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Original Research

Phosphate-Adsorbed by Concrete-Based Layered Double Hydroxide: A Slow-Release Phosphate Fertilizer

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Abstract

A novel multipoint titration coprecipitation method was used to prepare concrete-based layered double hydroxide (CLDH) to uptake phosphorus into slow-release phosphate fertilizer. Both the characteristics and the slow release of CLDH-P were investigated. Results showed that the multipoint titration method was efficient for coprecipitation. P-loaded CLDH under weak acid conditions (CLDH-P_1) contained mainly Al-P and Ca-P ($CaHPO_4 \cdot 2H_2O$, DCPD), while the content of Ca-P greatly increased in the product under weak alkaline conditions (CLDH-P_2). The slow-release effects of the two samples in soil leaching columns were significantly better than triple superphosphate (TSP). CLDH-P_1 was preferably used for mung bean growth promotion due to its better availability. The dry weight of CLDH-P_1 mung bean increased by 33% in 40 days, which was obviously better than that of the TSP group. In addition to phosphorus, the nutrient elements Ca and Mg were also enriched in mung bean plants. The results revealed an economical and sustainable candidate for phosphorus recovery.

Keywords: layered double hydroxide, multipoint titration; waste concrete, slow-release phosphate fertilizer, available phosphorus

Introduction

Nowadays, the rapid growth of the world population requires more agricultural output. To optimize and maximize agricultural productivity, various strategies have been implemented, including genetic improvement of crops, agronomic management, and fertilizer application [1, 2]. Fertilizer application has been proven to be an economical and effective way to maximize soil productivity. However, the negative effects of fertilization have also emerged. In China, the consumption of quick-acting phosphate fertilizer has increased significantly in the past few decades, of which less than 30% can be utilized [1, 3]. The large amount of phosphorus retained in the soil was either fixed by the soil into insoluble and inert components, infiltrated into groundwater, or flowed into the river, resulting in eutrophication of the water body and deterioration of the ecological environment [4-6]. Thus, it is urgent to improve the agronomic effectiveness of phosphate fertilizer.

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Slow-release phosphate fertilizer was proposed to increase agronomic effectiveness by gradually supplying phosphorus to the rhizosphere of plants to match the requirements of plant growth in the growing season [7]. The current types of slow-release phosphate fertilizer included polymer-coated phosphate and P-laden materials with slow-release properties [7- 9], among which the P-laden LDHs (layered double hydroxides) were more attractive due to their potential benefits in phosphorus recycling and environmental protection. LDHs is a type of lamellar anionic clay whose laminate is constructed by an octahedron composed of divalent and trivalent metal ions. The formula for LDHs were $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{z+}[A^{n-}]_{z/n}\cdot mH_2O$, where An- is the interlayer anion, and X is defined as the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$ [9]. The high affinity of LDHs for phosphorus makes it an excellent dephosphorization agent for wastewater; meanwhile, the adsorbed phosphorus can be released slowly through anion exchange or dissolution in the soil environment [9]. Qiao proved that P-LDH released phosphorus gradually to promote the growth of soybean plants and obtained better fertilizer effectiveness than TSP fertilizer [10]. Wan confirmed that P-loaded biochar-LDHs promoted the growth of lettuce seedlings, leading to a 150% increase in biomass [11]. These results demonstrated the attractivity of phosphorus recovery from sewage. However, most researchers synthesized LDHs with pure chemical reagents, and the preparation was time-consuming, which restricted their further application.

In this work, CLDH was prepared using an efficient multipoint titration method from waste concrete to uptake phosphorus into slow-release phosphate fertilizer. The slow-release effectiveness as well as the fertilization effectiveness of CLDH-P were investigated. The objectives of this study are to (1) seek an efficient and cheap preparation method for slow-release phosphate fertilizer, (2) elucidate the slow release, transformation, and availability of phosphorus from CLDH-P in soil, (3) assess the fertilization effectiveness of CLDH-P on plant growth.

Materials and Methods

Preparation of CLDH-P Fertilizers

Weathered concrete from waste buildings was crushed into powder (<0.1 mm). The main components of concrete powder were O, Ca, Si, Mg, Al, and Fe, which accounted for 36.8%, 28.2%, 11.6%, 5.2%, 4.8%, and 3.4%, respectively. All chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Solutions were prepared with ultrapure water.

5.0 g concrete powder was leached in 100 mL of 1 M HCl solution for 24 h (180 r/min, 40ºC). The filtrate was added to 2.8 g of $AlCl_3\cdot 6H_2O$ to be a metal solution. It is worth mentioning that multipoint titration was used to replace the traditional single point titration to obtain higher reaction efficiency and homogeneous reaction conditions. Metal solution and 2 M NaOH solution were dropped into the coprecipitation bulk solution by a multi-channel syringe pump. The number of channels for the two solutions was 9 and 1, respectively. Alkali solution was in the center, with metal solution distributed equidistantly around it. The titration outlet of the reaction solution was controlled at 0.1mm to reduce the droplet size. The previous experiments showed that this multipoint titration device replaced the traditional large droplets with small and dispersed droplets, which not only improved the reaction efficiency, but also made the product smaller in size and more uniform in morphology. The bulk solution pH was kept at 11.5 and the temperature was maintained at 40ºC. The slurry was aged for 2 h at 85ºC. The product was washed, then filtered and dried to be CLDH.

