay of early stage seedling growth was used to evaluate the impact of LDHs on lettuce leaves growth (Figure 5a). The concept and findings from this study explore a solution for recycling waste carbon to reclaim P in water and back to soils to boost food production.

Zn-based LDHs also show high potential in phosphate recycling and slow-release phosphate fertilizer. The sorption capacity of up to 22 mg of P/g with 90% phosphate removal efficiency by using the $Zn_{1.5}Al$-LDH was reported.[14] Either the Zn/Al molar ratio increases or decreases, the phosphate adsorption capacity can only remain at 70%. The results indicated that a lower metal molar ratio produces a high charge density in the layers, forming metal hydroxide groups that compete with the active adsorptive sites. On the other hand, the higher metal molar ratio causes the precipitation of zinc hydroxides. The results are similar to a recent comparison of adsorption and desorption of phosphate using ZnAl-NO_3-LDH, reporting that the lowest phosphate uptake of 1.97 mmol/g was obtained as the Zn/Al ratio increased to 3.[89] The low phosphate desorption rate ranging from 20 to 35% in a

Table 1. Application of Typical LDHs in Phosphate Adsorption/Desorption[a]

LDH type	Molar ratio	Textural properties	Adsorbent (g/L)	pH	Intercalation anion	Adsob capacity	Reg soln	Reg efficiency (%)	Reg cycle	Retained adsorption ratio (%)	Ref
CaFe	2:1		0.3	7	NO_3	47.4 mg of P/g	NaOH	91			97
MgAl	3:1	Pore:19 nm SSA: 84 m²/g	1	8.5	NO_3	98.3 mg of P/g	NaOH	<7	4	64	98
ZnAl	1.25:1	Pore: 11.7 nm SSA: 64.9 m²/g	1	7.6	NO_3	90.1 mg of P/g					14
MgAl	2:1	Pore: 19 nm SSA: 13.4 m²/g	0.3	5.5	Cl	76.1 mg of P/g					67
MgAl	4:1	SSA: 64.4 m²/g	5	7	NO_3	0.28 mmol/g	0.03 M KCl	22.5	5	15.7	133
CaAl	2:1		0.5	7	Cl	133.33 mg of P/g					121
ZnAl	3:1	Pore: 3.6 nm SSA: 133.2 m²/g	1–5	4.2	NO_3	102 mg of P/g					92
MgMn	3			8.5	Cl	7.3 mg of P/g	5 M NaCl + 0.1 M NaOH	82	7		134
ZnAl		SSA: 129 m²/g		6.5	CO_3	39.9 mg of P/g					135
CaFe	2:1		1	7	Cl	130 mg of P/g					115
ZnFe	2		0.5	2	SO_4	100%					136
ZnAl	2:3		5	7	NO_3	2.72 mmol/g	0.03 M KNO_3	36.3	5		89
ZnFe	2:1		0.5	6		36 mg of P/g	0.1 M NaOH + 0.1 M KNO_3 / 0.1 M NaOH + 0.1 M NaCl	84 / 80	6	72	119
MgAl	2:1	SSA:210 m²/g	1	6		84.4%	4 M NaCl + 0.1 M NaOH	80	3	~75	118
CaCr	2:1		2			98 mg of P/g					137
ZnAl			1	7.3	PMA	64.79 mg of P/g	0.1 M NaOH		3	83.5	138

[a]SSA, specific surface area; L, loading amount; DBS, dodecylbenzenesulfonate; Reg, regeneration; Ref, reference.
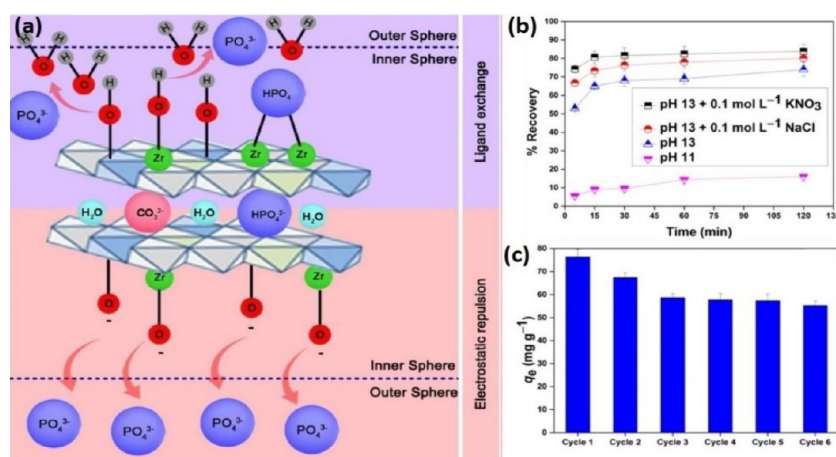
Figure 6. Investigation of P desorption from LDHs. (a) Proposed mechanism of phosphate desorption from am-Zr/MgFe-LDH by NaOH solution. (b) Influence of pH value and the composition of the solution on phosphate desorption from ZnFe-LDH. The results showed that NaOH + KNO₃ could reach a higher desorption percentage of 84%. (c) LDH showed excellent reusability for six cycles, where the adsorbent retained ~72% of its phosphate adsorption capacity. (Panel a reprinted with permission from ref 129. Copyright 2021 IOP Science. Panels b and c reprinted with permission from ref 119. Copyright 2020 Elsevier.)

0.03 M KNO₃ electrolyte, similar to the ionic strength of soil solutions, indicated that the synthesized LDH has potential for slow-release phosphate fertilizer. Gupta et al. demonstrated the synthetic ZnFe-LDH possesses a phosphate adsorption capacity of ~36 mg/g within 5 min coupled with excellent selectivity.[119] In XPS analysis, a larger binding energy difference can be observed for Zn 2p and Fe 2p peaks at pH 5 compared to that at pH 8, showing that the complexation mechanism dominated. For phosphate adsorption at pH 8, the Raman and XRD analyses showed no significant change between P-adsorbed LDH and pristine LDH, implying the ion exchange-controlled mechanism. Based on the kinetic analysis and comprehensive spectroscopic evidence, predominant mechanisms involved in the phosphate adsorption of ZnFe-LDH have been illustrated in Figure 5b. Calcium, which plays essential roles in both plant nutrition and soil health,[120] has been used to produce Ca-based LDHs for phosphate adsorption and fertilizer. Various Ca-based LDHs have been reported to possess high adsorption capacities up to 130 mg of P/g.[115,121,122] At high phosphate concentration ($[PO_4] > 100$ mg/L), the dissolution of Ca^{2+} from the LDH structure led to precipitation as hydroxyapatite, achieving high phosphate adsorption capacity. While at low phosphate concentration, ferrihydrite-like $Fe^{III}Ca^{II}$ disordered agglomerates formed and contributed to phosphate adsorption, where an agglomeration of nanocrystals can be confirmed by TEM analysis, as shown in Figure 5c.

