Journal of Tropical Plant Physiology 15(1) (2023):1-12
https://doi.org/10.56999/jtpp.2023.15.1.25

Effects of Zinc-Layered Hydroxide on Controlled Release of Plant Nutrients and Growth Performance of Kelempayan (*Neolamarckia cadamba*) Seedlings

Rozita Ahmad[1]*, Nor Farhana Khadiran[1], Mohd Zobir Hussein[2], Tumirah Khadiran[3], Siti Salwana Hashim[1], Zulkharnain Zainal[2], Wan Rasidah Kadir[1] and Norhayati Hashim[4]
[1]Forestry Biotechnology Division, Forest Research Institute Malaysia, 52109 Kepong, Selangor, Malaysia
[2]Institute of Nanoscience and Nanotechnology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[3]Forest Product Division, Forest Research Institute Malaysia, 52109 Kepong, Selangor, Malaysia
[4]Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Selangor, Malaysia
**Email: rozita@frim.gov.my*

Received: 15 March 2022; Revised: 9 January 2023; Accepted: 31 January 2023; Published: 1 June 2023

ABSTRACT

The loss of nutrients from conventional fertilisers is often encountered by the agricultural industry. Slow-release fertilisers by nanotechnology application can maintain nutrient availability for effective plant growth. Zinc-layered hydroxide nanohybrids have been little explored as controlled release systems of functional anions, unlike the Layered Double Hydroxides (LDH) that belong to the same family of anionic clays. The objective of the study was to investigate the effectiveness of zinc-layered hydroxide nanohybrid containing plant nutrient anions as a controlled-release formulation. Two nano-delivery materials namely zinc-layered hydroxide nitrate (ZLN) and zinc-layered hydroxide phosphate (ZLP) were successfully synthesised through the co-precipitation and anion exchange methods. The PXRD patterns of the resulting nanohybrids, ZLN and ZLP recorded basal spacing of 9.57 and 6.78Å, respectively, at a lower 2ϴ angles range of 0-60°. FTIR analyses confirmed the formation of host-guest nanohybrid which comprised the characteristic bands of nitrate and phosphate. Thermogravimetric analyses showed the thermal stability of the nanohybrid obtained where the capability of the host material to function as a controlled release agent was determined through a controlled release study. Controlled release of plant nutrient sources, nitrate and phosphate from their respective nanohybrids were evaluated using various release medium solutions. The accumulated release of guest anion from interlayer zinc layered hydroxide (ZLH) nanohybrid into pH 4 solution was observed to be faster than pH 6.5. A higher concentration of sodium carbonate solution showed an increase in the percentage release for both nitrate and phosphate anions into the release medium. A plant growth trial using Kelempayan (*Neolamarckia cadamba*) seedlings showed that treatment with ZLN and ZLP recorded the highest biomass weight compared to application with commercial fertiliser and raw chemicals. The content of N, P and Zn in Kelempayan leaves showed the highest readings for similar treatment. The study found that ZLH has acted as a good host for inorganic plant nutrients with slow-release properties and thus has improved the growth performance of Kelempayan seedlings with better nutrient uptake.

Keywords: Fertiliser, nanohybrids, nitrate, phosphate, seedlings.

INTRODUCTION

The agriculture industry demands high fertiliser consumption to increase crop yield due to insufficient nutrients in the soil. However, most of the nutrients in the fertilisers are not fully absorbed by the plants. About 40 to 70% N and 80 to 90% P from normal fertiliser application are lost to the environment through

ISSN No 1985-0484

leaching, degradation and evaporation, resulting in undernourished soil conditions and pollution (Preetha and Balakrishnan, 2017). One approach to minimise these losses and curb pollution is the use of controlled release formulation (CRF). However, some of the CRF materials have drawbacks because they contain additives such as plasticisers, fillers, antioxidants and stabilisers that remained after the application were completed (Zobir et al., 2021). This is detrimental as it could pollute the environment and become a risk to living things. A suitable CRF material that is environmentally friendly is required to deliver the functional agent efficiently and slowly. Given the current global climate change, nanomaterials offer an alternative medium through the use of encapsulated and nanogel-based fertilisers for the release of nutrients. This method has led to a 6 to 17% increase in plant productivity (Madzokere et al., 2021).