CLDH-P was prepared by the adsorption method with CLDH and 300 mg/L KH_2PO_4 solution in a solid/liquid ratio of 1:100. The adsorption was carried at room temperature for 24 h. The present study has confirmed that a high phosphate content of CLDH-P could be obtained under equilibrium pH 6~9. To decrease the influence of fertilization on soil pH, two kinds of P-loaded samples, named CLDH-P1 and CLDH-P_2, were prepared under the equilibrium pH conditions of weak acid (about 6.5) and weak alkali (about 8), and the corresponding initial pH was 3 and 5, respectively.

Column Leaching Test

The column leaching test was designed according to the method described by Tang [12]. The column was 0.35 m high, with an inner diameter of 0.08 m. The column was perforated at the bottom to collect the leachates. 2 kg dry local calcareous soil (bulk density 1.4 g/cm^3, pH 8.0) was packed into the column, and the top and bottom of the soil were filled with 2 cm of sea sand. 3.0 g powdered TSP (20.0% wt. P) or 3.7 g CLDH-P_1 (16.1% wt. P) or 3.5 g CLDH-P_2 (17.2% wt. P), which contained the same phosphorus content, were encapsulated into a mesh bag and buried 5 cm beneath the surface soil. Fine netting was employed at the column bottom to avoid soil loss into the leachates. 750 mL water was added to the column until it reached soil-water saturation. The column was leached with water at a rate of 700 mL/d. The leachates were collected to measure phosphate every 12 h, and the average concentration of two times was the daily concentration. Each fertilizer had three parallel leaching columns, among which one was used for the test of the 30-day cumulative release rate. The other two were operated for 80 days for leaching data collection. Additionally, a controlled column was applied with water influent. The P release rate was investigated according to the method described by Tang et al. [12].

Sequential Extraction of Phosphorus

P fractions in CLDH-P and soil were sequentially extracted from 2.0 g of dried sample according to the literature [13-15]. Four fractions, including weakly bound P (W-P), Fe/Al-associated P (Fe/Al-P), Ca/Mg-associated P (Ca/Mg-P), and P in stable compounds (S-P), were obtained through sequential extraction. The sample was sequentially extracted in 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M HCl at room temperature for 16 h (S/L = 1:50). Finally, the residual was extracted in 20 mL of 12 M HCl (80ºC, 1 h) to determine S-P. For the soil sample, W-P and Fe/Al-P were defined as available P for plants [13-16].

Cultivation Experiment of Mung Bean

30 mung bean seeds were first washed with deionized water and then cultivated in a Petri dish. To provide sufficient moisture and fertilizer, 10 mL of deionized water and CLDH-P1 were added to the Petri dish. The seeds and fertilizer were separated by filter paper. A series of samples with different fertilizer dosages were cultured in the dark at 25ºC for 5 days. Each sample was three parallel. After 5 days, the growth indexes were measured.

4 kg of dry calcareous soil was first mixed with 1.15 g of urea and 1.32 g of KCl, and then packed into the pot. CLDH-P1 or TSP were buried as basal fertilizer to amend phosphorus, with a P dose of 0 and 30 mg P/kg soil. The fertilization rate refers to the previous research results on calcareous soil fertilization [7, 17, 18]. Each pot was planted with 5 mung bean seedlings precultured for 5 days, and the seedlings were similar in size. The fertilization groups and control group were cultured in a growth chamber at 20±0.5ºC with a daily photoperiod of 16 h. Each group was in three replicates. After 40 days, the shoots were harvested and the growth indexes measured. Dry weight was analyzed after drying at 60ºC for 48 h [10, 19]. The dry shoots were digested in boiling HNO_3 to analyze the characteristic elements by ICP-OES.

Characterization

The morphology of samples was investigated with a scanning electron microscope (SEM, Zeiss-Supra 55 VP), which was equipped with an energy spectrometer (Bruker EDS QUANTAX). X-ray diffraction (XRD) was conducted on a D/MaX-2500PC diffractometer (at 40 kV and 100 mA, Cu/kα). FTIR spectra were collected on IRAffinity-1s FTIR (Shimadzu IRAffinity-1s, Japan, KBr method). Specific surface area and pore volume were determined by N2 adsorption-desorption isotherms at -196ºC (Micro Active ASAP 2460, USA). The elemental composition of concrete was analyzed by X-ray fluorescence spectroscopy (XRF, PANalytical-Axios).