3.2. Phosphate Desorption and LDHs Regeneration. Since phosphate is the primary source of nutrients for crop production,[123] there is an emerging demand for the recovery and reuse of nonrenewable phosphate.[124] Therefore, the versatile LDHs are tempting materials for designing favorable adsorbents that can repeatedly uptake excessive P-nutrient from water and gradually release it for agricultural production (Table 1).[125] Generally, abundant and low-cost alkali salts, such as KCl,[126] NaOH, NaCl,[127] and KNO₃,[40] are widely used to release the phosphates from LDHs. These salts can easily interact with LDHs because they can serve as Lewis bases and form ligands with the metal cations on the LDH surface, leading to the replacement of adsorbed phosphate.[128] For instance, the phosphate desorption of P-loaded CaFe-LDHs

was successfully performed using a 5% NaOH solution for 20 cycles with a desorption efficiency of 88%.[97] As the NaOH concentration increased to 20%, a higher desorption efficiency of 91% was achieved within four recycles, demonstrating the regeneration concentration's influence. In the 0.001 M NaOH solution, only ~16% of adsorbed phosphate can be recovered from ZnFe-LDH even after 2 h of contact duration. In contrast, the desorption study conducted at 0.1 M NaOH can reach up to ~70% of phosphate recovery.[119] The results agree with the previous literature that at a higher pH, the presence of competitive OH⁻ for the binding sites and the increased electrostatic repulsion facilitate the release of phosphate.[68] Nuryadin et al. precipitated P to hydroxyapatite (HAP) by adding CaCl₂ to a phosphate regeneration solution to promote phosphate recovery. The mechanisms of phosphate desorption by ligand exchange and electrostatic repulsion are shown in Figure 6a.[129] However, the major problem of the regeneration process using a high concentration of NaOH is the disposal of a high alkaline desorption solution. Therefore, the addition of metal ions in the P desorption process from LDHs has been proposed to tackle this issue.[130] Albeemi et al. investigated P removal and recovered by using Nanoscale zero valent iron (NZVI), the higher P recovered at pH-12.[131] Besides, the pH of the phosphate regeneration solution decreased from around 11 to the range of discharge standard ($6 <$ pH < 9).[132] Consequently, not only the P can be recovered effectively but also the pH of the regeneration solution can be reduced. Interestingly, other alkali salts such as NaCl display inefficient phosphate desorption performance due to the low affinity of chloride ions toward the LDHs layer. However, the combination of NaOH and NaCl significantly improves the phosphate desorption rate. The desorption behavior of GO/MgMn-LDH was investigated by sonication in 0.1 M NaCl and NaOH mixture, and the desorption efficiency of 85.8% was more significant than that in NaCl or NaOH alone.[80] Das et al. also reported that the combination of NaOH and NaCl exhibited more effective phosphate desorption by 10% than NaOH alone.[118] In panels b and c of Figure 6, a mixture containing NaOH + KNO₃ showed higher phosphate desorption than NaOH + NaCl, where only 11−19% loss in
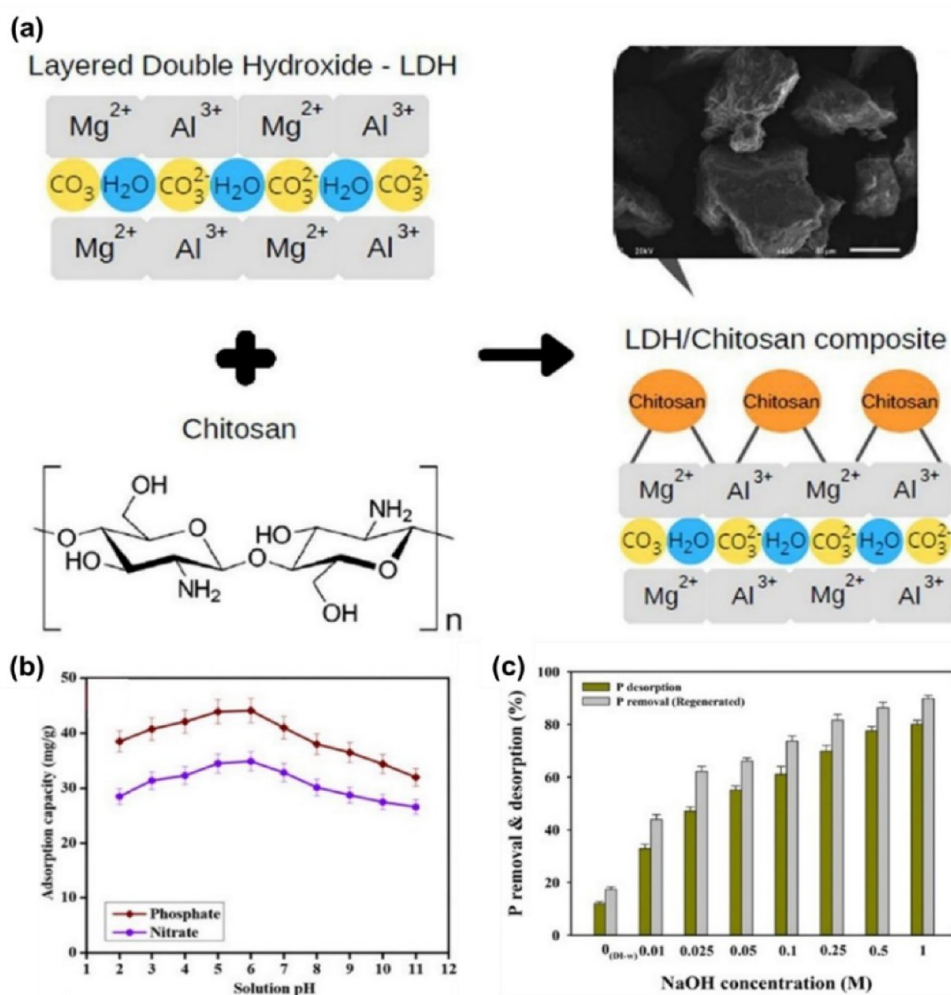
Figure 7. Phosphate adsorption/desorption performances by LDH/carbon materials composites. (a) Schematic mechanism of prepared LDH/chitosan composite. (b) Adsorption capacity of different pH and (c) NaOH concentration of desorption performance. (Panel a reprinted with permission from ref 148. Copyright 2023 Elsevier. Panel b reprinted with permission from ref 150. Copyright 2019 Elsevier. Panel c reprinted with permission from ref 149. Copyright 2019 Elsevier.)

adsorption capacity can be observed for ZnFe-LDH after six cycles of phosphate adsorption−desorption test.[119]

Considering the practical applications in the agricultural industry, avoiding the use of the highly alkaline solution to regenerate the P-adsorbed LDHs is a crucial challenge. Halajnia et al. reported a phosphate desorption rate of 15.7% from MgAl-LDH using a 0.03 M KCl solution.[133] More recently, a higher phosphate desorption rate of 36.3% was achieved for ZnAl-LDH by five successive desorption steps using 0.03 M KNO₃ as the regeneration electrolyte.[89] The partially reversible adsorption−desorption process indicated chemisorption behavior. The implications of these studies applying an electrolyte concentration similar to that of soil solutions validate the potential of LDHs as a slow-release phosphate fertilizer in agriculture.