Layered metal materials such as layered hydroxide salt (LHS) and layered double hydroxide (LDH) incorporated with active agents within the interlayer space will form new layered material with improved properties (Ruiz et al., 2019; Zobir et al., 2021). This type of material provides a platform for various applications such as chemical sensors (Isa et al., 2012), herbicides (Hashim et al., 2014a), drug delivery (Nabipour et al., 2015; Najem Abed et al., 2017) and controlled release formulation (Saifullah et al., 2013; Biswick et al., 2010). Studies are using layered metal hydroxide as a fertiliser delivery system. The layered double hydroxide matrix material was used as a carrier for nitrogen fertiliser (Berber et al., 2014) and zinc hydroxide nitrate nanocrystals as leaf suspension fertiliser (Li et al., 2012). However, not many studies have been conducted on the use of zinc-layered metal hydroxide (ZLH) as inorganic ion storage for fertiliser delivery systems. A simple synthesis method (Hashim et al., 2014b) and no aluminium used in ZLH, can prevent the increase of soil acidity during the anion exchange process (Ahmad et al., 2015).

$Zn_5(OH)_8(NO_3)_2.2H_2O$ has an empirical formula of $M^{2+}(OH)_{2-x}(A^{m-})_{x/m}\cdot nH_2O$ where M^{2+} refers to the metal cations for example Mg^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+} and Cu^{2+} while A^{m-} as the counter anions such as Cl^-, PO_4^{2-}, NO_3^- and SO_4^{2-}. This brucite-like structure consists of a positively charged metal hydroxide nanolayer and interlayer anions containing exchange anions and water molecules (Cursino et al., 2015) and acts as host matrices for various guest anions (Zobir et.al., 2021). The nanolayered material can undergo an exchange process with exchangeable anions in the solution, depending on the affinity of existing anions in the solution (Ahmad et al., 2018). The ability of the host material to act as a controlled release agent can be determined by a controlled release study. The behaviour of the encapsulated active ingredient in the nanohybrid material was investigated by dispersing the nanohybrid in a selected medium solution over time (Hashim et al., 2018). The use of ZLH as a matrix, particularly in fertiliser delivery systems, is very limited and needs to be explored (Khadiran et al., 2021). Based on its unique anion exchange properties and zinc being an important macronutrient for plant growth, a study on ZLH is worth looking into. This study reported on the controlled release formulation of a plant nutrient source by forming zinc-layered hydroxide nanohybrids as a host matrix for nitrate and phosphate anions. The properties of the nanohybrids were investigated on their formation, thermal stability and controlled release performance. A plant growth study was set up to determine the effects of ZLN and ZLP on the growth and nutrient uptake in Kelempayan (*Neolamarckia cadamba*) seedlings with comparison to commercial fertiliser, raw chemicals and control.

MATERIALS AND METHODS

Synthesis of ZLN and ZLP

The ZLN and ZLP were prepared by a two-stage process which is the co-precipitation and anion exchange method. First, the co-precipitation method was used to synthesise zinc-layered hydroxide nitrate (ZLN), while zinc nitrate hexahydrate, $Zn(NO_3)_2\cdot 6H_2O$ acts as a ZLH precursor. NaOH solution (1.0 mol/L) was added slowly into 10 mL of 3.0 mol/L zinc nitrate solution. The pH value of the solution was adjusted to 7 and achieved by magnetic stirring for 2 h. The precipitate obtained was washed with deionised water, separated by a centrifuge and oven-dried at 70 °C for 72 h or until fully dried.

ZLP was prepared using the anion exchange method. Firstly, 0.2 g of ZLN was dissolved in 50 mL of deionised water. This was followed by adding 20 mL of 0.3 mol potassium dihydrogen phosphate,

(KH_2PO_4) slowly into the ZLN solution and vigorously stirred for 3.5 h at room temperature. A solution of 1.0 mol/L of NaOH was slowly added until pH 8 was obtained. The slurry obtained was washed with deionised water, separated by a centrifuge and oven-dried at 70 °C for 72 h or until fully dried. The sample produced was ground into a fine powder and kept in a sample bottle for characterisation purposes.