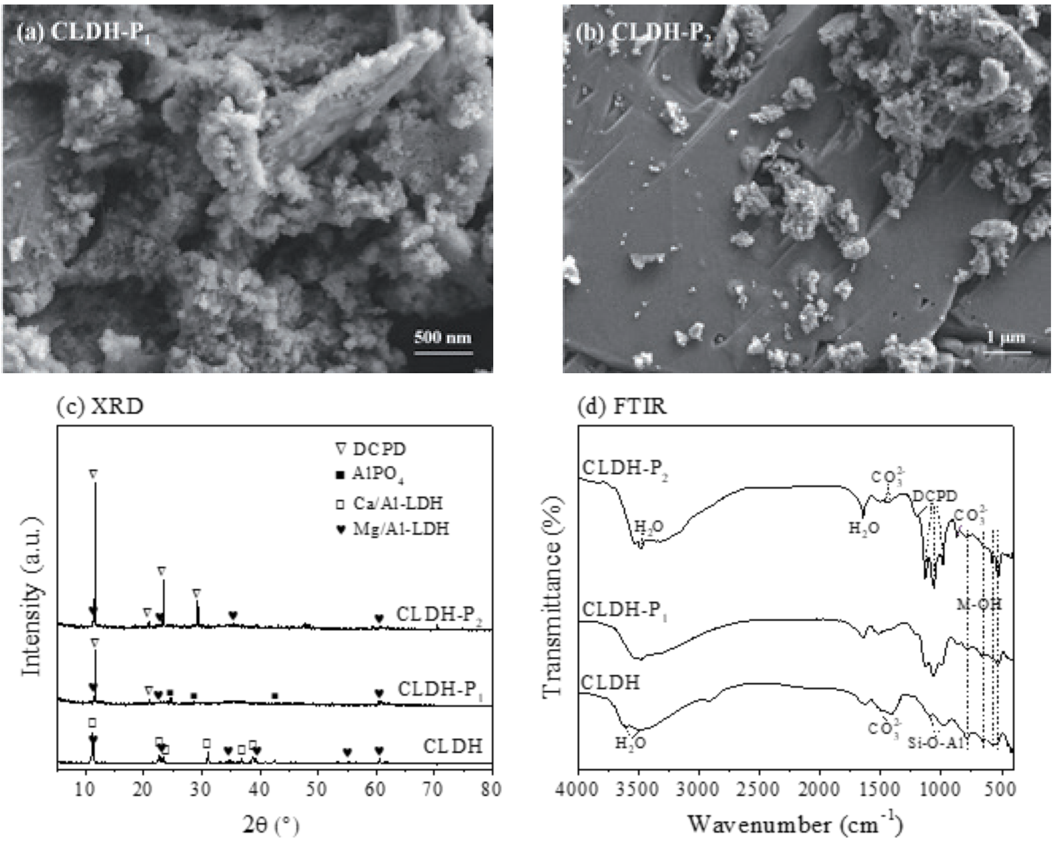


Fig. 1. Characterization analysis of CLDH-P.

Results and Discussion

Characteristics of CLDH and CLDH-P

Fig. S1 shows the morphology of CLDH. Abundant pores and submicron-scale laminations were observed, which provided a large specific surface area and more active sites for phosphorus adsorption. As shown in Table 1, CLDH had a large surface area and a positive charge, and the phosphorus holding capacity q_m was 172.3 mg/g. Compared with the works with single-point titration method, the preparation time of CLDH for multipoint titration was significantly shortened. This indicated that the multipoint titration method is an efficient and stable way to prepare LDHs.

After phosphorus adsorption, flake crystals and flocs rich in phosphorus were observed (Fig. 1), and the CLDH-P_2 appeared more compact. In Fig. 1c), the flake crystal in both CLDH-P_1 and CLDH-P_2 was confirmed to be DCPD ($CaHPO_4 \cdot 2H_2O$, PDF #01-072-0713), and $AlPO_4$ (PDF #00-046-0695) was also detected in CLDH-P_1. In addition, Ca/Al-LDH and Mg/Al-LDH (corresponding to PDF# 04-010-4677 and PDF# 00-035-0965, respectively) were detected in CLDH, but Ca/Al-LDH disappeared in CLDH-P. In Fig. 1d), the characteristic peaks of DCPD, namely the water molecule at 3542/3487/1651 cm^{-1} in CLDH-P_1 (or 3538/3485/1647 cm^{-1} in CLDH-P_2), and O-P-O vibration at 996/1064/1133/1206 cm^{-1}, was identified in CLDH-P samples. The absorption bands of M-O/OH (M is Ca, Mg, or Al) were presented in all the samples (530/580, 660, and 781 cm^{-1}). Vibration of CO_3^{2-} was detected at 1518/1455/1416/1411 cm^{-1} and 869 cm^{-1}, indicating the participation of atmospheric CO_2 during sample preparation.