3.3. LDH Composites. Though LDH-based adsorbents have been reported to successfully uptake and recycle P from wastewater, some works still face low stability and destruction of the LDHs structure during the adsorption−desorption process or acidic pH conditions. Therefore, current developments in material science focus on designing new LDH-composites with multifunctionality and enhanced efficiency of phosphate adsorption/release. Carbon related materials are widely used for P adsorption−desorption applications in wastewater treatment. Bio-carbon (BC),[139] activated carbon (AC),[140] and graphene-related materials,[141] due to the various functional groups, high specific surface area, and hierarchical porosity, are usually combined with LDHs to enhance the phosphate adsorption−desorption behaviors synergistically.[142,143] Peng et al. synthesized corn straw biochar-supported MgAl-LDH composites under various pyrolysis temperatures.[144] The results demonstrated produce exfoliated LDH dispersion with enlarged interlayer spacing, high specific surface area, and porosity, leading to superior adsorption capacities toward P and Cu ions. Porous biochars pyrolyzed at higher temperatures can serve as promising support to effectively exfoliate the nanosized LDHs by aqueous miscible organic solvent treatment, allowing long-term reusability for sustainable wastewater management. A recent study by Bolbol et al. proposed pine cone-derived LDH/BC as a sorbent for removing aquatic phosphorus.[145] Results showed that the P sorption on LDH/BC was pH-dependent, where the maximum P adsorption capacity was obtained at the pH value ranging from 2 to 4, agreeing with previous works.[72,89,146] Not only can the BC structure prevent LDHs from aggregation, thereby reducing active adsorption sites, but also the H-bond between

Table 2. Application of LDH Composites in Phosphate Adsorption/Desorption[a]

Composites	LDH	Composite material	Exp P concn, Ads, Temp	Adsorp capacity of pristine LDHs (mg of P/g)	Adsorp capacity of LDH composites (mg of P/g)	Reg soln	Reg efficiency (%)	Reg cycle	Retained adsorp ratio (%)	Ref
Carbon-based	MgAl	Chitosan	P concn: 50 mg/L; Ads: 1 g/L; Temp: RT	54.9	106.3	NaOH	68.6			148
	MgMn	Reduced GO	P concn: 0.1 mg/L; Ads: 1 × 1 cm² electrode /(200 mL)	26.0	70.8	0.01 M NaCl and NaOH	35.6	3		79
	ZnAl	Activated carbon from banana bract	P concn: 22.22 mg/L; Ads: 0.1 g/(50 mL)		80.3	0.1 M NaOH		7		150
	FeMg	Biochar from Douglas fir	P concn: 50 mg/L; Ads: 1 g/L; Temp: 25 °C	243.3	1279.6	1 M NaOH	8.7 mg of P/g	3	38	172
	NiFe	Reduced GO	P concn: 300 ppm		270	0.1 M NaNO₃		10	85	173
Magnetic materials	MgAl	Fe₃O₄	Ads: 1 g/L	Fe₃O₄: 4.6	33.4					174
	MgAl	Fe₃O₄ and SiO₂	P concn: 1 mg/L; Ads: 10 g/mL; Temp: RT		57.07	10 mM NaNO₃ + 100 mM NaOH		5	94.5	175
	ZnFe	MnFe₂O₄	P concn: 50 mg/L; Temp: RT	84.48	94.52	0.1 M NaOH		5	70	155
	MgAl	Al-doped Fe₂O₃	P concn: 1 mg/L; Ads: 5 g/(25 mL); Temp: RT		93.06	2 M NaOH / 1 M NaOH / 0.5 M NaOH / 0.1 M NaOH	80.8 / 80.1 / 76.7 / 70.2	4	65.2	176
Other materials	MgFe	PVDF, PVA, PEG (polymer)	P concn: 2 mg/L; Ads: 50 g/mL; Temp: 30 °C		8	1 M NaOH	90.26	3	81.35	177
	MgAl	ZIF-8 (zeolite)	P concn: 30 mg/L; Ads: 1 g/mL	36.18	68.53	1 M NaOH		4	41	162
	MgAl	Zr		69.64	99.35			5	51	178
	MgFe	ZrO₂	P concn: 10 mg/L; Ads: 0.1 g/L	17.99	35.40	2 M NaOH	87.37	7	78	170

[a]Concn, concentration; Ads, adsorbent concentration; Temp, temperature; P, phosphate; Reg, regeneration.
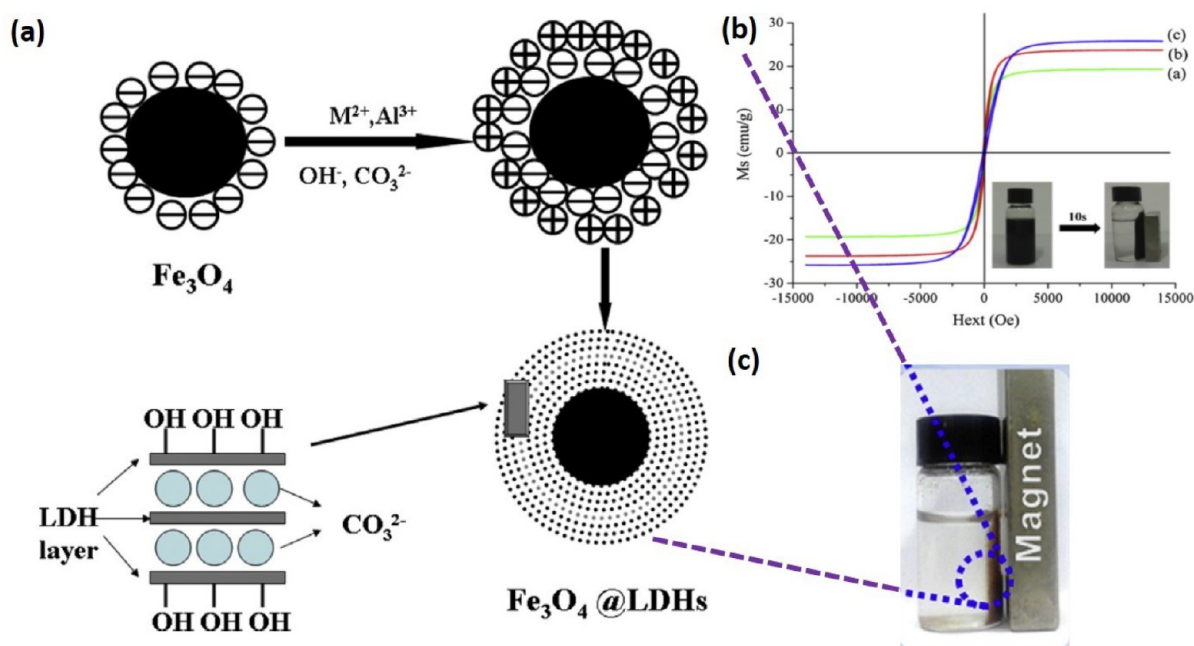
Figure 8. Phosphate removal by LDH/magnetic materials composites. (a) Schematic representation of the preparation of Fe_3O_4@LDHs. (b) Magnetization curves of LDH composites. (c) Photograph of P-adsorbed magnetic LDH composite separated by applied magnetic force. (Panels a and b reprinted with permission from ref 157. Copyright 2015 Elsevier. Panel c reprinted with permission from ref 159. Copyright 2020 Elsevier.)