Characterisation of Nanoparticle

Powder X-ray diffraction (PXRD) patterns were recorded at 2–60° on a Shimadzu XDR-6000 diffractometer operated at CuKα radiation at 40 kV and 30 mA. Fourier transform infrared (FTIR) spectra of the materials were determined at the range of 400 to 4000 cm^{-1} using a KBr disc method on a Perkin-Elmer 1725X spectrophotometer. The thermal properties of samples were determined by Thermogravimetric analysis (TGA) (Q500 V20.13 Build 39, TA Instrument) with a heating rate of 5 °C/min between 25 to 400 °C under a nitrogen atmosphere. The surface morphology of ZLN and ZLP were captured under the high-resolution field emission electron microscopy (FESEM), JSM-6400.

Controlled Release Study

The controlled release study on nitrate and phosphate from the respective ZLN and ZLP nanohybrid was monitored in the following medium: carbonate buffer solution at pH 4, pH 6.5 and sodium carbonate solution at 0.005 M and 0.1 M. Approximately 0.1 g of each nanohybrid was dispersed in 20 mL of individual media solution. At the real-time interval, the solution was filtered through a Whatman filter paper No. 2. The solution collected was analysed using the flow analyzer (FIA) and inductive coupled plasma-optical emission spectrometer (ICP-OES) to determine the concentration of nitrate and phosphate, respectively. The results from the instrument were plotted to obtain the release profile of anions from the respective nanohybrid.

Biomass and Plant Nutrient Analysis

A short-term plant study using Kelempayan seedlings was conducted at FRIM nursery. Four treatments consisted of control as T1, commercial fertiliser (NPK green) as T2, T3 for raw chemicals and ZLN and ZLP as T4. The raw chemical comprised zinc nitrate hexahydrate and potassium dihydrogen phosphate. The amount of nitrogen and phosphorous was kept at 0.0012 g N and 0.0005 g P for all treatments in T2 to T4. Kelempayan seedlings were germinated on a sand bed for 2 months before being transferred to a polybag containing topsoil at 20 replicates per treatment. The height of the plant was measured every month for a period of 4 months. After 4 months, destructive sampling was carried out and the biomass of the plant was weighed. The leaf samples were then dried at 60 °C and ground into fine powder. A 0.3 g of the ground leaf samples were digested using 3 mL of nitric acid and 2 mL of hydrogen peroxide in a microwave digester. After cooling, the digest was transferred to a 50 mL volumetric flask and made up to the volume. The concentration of P and Zn in the digest was analysed using ICP OES to determine nutrient plant uptake. While the N content of the ground leaf samples was measured by combustion method with a CNS analyser FP 528.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction

The powder X-ray diffraction patterns of ZLN and ZLP are displayed in Figures 1A and B, respectively. Both the nanohybrids showed sharp reflection peaks with basal spacing at, 9.57 and 6.78 Å, respectively. This basal spacing from ZLN agreed with a study reported by Nabipour et al. (2015). The ZLN produced a well-ordered 2D nanolayered structure with four reflection peaks at 9.57, 4.83, 3.11 and 2.39 Å. The intercalation of phosphate anions in the interlayer region caused shifts at the high 2Θ angle due to decreasing values of the basal spacing (Woo et al., 2011). ZLP also exhibited sharp symmetric peaks with four series of reflection peaks recorded at 6.78, 3.40, 2.26 and 1.70 Å. The sharp symmetric peaks with a series of diffraction peaks indicated that ZLN and ZLP have good two-dimensional (2D) stacking layered crystalline structures. Sarijo et al. (2010) suggested that sharp and intense peaks from PXRD revealed a high crystallinity of the nanocomposite.