Fig. 2 demonstrates that CLDH-P_1 contained more Fe/Al-P (57%), while CLDH-P_2 contained more Ca/Mg-P (59%). Considering the lower content of Fe detected in CLDH-P samples, Al-P should be the major component of Fe/Al-P. In addition, W-P accounted for 17%-20% of the two samples, suggesting that weak adsorption played an important role.

The CLDH-P samples contained mainly Al-P, Ca/Mg-P, and weakly adsorbed P, which could be explained as the results of CLDH dissolution,

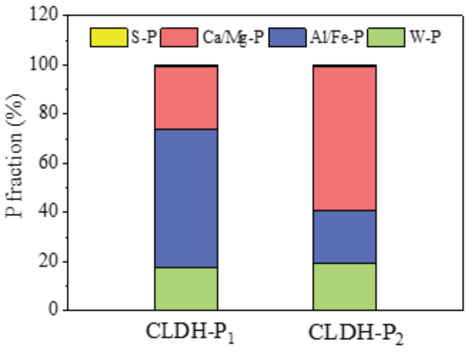
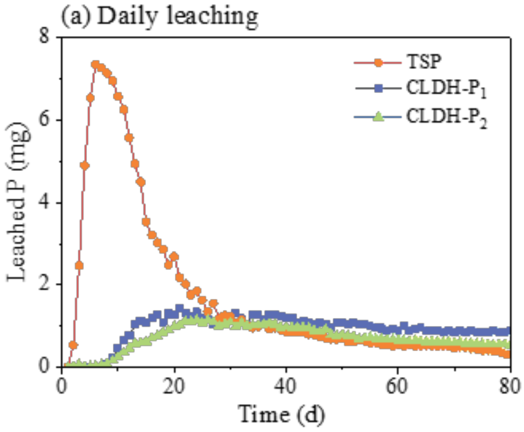


Fig. 2. Phosphorus composition of CLDH-P.

(a) Daily leaching



(b) Cumulative leaching

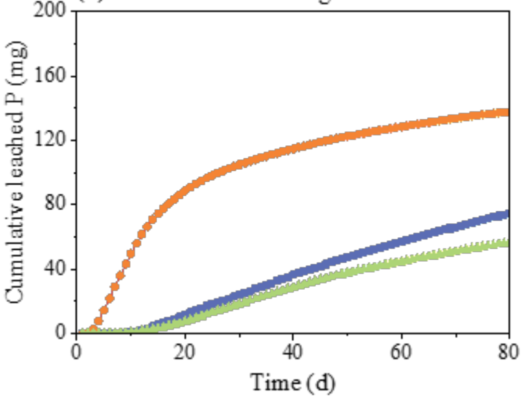


Fig. 3. The slow-release effect of CLDH-P.

Table 1. Comparison between CLDH and LDHs in other works.

Samples	Surface area (m^2/g)	Zeta potential* (mV)	q_m (mg P/g)	Preparation time (h)	Ref.
Mg/Fe/La-LDH	86.2	-20	19	>18	[20]
Fe_3O_4/Zn/Al/Fe/La-LDH	268.7	-	119.2	>18	[10]
Ca/Mg/Al-LDH	46.7	-	77.1	>24	[21]
Mg/Al-LDH	124	26	127.2	>18	[22]
CLDH	170.2	38.5	172.3	3	This work

* Corresponding pH was 7.

phosphate precipitation, and surface adsorption [23, 24]. Ca/Al-LDH phase in CLDH tended to dissolve in phosphate solution. The released Ca^{2+} and Al^{3+} subsequently precipitated PO^{3-} into DCPD and AlPO. Meanwhile, the insoluble Mg/Al-LDH and amorphous $Al(OH)_3$ adsorbed phosphorus through anion exchange or surface adsorption [24]. CLDH-P_1 was obtained from a weak acid environment where the precipitation of $AlPO_4$ was dominant. Besides, the protonation of the solid surface in an acidic environment facilitated the exchange and surface adsorption of phosphate anion. For CLDH-P_2, the phosphorus precipitation was mainly calcium phosphate as pH increased.

Slow Release of CLDH-P in the Soil Leaching Column

Fig. 3 shows the leaching of P-fertilizer in the calcareous soil column. The peak of leached P from the TSP column appeared on the 6th day (7.36 mg/L), whereas no obvious peak was observed for the CLDH-P_1 and CLDH-P_2 columns. The P-leaching of CLDH-P samples was slower and more stable than that of TSP. The cumulative P-leaching of CLDH-P_1 and CLDH-P_2 was 54% and 41% that of TSP in 80 days.