LDH/BC and anions can foster phosphate adsorption. MgAl-LDH (3:1) can also grow on ball-milled biochar (BMBC) by co-precipitation, demonstrating a higher phosphate adsorption capacity of 52.6 mg of P/g at pH of 3[147] indicating the surface area dominated effect. Ribeiro et al.[148] investigated the P adsorption−desorption performance of the MgAl-LDH/chitosan shown in Figure 7a, showing two-times higher P adsorption and desorption performance compared to bare chitosan and LDH (Table 2). Similarly, ZnAl-LDH was grafted on banana bract-derived AC, which showed non-expensive, high surface area, universally accessible, and multiple reactive groups (carbonyl, hydroxyl, carboxylic, and phenolic groups), facilitating phosphate adsorption.[149] The phosphate adsorption mechanisms, such as ion exchange, surface complexation, and electrostatic attraction, were investigated in detail. The results also indicated pH-dependent phosphate adsorption behavior. The phosphate adsorption at alkaline conditions (NaOH) produced a negatively charged layered surface, which generates electrostatic repulsion between the phosphate ion and adsorbent as well as competitive OH^-, leading to decreased adsorption efficiency (Figure 7b), as discussed in the previous section.[150] The desorption test of the P-loaded LDH/AC composite was also performed with a solution of NaOH in different concentrations (Figure 7c). The regeneration results achieved a high P desorption efficiency of 78% after five consecutive adsorption/desorption cycles.[149] Graphene oxide (GO), a two-dimensional material, also attracts extensive attention for wastewater treatment[151] Nevertheless, the low selectivity toward pollutants of interest limits the practical applications of GO.[152] Therefore, Lai et al. prepared biotemplated GO/MgMn-LDH composites with a significantly improved phosphate adsorption capacity of 244.08 mg of P/g.[80] Such a high adsorption capacity resulted from intercalated biochemical substances from natural leaves, which not only provided a high surface area of 91.39 m^2/g with mesoporous structure but also contributed to H-bond with phosphate. The

P desorption performance was tested using the combination of 0.1 M NaCl and NaOH solution and achieved a desorption rate of 85.8%. The desorption can also maintain efficiency up to 80% after three phosphate uptake-release processes, which exhibited the alternative potential for phosphate management in wastewater with enhanced P adsorption/release performances.

Though intensive research has demonstrated that different adsorbents can effectively adsorb phosphate in wastewater with solid physicochemical properties characterization,[153] how to separate the P-loaded adsorbent from the aqueous solution after the adsorption process becomes a crucial issue. Filtration and centrifugation are the most common techniques to separate the adsorbent from the aqueous solution, which limits the scalable practices in real water.[88,111] Therefore, the magnetic separation technology has arisen broad interest, which can easily separate the adsorbents from the solution by applying the external magnetic field.[154] To tackle this bottleneck, the combination of magnetic Fe_3O_4 nanoparticles with LDH has been proposed to effectively remove adsorbents from the aqueous solution after the phosphate adsorption process.[40,155] Fe_3O_4 has been considered a promising adsorbent due to its superparamagnetic properties, durability, low toxicity, low cost, high biocompatibility, chemical stability, and large surface area.[156] Yan et al. prepared ZnAl-LDH/Fe_3O_4 composite with a core−shell structure for phosphate adsorption with easy magnetic separation.[157] Figure 8a illustrates the synthesis mechanism of Fe_3O_4@LDH composites through the electrostatic attraction between the positive metal cations and negatively charged functional groups on the ferric oxide surface. The superior phosphate adsorption capacity of 36.1 mg of P/g was contributed from a high surface area of 133 m^2/g with mesoporous-sized ZnAl-LDH nanoparticles. Panels b and c of Figure 8 clearly demonstrate the separation of LDH adsorbent from aqueous solution under magnetic force, displaying a ferromagnetic LDH composite
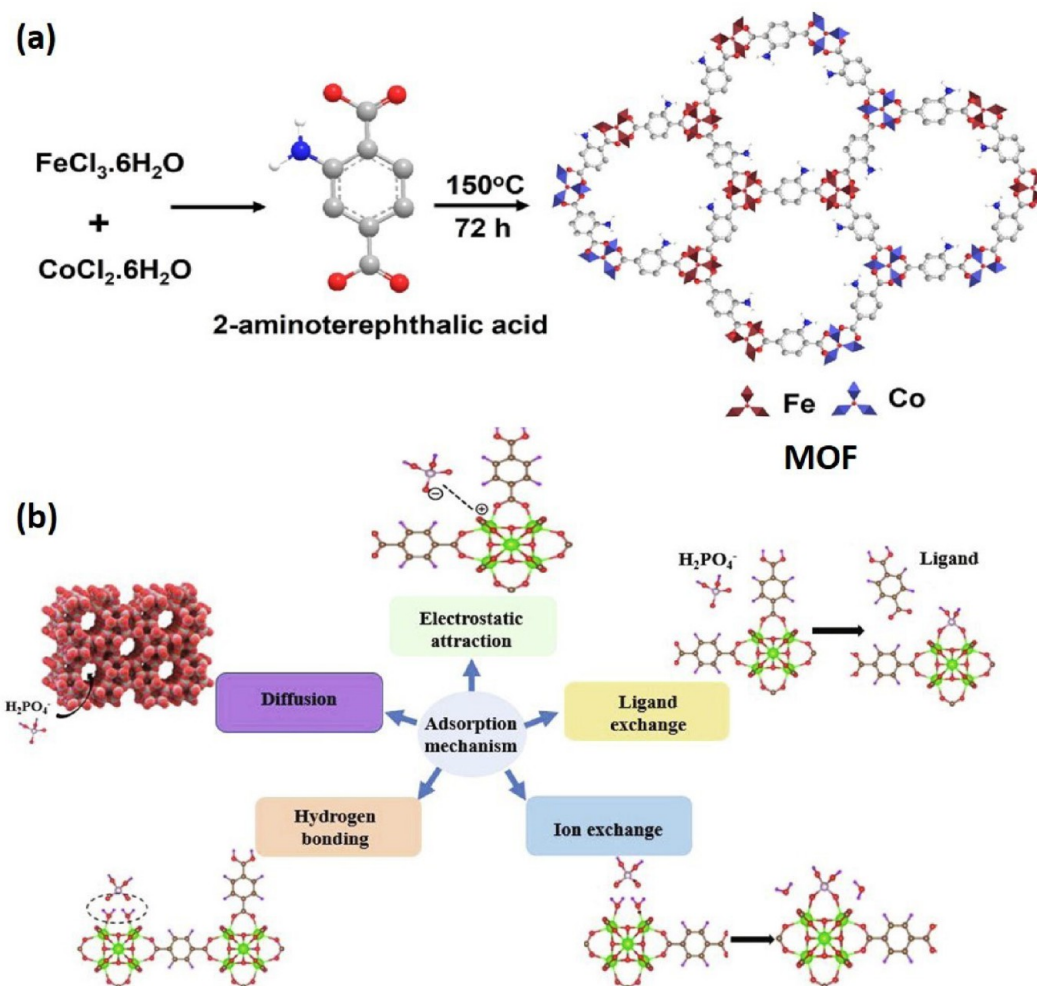
Figure 9. Pollutant removal by MOFs materials composites. (a) Schematic illustration of preparing MOFs. (b) Different mechanisms of P removal using LDH/MOF. (Panel a reprinted with permission from ref 164. Copyright 2023 Elsevier. Panel b reprinted with permission from ref 163. Copyright 2022 Elsevier.)