Phosphorus Distribution in Soil

The migration and availability of phosphorus were not as good as those of other nutrients in the soil. Due to the adsorption and fixation of soil, phosphorus released by fertilizer was firstly transformed into available phosphorus easily adsorbed by plants and then gradually passivized into Ca/Mg-P and S-P that were difficult to use [15]. Fig. 4 showed that after 80 days' leaching, the abundance of available phosphorus in the topsoil of all the columns was close to the soil background value, while the content of available P decreased with the increase in soil depth below the fertilizer burial site. The available P content changed obviously in the range from the fertilizer site to 25 cm soil depth, meaning that the transformation of released P was mostly completed in the soil layer near the fertilizer site. The available P content in the CLDH-P1 soil was higher than the background at all depths below the fertilizer site, indicating that phosphorus transformation was still in progress. Ivan suggested that phosphorus released from fertilizer in calcareous soil would soon be immobilized and become non-bioavailable, but the passivation could be inhibited by slowing down the release rate of phosphorus [25]. This was confirmed by the result of Fig. 4.

Phosphorus is one of the major macronutrients that functions as a promoter of plant growth, root development, flowering, and ripening. As a shallow-rooted plant, mung bean develops 80% of its roots within 30 cm soil depth [26]. The active range of CLDH-P_1 in soil could embrace the growth range of mung bean roots under appropriate burial depths. Considering the stable release effectiveness and more available phosphorus content, CLDH-P1 was selected for the planting test.

Fertilization Effect

An appropriate amount of phosphorus fertilizer can promote plant growth; however, overfertilization of phosphorus will not only cause waste, but also lead to smaller leaves, the shrinking of vegetative bodies, and premature plant maturity [27]. Table S1 showed that the application of CLDH-P1 at a certain dose promoted germination and the root and leaf growth of mung bean sprouts. However, overfertilization inhibited the germination and growth of mung bean sprouts (e.g., 0.4 g).

In Fig. 5, the 40-day growth index showed that the fertilization groups increased in their root/pod length (L), fresh/dry weight (W), plant height (H), and leaf area (A). The CLDH-P1 group had sturdy rhizomes and flourishing leaves compared to the control group, and the number of flowers and pods increased significantly.

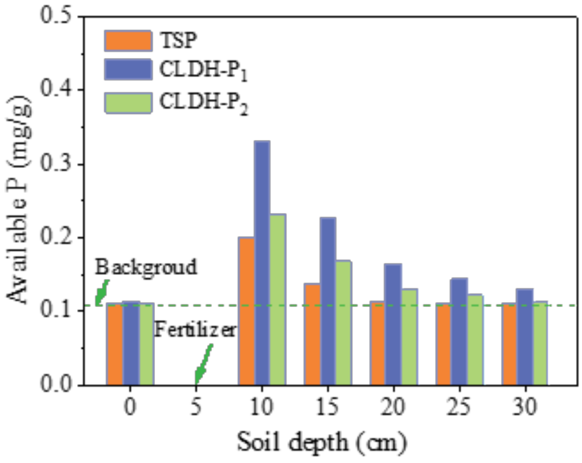


Fig. 4. Available P distribution in soil.

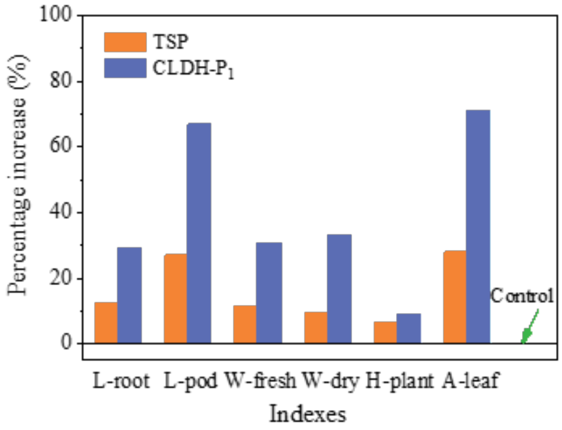
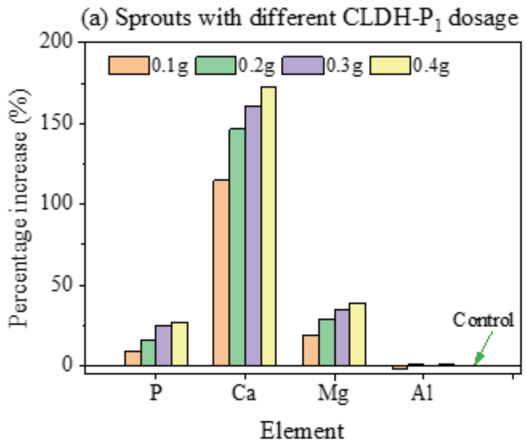


Fig. 5. Improvement of mung bean growth indicators by fertilization.



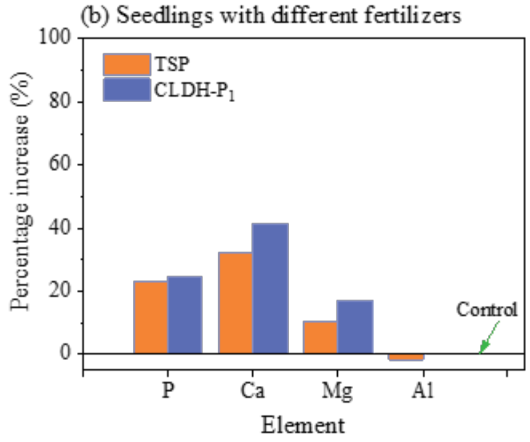


Fig. 6. Enrichment of nutrient elements in mung bean sprouts and seedlings.

Compared with the control group, the fresh weight, and the dry weight in the CLDH-P_1 group increased by 31% and 33%, respectively, which were higher than those of the TSP group. Thus, CLDH-P_1 fertilizer could promote the growth of mung beans with higher biomass.

In addition to phosphorus, the Ca and Mg in LDH-P were the essential macronutrients for plants and animals. Ca is the structural component of the cell wall and membrane, serves for charge balance and osmotic regulation, and participates in cell and system signal transduction [28]. Mg is one of the elements that constitute chlorophyll and participates in the physiological processes of animals. Nevertheless, Al in LDH-P might be biologically toxic. Therefore, it is necessary to investigate the enrichment of the above elements in mung bean growth.

Fig. 6 showed that P, Ca, and Mg were significantly enriched in mung bean sprouts and mung bean seedlings in the P fertilizer groups. The enrichment of the above elements in mung bean sprouts increased with the increase in CLDH-P_1 dosage. Moreover, the CLDH-P_1 seedling showed better nutrient enrichment than the TSP group. The contents of P, Ca, and Mg in the CLDH-P_1 mung bean seedling increased by 25%, 41%, and 17%, respectively, compared with the control group. The Al content was less than 0.05 mg/g in all the samples, and no enrichment was found in the CLDH-P_1 mung bean sprout or seedling. This indicated that the dissolved aluminum content in the culture medium or soil was very low. It is known that the Al in the soil will be passivated if the soil pH is higher than 5.7, which is harmless to plants [1]. In other words, even when Al was released from CLDH-P_1 into the calcareous soil, it would be quickly fixed by the solid phase.

Table 2 compares CLDH-P_1 with other mew slow-release P fertilizers. It can be concluded that CLDH-P_1 contained a more active ingredient and a more stable release rate, which indicated that better application effectiveness could be obtained by CLDH-P_1. Namely, it can not only ensure sufficient phosphorus fertilizer, but also not cause too fast phosphorus loss due to early rapid release. However, there are many works to be carried out, such as the application effectiveness of different soil types and different plants

Conclusions

CLDH was prepared by a novel multipoint titration method from waste concrete to uptake phosphorus to be a slow-release phosphate fertilizer. CLDH with a large surface area and a large P-uptake capacity was obtained. The cumulative P-leaching of CLDH-P was 41%-54% that of TSP in 80 days. CLDH-P_1 proved to release

Table 2. Comparison of slow-release effects of different slow-release phosphate fertilizers.

Type	P content (%)	Soil pH	Average P-release rate [mg/(g·d)]		Ref.
Straw cellulose-P	1.3	7.0-9.0	42 (15 days)	25 (30 days)	[29]
Activated lignite-P	2.2	6.3	13 (30 days)	10 (90 days)	[12]
Struvite	9.7	7.9	6 (30 days) ^{a}	4 (56 days) ^{a}	[30]
Fiber absorbent-P	0.14	-	18 (30 days)	10 (60 days)	[31]
NPK compound fertilizer	3.2	6.5-9.0	12 (28 days) ^{a}	6 (70 days) ^{a}	[32]
CLDH-P_1	16.1	8.0	8.3 (30 days)	7.2 (80 days)	This work

^{a} Phosphorus fixed in the soil was not included phosphorus stably with more available phosphorus for plants. Further, CLDH-P1 was confirmed to provide mung bean has a higher production of dry matter, a more developed root, and a higher content of beneficial elements (P, Ca, and Mg) when compared to that of TSP. The results of this work assure that CLDH-P has great application potential as a new type of slow-release P fertilizers.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