material for practical wastewater treatment. In a recent work by Lee and Kim, the prepared magnetic LDHs exhibited good paramagnetisms.[158] The superior phosphate uptake capacity obtained at 39.1 mg of P/g for LDH/magnetic composite due to the enhanced surface area of 73.3 m²/g. The initial P concentration (10 mg of P/L) decreased to 6.4 mg of P/L for the first 2 h reaction time and then reached the saturation of 3.1 mg of P/L after reaction for 12 h. Most magnetic LDH composites demonstrate stable phosphate adsorption performance between pH 4 and 10. The adsorbed P could be successfully recovered using the NaNO₃-NaOH solution, and the regenerated LDH composites could be reused for the following phosphate adsorption process. Due to enhanced adsorption capacities, ease of the magnetic separation process, high stability, and good reusability, LDH/magnetic materials composites are expected to be applied in practical phosphate removal from real water.

Metal−organic frameworks (MOFs) are formed by cross-linking organic−inorganic molecules via coordination covalent bonds, which possess a 3D porous crystalline structure with a high surface area (7800 m²/g), as presented in Figure 9a.[160] Additionally, the stretchable bonds in the structure enable MOFs to be a promising adsorbent for pollutants adsorption. Their structure can be regulated by selecting different metal ions and organic bridging ligands, allowing us to modulate their properties, such as porosity, surface area, richness of active sites, and functionality. For example, Xie et al. proposed a Fe-based MOF, MIL-101, and NH₂-MIL-101 to remove phosphate from aqueous solutions.[161] NH₂-MIL-101 has a higher adsorption capacity than MIL-101, which may result from the amine functional groups that can interact with phosphate ions, and the different mechanisms were discussed in Figure 9b. In a recent study by Dai et al., MgAl-LDH@ZIF-8 composites were prepared by in situ growth of zeolite imidazole framework-8 (ZIF-8) on MgAl-LDH for phosphate removal in wastewater.[162] Compared with pure ZIF-8 and MgAl-LDH, the prepared LDH/MOF composite has a higher phosphate removal efficiency of up to 99%. However, there are still some challenges in preparing LDH/MOF composites due to the water-resistant property of MOFs, making it inevitable to use toxic solvents, such as methanol, DMF, etc., in the synthesis process. Besides, though various approaches have been achieved to fabricate LDH/MOF composites for pollutants adsorption application, almost no study can be found for selective P removal.[163] Consequently, it is worth exploring new strategies for developing a green and economical preparation of LDH/MOF composites for sustainable P adsorption−desorption applications.
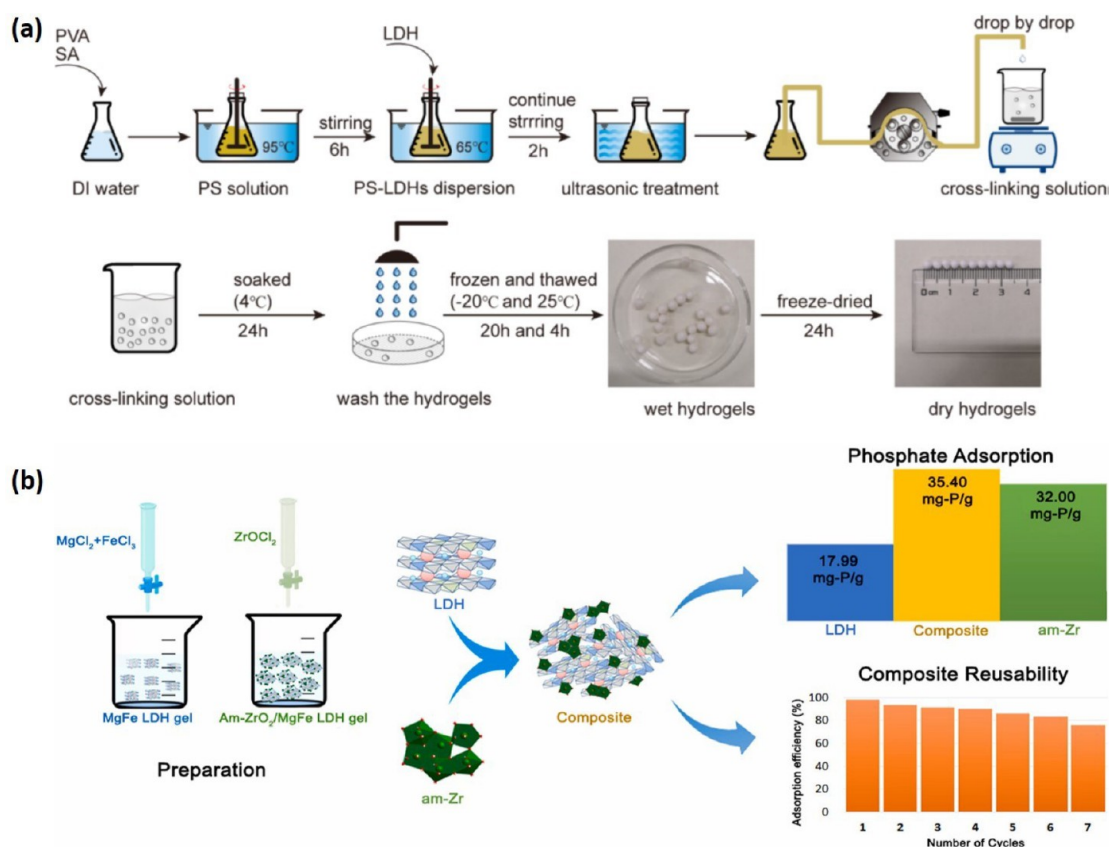
Figure 10. Phosphate removal by versatile LDH composites. (a) Preparation of hydrogel beads of PS-LDH. (b) Phosphate adsorption−desorption schematic illustration of amorphous ZrO$_2$/MgFe-LDH. (Panel a reprinted with permission from ref 68. Copyright 2022 Elsevier. Panel b reprinted with permission from ref 170. Copyright 2021 Elsevier.)