References

1. BENÍCIO L.P.F., CONSTANTINO V.R.L., PINTO F.G., VERGÜTZ L., TRONTO J., DA COSTA L.M. Layered double hydroxides: new technology in phosphate fertilizers based on nanostructured materials. ACS Sustain. Chem. Eng., **5** (1), 399, **2017**.
2. ZHANG M., GAO B., CHEN J., LI Y., CREAMER A.E., CHEN H. Slow-release fertilizer encapsulated by graphene oxide films. Chem. Eng. J., **255**, 107, **2014**.
3. JOHNSTON A.E., POULTON P.R., FIXEN P.E., CURTIN D. Chapter five-phosphorus: its efficient use in agriculture. Adv. Agron., **123**, 177, **2014**.
4. EVERAERT M., WARRINNIER R., BAKEN S., GUSTAFSSON J.P., VOS D.D., SMOLDERS E. Phosphate-exchanged Mg-Al layered double hydroxides: a new slow release phosphate fertilizer. ACS Sustain. Chem. Eng., **4**, 4280, **2016**.
5. LI Y., LI J., GAO L., TIAN Y., LIN W.X. Irrigation has more influence than fertilization on leaching water quality and the potential environmental risk in excessively fertilized vegetable soils. Plos One, **13**, 1, **2018**.
6. LUSTOSA FILHO J.F., BARBOS C.F., CARNEIRO J.S. D.S., MELO L.C.A. Diffusion and phosphorus solubility of biochar-based fertilizer: visualization, chemical assessment and availability to plants. Soil Till Res., **194**, 104298, **2019**.
7. EVERAERT M., DEGRYSE F., MCLAUGHLIN M.J., VOS D.D., SMOLDERS E. Agronomic effectiveness of granulated and powdered p-exchanged Mg-Al LDH relative to struvite and MAP. J. Agric. Food Chem., **65**, 6736, **2017**.
8. CRUZ D.F., BORTOLETTO-SANTOS R., GUIMARÃES G.G.F., POLITO W.L., RIBEIRO C. Role of Polymeric Coating on the Phosphate Availability as a Fertilizer: Insight from Phosphate Release by Castor Polyurethane Coatings. J. Agric. Food Chem., **65**, 5890, **2017**.
9. KONG L., TIAN Y., WANG Y., YANG N., LI L., PANG Z., HUANG X., LI M., ZHANG J., ZUO W. Periclase-induced generation of flowerlike clay-based layered double hydroxides: a highly efficient phosphate scavenger and solid-phase fertilizer. Chem. Eng. J., **359**, 902, **2019**.
10. QIAO W., BAI H., TANG T., MIAO J., YANG Q. Recovery and utilization of phosphorus in wastewater by magnetic Fe3O4/Zn-Al-Fe-La layered double hydroxides (LDHs). Colloid. Surface. A, **577**, 118, **2019**.
11. WAN S., WANG S., LI Y., GAO B. Functionalizing biochar with Mg-Al and Mg-Fe layered double hydroxides for removal of phosphate from aqueous solutions. J. Ind. Eng. Chem., **47**, 246-253, **2017**.
12. TANG Y., WANG X., YANG Y., GAO B., WAN Y., LI Y., CHENG D. Activated-lignite-based super large granular slow-release fertilizers improve apple tree growth: synthesis, characterizations, and laboratory and field evaluations. J. Agric. Food Chem., **65**, 5879, **2017**.
13. BRAOS L.B., BETTIOL A.C.T., DI SANTO L.G., FERREIRA M.E., CRUZ M.C.P. Dynamics of phosphorus fractions in soils treated with dairy manure. Soil Res., **58**, 289, **2020**.
14. PENG Y., ZHANG T., TANG B., LI X., CUI S., GUAN C., ZHANG B., CHEN Q. Interception of fertile soil phosphorus leaching with immobilization materials: Recent progresses, opportunities and challenges. Chemosphere, **308**, 136337, **2022**.
15. ZHU X., FANG X., WANG L., XIANG W., ALHARBI H. A., LEI P., KUZYAKOV Y. Regulation of soil phosphorus availability and composition during forest succession in subtropics. Forest Ecol. Manag., **502**, 119706, **2021**.
16. WEI W., ZHANG S., WU L., CUI D., DING X. Biochar and phosphorus fertilization improved soil quality and inorganic phosphorus fractions in saline-alkaline soils. Arch. Agron. Soil Sci., **67**,1177, **2020**.
17. AIMEN A., BASIT A., BASHIR S., ASLAM Z., SHAHID M.F., AMJAD S., MEHMOOD K., ALJUAID B.S., EL-SHEHAWI A.M., ZUAN A.T.K., FAROOQ S., LI Y. Sustainable phosphorous management in two different soil series of Pakistan by evaluating dynamics of phosphatic fertilizer source. Saudi J. Biol Sci., **29**, 255, **2022**.
18. WAHID F., SHARIF M., FAHAD S., ADAN M., KHAN I. A., AKSOY E., ALI A., SULTAN T., ALAM M., SAEED M., ULLAH H., BASIR A., NOOR M., KHAN N. A. Arbuscular mycorrhizal fungi improve the growth and phosphorus uptake of mung bean plants fertilized with composted rock phosphate fed dung in alkaline soil environment. J. Plant Nutr., **42**, 1760, **2019**.
19. BUATES J., IMAI T. Assessment of plant growth performance and nutrient release for application of phosphorus-loaded layered double hydroxides as fertilizer. Environ. Technol. Inno., **22**, 101505, **2021**.
20. WANG X., WU L., HUANG Y., LI J., HUA G., LIU C., LI N., LAI B. Efficient removal and selective recovery of phosphorus by calcined La-doped layered double hydroxides. J. Water Process Eng., **47**, 102722, **2022**.
21. ZHANG W., DONG T., CHENG H., WU H., WU C., HU A., WANG D. Preparation of composite sludge carbon-based materials by LDHs conditioning and carbonization and its application in the simultaneous removal of dissolved organic matter and phosphate in sewage. Chemosphere, **270**, 129485, **2021**.
22. ZHANG Z., YAN L., YU H., YAN T., LI X. Adsorption of phosphate from aqueous solution by vegetable biochar/layered double oxides: Fast removal and mechanistic studies. Bioresource Technol., **284**, 65, **2019**.
23. BERNARDO M.P., MOREIRA F.K.V., RIBEIRO C. Synthesis and characterization of eco-friendly Ca-Al-LDH

loaded with phosphate for agricultural applications. Appl Clay Sci., **137**, 143, **2017**.