The growing requirement for crop productivity has aroused intensive attention to nutrient management. Significant progress has been achieved in phosphate adsorption from water by assembling LDHs on other functional materials to surmount the limitations of bare LDHs.[165] Polyvinyl alcohol (PVA) can be gelled to hydrogels through a simple physical or chemical cross-linking process.[166] These hydrogels commonly possess three-dimensional porous scaffolds with a large surface area of up to 56.07 m^2/g, which can be incorporated with LDHs for efficient P adsorption. Feng et al. developed a simple process by mixing PVA with sodium alginate (SA) to solve the insoluble problem in the aqueous solution, thereby obtaining a uniform dispersion for the preparation of LDH/polystyrene (PS) composite, as shown in Figure 10a.[68] A recent study also elaborated on the mechanism of the gelation process that can improve the affinity between the PS-La-LDH hydrogel and phosphate. Moreover, zirconia (Zr) has been reported to synthesize Zr-MgAl-LDH through a low-energy-consumed and eco-friendly process for phosphate removal.[167] The characterization results indicated that Zr-MgAl-LDH had low crystallinity, suggesting the formation of amorphous ZrO$_2$. It indicated that Zr was easily hydrolyzed to form a tetranuclear structure with a large amount surrounding hydroxyl ions, which can facilitate the ion exchange and ligand exchange processes with phosphate ions.[168] There is an intense interest in growing zirconium hydroxides or ZrO$_2$ on the LDH layers, which can control the crystal crystallinity and produce desired nanosized adsorbents for phosphate adsorption−desorption.[169] Nuryadin et al. synthesized amorphous ZrO$_2$/MgFe-LDH composites (Figure 10b) and studied the phosphate

adsorption−desorption behavior by different molar ratios of components in LDH composites.[170] The addition of ZrO$_2$ can improve the adsorption process even at low pH. In addition, the calcination process has been widely reported to significantly enhance the P adsorption performance due to the memory effect that collapsed layered structures can adsorb phosphate ions for reconstruction. Chitrakar et al. prepared Zr-modified MgFe-LDH and added Na$_2$CO$_3$ into the reaction solution, where the carbonate ions can play the role of exchangeable ions for phosphate adsorption.[171] Zr-modified MgFe-LDH material exhibited a poorly crystalline structure during the reassembly of LDH, facilitating the P adsorption process due to the weak interaction between LDH layers and intercalated anions.

In conclusion, innovative composite materials with enhanced P adsorption−desorption performance can undoubtedly be prepared by assembling LDHs with other desired functional materials. Given the considerable efforts and the remarkable performance obtained (summarized in Table 2), the potential of LDH composites as nanofertilizers is becoming real regarding solutions for phosphate management to meet the increasing food demand.

4. LDH-BASED MATERIALS AS SLOW-RELEASE FERTILIZERS

Conventional agricultural techniques are often associated with the intensive use of fertilizers to meet the growing requirement for food, leading to the inefficient use of nutrients by plants and severe damage to the environment. Not only is excessive
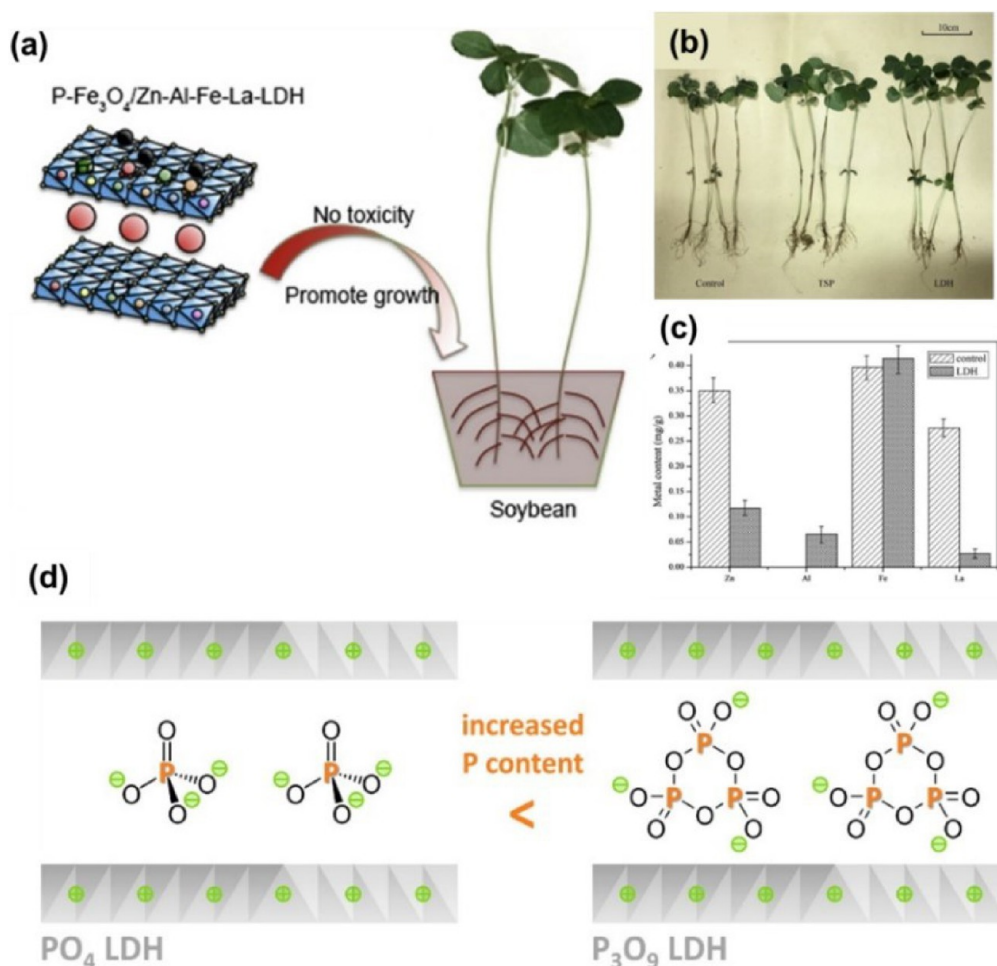
Figure 11. Practical applications of SRF by LDHs. (a) Schematic presentation for growth of soybean plants by using P-adsorbed LDH. (b) Comparison of soybean plant heights after 28 days of growth, and (c) metal content analysis of plant leaves. (d) Schematic illustration of enhanced phosphorus content of LDH-fertilizers by intercalating polymeric phosphate. (Panelss a−c reprinted with permission from ref 181. Copyright 2019 Elsevier. Panel d reprinted with permission from ref 186. Copyright 2022 Elsevier.)

phosphate fertilizer unproductive for crop growth due to its insolubility but it also leads to eutrophication. Hence, using SRF, which can avoid excessive application of phosphate and provide more constant phosphate availability over a long release time, has drawn significant attention to soil fertilization. SRFs are mainly utilized for fertilizer management in agriculture to steadily provide nutrients to plants for an extended period compared to fast-release fertilizers.[179] According to the Association of American Plant Food Control Officials (AAPFCO), SRFs are defined as fertilizer carriers that can delay or prolong the nutrients accessibility for plant uptake, which allows longer nutrients supply for plants than typical nutrient fertilizers such as urea, ammonium phosphate, or potassium chloride.[180]

Several pioneering endeavors have been made by employing phosphate-loaded LDHs as effective slow-release substrates for phosphate ions. Qiao et al. reported the recovery of phosphorus from wastewater by magnetic Fe_3O_4/Zn-Al-Fe-La LDH.[181] The co-produced metal hydroxides on the magnetic Fe_3O_4/Zn-Al-Fe-La-LDH could facilitate the P adsorption capability of 169.5 mg of P/g by the ion-exchange process, contributing to higher P adsorption ability than that of other binary and ternary metal LDHs. The P-adsorbed LDH was subsequently used as SRF to increase the growth of the soybean *Glycine max* (Figure 11a). After 4 weeks, soybean height attained had a higher value than that of commercial (TSP) fertilizers, as shown in Figure 11b. ICP-OES confirmed that the LDH was stable after the phosphate adsorption−desorption process and did not leach their metal ions into water and plant, proving the nontoxicity. Moreover, the trace elements for the growth of soybean plants showed reduced Zn and increased Fe concentrations (Figure 11c), indicating the metal regulation ability for plant growth. Koliraj et al. synthesized colloidal NiAl-LDH by ultrasonication for phosphate removal/recovery in the growth of green seaweed *Ulva lactuca*.[74] NiAl-P-LDH displayed a 14.3% plant growth rate, while the KH_2PO_4 medium showed only 13.5%, exhibiting a promising alternative of fertilizer for green algae. As for the release kinetics of phosphate intercalated in LDH interlayer, Woo et al. investigated the P-release kinetics by using the P-loaded CaFe-LDH in weakly acidic media (pH = 5.2).[182] Among the present kinetic equations, the modified Freundlich model showed a well-fitted r^2 value of 0.986, in contrast to dissatisfied r^2 values obtained for the first-order kinetic model ($r^2 = 0.944$) and the parabolic diffusion model ($r^2 = 0.966$), suggesting heterogeneous diffusion processes of the intercalated phosphate from the LDH.[183] Nevertheless, the calculated rate coefficient (k_d) was ∼0.6834−0.7614, indicat-
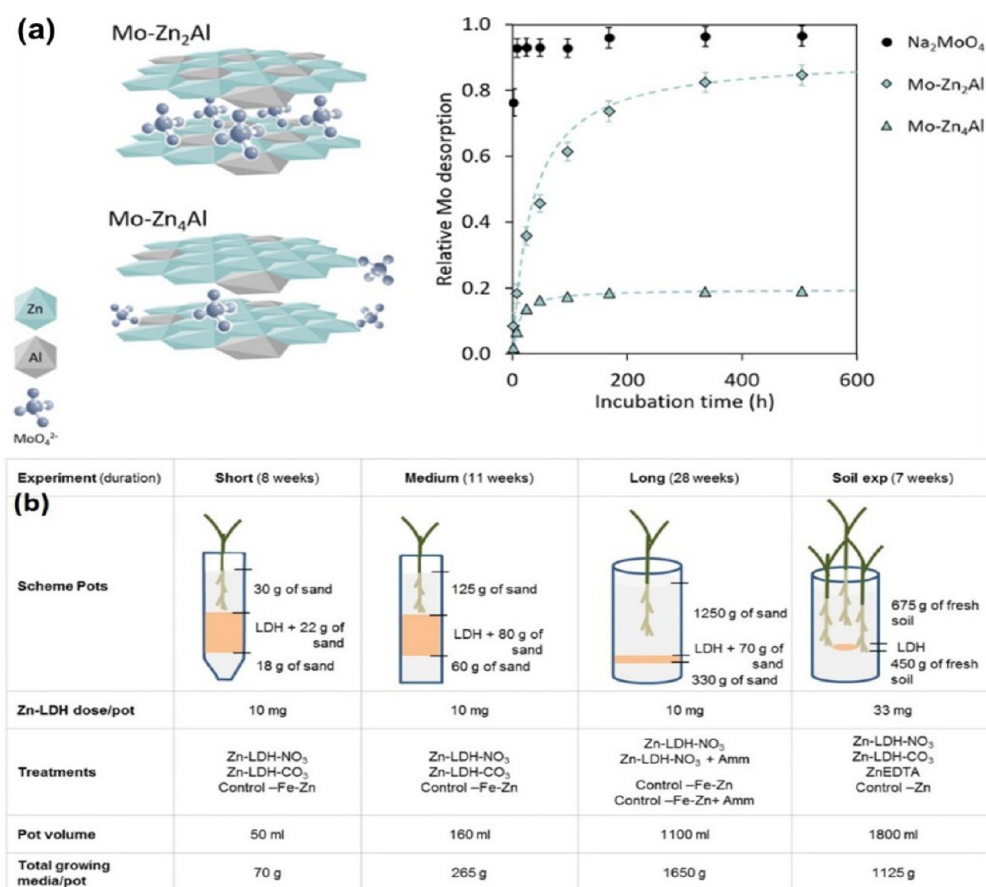
Figure 12. LDH-based SRFs for various nutrients. (a) Mo-loaded ZnAl-LDH SRFs demonstrated slow and completed Mo release compared to Na$_2$MoO$_4$.. (b) Evaluation of Zn-doped MgFe-LDH as a Zn fertilizer for long-term usage. (Panel a reprinted with permission from ref 191. Copyright 2021 American Chemical Society. Panel b reprinted with permission from ref 193. Copyright 2017 Elsevier.)

ing a slower release of phosphate ions from the LDH lattice. Everaert et al. synthesized P-exchanged MgAl-LDHs with varying M^{2+}/M^{3+} ratios and investigated their fertilizer value.[184] The kinetics of P release from LDHs was observed to be significantly slower compared to the other two soluble P fertilizers, namely, KH$_2$PO$_4$ and granular triple super phosphate. The phosphate desorption was described using first-order kinetics, and this ion exchange process suggesting that P-LDHs can effectively function as slow-phosphate-release materials for sustainable agricultural production. These promising results motivated Everaert's group to conduct further research on P-LDHs as effective SRF. They prepared P-exchanged MgAl-LDH as granulated fertilizer and compared it with monoammonium phosphate (MAP).[185] After 100 day incubation experiments, 74−90% of P remained within the LDH granule, confirming a slow-P-release property. Fertilizer use efficiency was examined by planting wheat (*Triticum aestivum*) for pot trials, along with acid and calcareous soil. However, due to the liming effect, the results did not find significant agronomic effectiveness for granulated LDHs as SRF for P uptake, especially in alkaline soil. Nevertheless, the report suggested LDHs can be applied in waste streams for phosphate recycling and in high-rainfall areas as SRF for minimizing P losses with eco-friendly properties. In a more recent study, Everaert et al. conducted dialysis and soil incubation experiments with PO$_4$-LDHs and P$_3$O$_9$-LDHs with various Mg/Al ratios to evaluate their P-release for fertilizers.[186] The results indicated the P$_3$O$_9$-LDH possessed

enhanced P adsorption capacities by 1.25−1.60-fold with slower P release than PO$_4$-LDH (Figure 11d). It is noteworthy that P$_3$O$_9$-Mg$_3$Al released polymeric-P, whereas P$_3$O$_9$-Mg$_2$Al released depolymerized PO$_4$, which results from the catalyzed degradation of P$_3$O$_9$ to linear polymeric P compounds by solid Al-oxyhydroxides. With soil incubation, the solubility of P from P$_3$O$_9$-LDH was initially lower but later converged to that of PO$_4$-LDH, likely due to the continuous hydrolysis process. This study highlights the potential of polyphosphate-loaded LDHs as an alternative to SRF with enhanced long-term P availability.