24. LUNDEHØJ L., CELLIER J., FORANO C., NIELSEN U.G. Atomic level understanding of orthophosphate adsorption by magnesium aluminum-layered double hydroxides a multitechnique study. J. Phys. Chem. C, **123**, 24039, **2019**.
25. ANDELKOVIC I.B., KABIRI S., TAVAKKOLI E, KIRBY J.K., MCLAUGHLIN M.J., LOSIC D. Graphene oxide-Fe(III) composite containing phosphate-A novel slow release fertilizer for improved agriculture management. J. Clean. Prod., **185**, 97, **2018**.
26. ZHOU H., ZHENG D., FENG N., XIANG H., LIU Y., LIANG X. Grain yield in mungbean (*Vigna Radiata*) is associated with spatial distribution of root dry weight and volume. Legume Res., **43**, 408, **2020**.
27. KAMINSKY L.M., THOMPSON G.L., TREXLER R.V., BELL T.H. Medicago sativa reduced biomass and nodulation when growth with soil microbiomes conditioned to high phosphorus input. Phytobiomes J., **2**, 237, **2018**.
28. LUX A., KOHANOVA J., WHITE P.J. The secrets of calcicole species revealed. J. Exp. Bot, **72**, 968, **2021**.
29. WANG X., LÜ S., GAO C., FENG C., XU X., BAI X., GAO N., YANG J., LIU M., WU L. Recovery of ammonium and phosphate from wastewater by wheat straw-based amphoteric adsorbent and reusing as a multifunctional slow-release compound fertilizer. Acs Sustainable Chem. Eng. **4**, 2068. **2016**.
30. HU P., ZHANG Y., LIU L., WANG X., LUAN X., MA X., CHU P.K., ZHOU J., ZHAO P. Biochar/struvite composite as a novel potential material for slow release of N and P. Environ. Sci. Pollut Res., **26**, 17152. **2019**.
31. ZHANG L., LOH K.C., SARVANANTHARAJAH S., SHEN Y., TONG Y.W., WANG C.H., DAI Y. Recovery of nitrogen and phosphorus nutrition from anaerobic digestate by natural superabsorbent fiber-based adsorbent and reusing as an environmentally friendly slow-release fertilizer for horticultural plants. Waste Biomass Valori., **11**, 5223, **2020**.
32. LI J., LIU Y., LIU J., CUI X, HOU T., CHENG D. A novel synthetic slow release fertilizer with low energy production for efficient nutrient management. Sci. Total Environ., **831**, 154844, **2022**.

Supplementary Material

Table S1. Effect of fertilizer dosage on the early growth of mung bean sprouts

CLDH-P_1 dosage (g)	Root length (cm)	Fresh weight (mg/plant)	Dry weight (mg/plant)	Stem height (cm)	Germination percentage (%)	Leaf weight (mg/plant)
Control	4.53	341.94	31.87	11.25	96.67	24.57
0.1	5.26	379.22	34.03	11.59	100	26.39
0.2	5.67	471.35	38.42	12.83	100	29.79
0.3	6.62	502.85	39.41	12.88	100	34.26
0.4	5.33	363.92	32.85	10.92	97.78	25.52

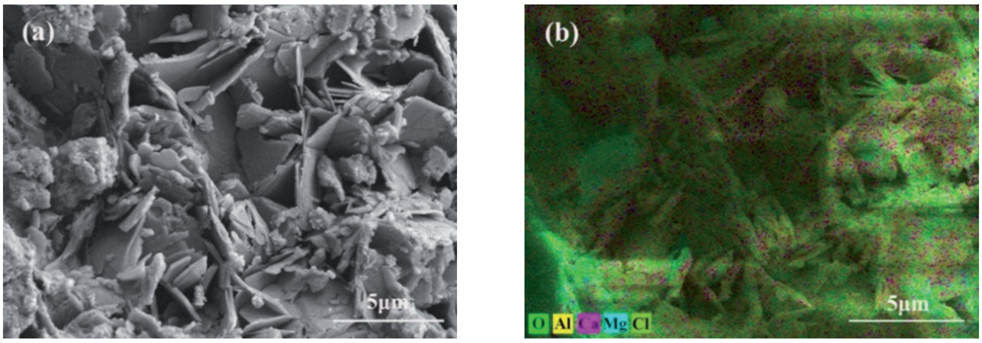

Fig. S1. SEM image a) and mapping b) of CLDH.