4.1. Composite LDHs for Phosphate Slow-Release Fertilizers. The use of novel LDH-based adsorbents presents a promising approach for removing P from contaminated waters and developing slow-release P-fertilizers. However, the efficiency of LDH-based SRFs may be affected by soil profiles and climatic conditions, which trigger calls for exploring new LDH-based SRFs with high stability and long-term nutrients availability for plant uptake.[187] Lohomusavi et al. synthesized an environment-friendly hybrid nanocomposite based on LDH nanosheets and the banana peel cellulose-*g*-poly(acrylic acid)/PVA (BPC-g-PAA/PVA) hydrogel for SRF of P and water retention.[188] The P release behavior of the nanocomposite was investigated at various pH values ranging from 2 to 7, which showed an increasing trend with increasing pH until it reached its maximum value at normal pH. At higher pH values, electrostatic repulsion between PO$_3$$^{-4}$ and carboxyl compounds decreased due to the reaction between sodium ions

and carboxyl groups, resulting in a slow release of phosphate. Besides, the phosphate release was slower when subjected to bivalent cations than monovalent cations, which may result from a greater cross-linking degree between bivalent cations and carboxyl groups in the LDH nanocomposite, leading to slower fertilizers release. Azimzadeh et al. synthesized MgAl-LDH composites with apple wood biochar (LDH-biochar) and hydrochar (LDH-hydrochar) to remove phosphate from aqueous solutions. P-loaded LDH-biochar/-hydrochar composites were then used as fertilizers for maize production in calcareous soils under controlled conditions.[189] The composites were found to significantly increase the availability of P compared to pristine LDH, and promote maize shoot and root growth over a pH range of 3−10. The use of P-loaded LDH-biochar/hydrochar composites as P fertilizers can therefore be an effective alternative to chemical fertilizers without any negative effects on plant growth.

4.2. Slow-Release of Other Nutrients by LDHs. Except for phosphate, other kinds of nutrients, such as nitrogen, zinc, and potassium, also play an essential role in the growth and productivity of crops in agriculture. Fortunately, several studies have investigated the use of LDHs as SRFs for different nutrients. Gogoi et al. synthesized NO_3^- intercalated ZnAl-LDH composites by co-precipitation as a nitrogen SRF for crop production,[190] demonstrating 90% (w/w) and 85.45% (w/w) of intercalated NO_3^- at pH values of 5.25 and 7, respectively were released in 30 days. The results showed that LDHs possess the ability to supply plants with accessible N for long periods, even in acidic soils. Everaert et al. proposed ZnAl-LDH loaded with molybdate (MoO_4) as a Mo SRF for legume crops, with up to 85% of total Mo released in a slow manner after a 3 week incubation.[191] This Mo-Zn_2Al-LDH proved to release Mo slowly and completely through solid-state diffusion and ion exchange processes (half-life of 35 h) by a pseudo-second-order kinetic model (Figure 12a). The results solidly confirmed the Mo mass balance between release and remaining in the LDH materials compared to that in Na_2MoO_4, showcasing the potential to replace other soil management (liming, organic matter application) for Mo deficiency. A pioneering finding from Borges et al. reported an SRF for releasing both phosphate and potassium by mixing MgAl-LDH with dipotassium hydrogen phosphate (K_2HPO_4).[192] The study also observed the thermal behavior of P/K release and found that the release of K^+ was almost completed at temperatures greater than 25 °C. At 10 °C, the release dropped to 75%, indicating that LDH-based SRF is convenient for a temperature range of 25−50 °C. López-Rayo et al. demonstrated the suitability of Zn-doped MgFe-LDH for use as a Zn fertilizer for long-term usage by evaluating its Zn release in short-term (8 weeks), medium-term (11 weeks), and long-term (28 weeks) experiments, as shown in Figure 12b.[193] The results showed that the release of Zn reached approximately 45% at pH 5.2, and the Zn concentrations in plants from Zn-doped MgFe-LDH were 9.5-fold higher than those in plants without Zn addition, confirming its capacity as a long-term Zn fertilizer.

5. PERSPECTIVES AND OUTLOOK

The growing global population has resulted in a heightened demand for food, triggering calls for solutions to food security in the future. In order to increase food production, conventional agricultural methods associated with overfertilization often result in inefficient nutrient management and potential environmental damage. It has put pressure on the development of sustainable strategies in crop production with minimal environmental risks. LDHs have emerged as a green nanomaterial in P fertilizers with slow-release property. This review discusses the fundamental mechanisms and summarizes the recent developments in LDH-based materials for phosphate removal/recovery. However, several important issues still require exploration in more detail before real-scale applications.

5.1. Dynamic Tailoring of Phosphate Adsorption/Release. Though LDHs have been successfully prepared with slow-release properties for adsorbed-P in various synthetic methods, the ability to dynamically tune the phosphate adsorption and release of LDH-based materials is still challenging. In recent years, some strategies have been proposed to affect the phosphate adsorption/release, for instance, adjustment of pH value in soil, where the shoot P uptake can increase by 4.5-fold for the P-LDH than for the KH_2PO_4 fertilizer in the acid soil.[184] However, leaching of the LDHs metal effluents into the aqueous solution at an acidic pH may lead to secondary pollution and reduction of reusability of the LDHs.

In a recent study, Lai et al. demonstrated a continuous electrosorption−desorption system, where the adsorbed phosphate can be quickly released by controlling the applied voltage within 5 min.[79] However, the electro-assistance mechanism was conducted under controlled conditions; hence, the challenge to realize a direct modulation of P adsorption/release by LDHs in real water is still nontrivial. Therefore, more research data are required concerning their stability and scalability in practical applications.

5.2. Evolution of Long-Term and Large-Scale Operation of Phosphate Management. In practical agricultural applications, LDHs, playing the role of phosphate SRF, should be able to run for days or even a month. However, during the long-term operation of the SRF, the removal/release mechanisms of phosphate may irreversibly change, affecting the phosphate sorption and desorption behavior. Besides, the change in the phosphate removal/release mechanism may be associated with metal-layered structural instability and dissolution; for example, Al^{3+} may release at a relatively low pH value and suppress root growth.[194]

Despite the excellent reusability of LDHs demonstrated in the beginning adsorption−desorption cycles, the performance of reused materials is not far from satisfactory. Besides, the phosphate adsorption tests are usually performed in controlled conditions with high phosphate concentrations, which is concerning due to the feasibility for real water in low phosphate concentrations and the presence of competing anions is concerning.

To improve the stability and reuse performances of LDHs, new research focused on developing new LDH-based composites, such as carbon-LDHs, magnetic materials-LDHs, and MOF-LDHs, on achieving higher phosphate uptake and recycling on the commercial scale. The criteria of LDH-based composites allow wide-range possibilities to design and tailor their various functionalities with the unique features of LDHs.

5.3. New Discoveries for Phosphate Management for Zero Hunger. The use of LDHs for removing phosphate from wastewater has been investigated for tens of years, though more knowledge in materials science, characterization techniques, and efficacy in field trials still requires more endeavors to integrate LDHs as sustainable nanomaterials in

crop production implementation. We expect this review to pave the way for designing new LDH-based technologies for long-term P management against available products, which are helpful for tackling the global food shortage challenge.

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Notes

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