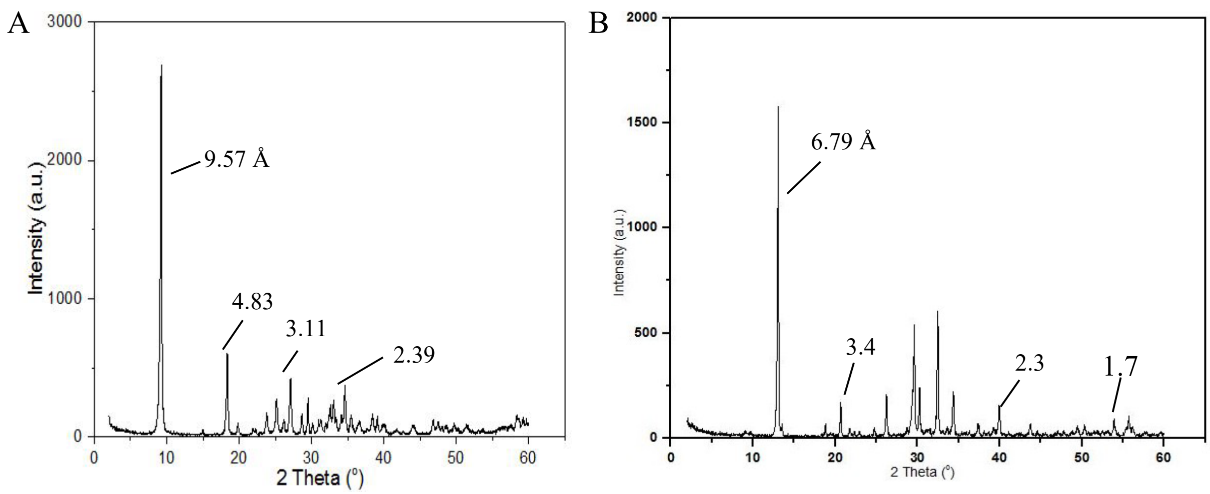


Figure 1. PXRD patterns of ZLN (A) and ZLP (B)

FTIR Spectroscopy

The FTIR spectra of ZLN and zinc nitrate hexahydrate is illustrated in Figure 2A. The presence of nitrate in ZLN was supported by a FTIR study by Nabipour et al. (2015) with bands found at 834 and 1384 cm^{-1} contributing to vibration modes of the nitrate ions. The FTIR spectra of ZLN have a similar characteristic bands of zinc nitrate hexahydrate with nitrate detected at bands 828 and 1387 cm^{-1}. The bands in ZLN were slightly shifted due to the interaction of nitrate anions with the ZLH interlayer. The FTIR spectra of ZLP and potassium dihydrogen phosphate are shown in Figure 2B. The existence of phosphate in ZLP was detected at the 1050 cm^{-1} band assigned to phosphate ion vibration (Woo et al., 2011). As predicted, the phosphate bands in ZLP slightly shifted from position 1076 cm^{-1} in potassium dihydrogen phosphate. The absence of peaks at 834 cm^{-1} and 1384 cm^{-1} suggested that the transformation of ZLN to ZLP has occurred through the anion exchange process (Khadiran et al., 2021). A broad absorption band was spotted at wavenumber 3397 cm^{-1} associated with the O-H stretching frequency of hydroxyl groups due to adsorbed interlayer water (Christy et al., 2019; Machado et al., 2010).

Thermal Analysis

The results of thermal behaviour for ZLN and ZLP examined by thermogravimetric analysis are summarised in Table 1. Four steps of weight loss were observed in ZLN while ZLP progressed mainly in three steps. The first step of thermal decomposition with minor weight loss was 3.75% at 125 °C for ZLN and 2.5% at 92 °C from ZLP. This was due to the elimination of water molecules that exist in the interlayer space (Muda et al., 2018). This was followed by two weight losses at 150 °C (5.00%) and 175 °C (3.75%) in ZLN while ZLP recorded a weight loss of 3.00% at 163 °C. This was associated with the dihydroxylation of hydroxide layers as well as partial decomposition of the intercalated nitrate and phosphate anions. The final step of decomposition was observed at 413 °C and 248 °C with 6.25% and 0.50% weight loss for ZLN and ZLP, respectively (Khadiran et al., 2021). This corresponded with the combustion of organic or inorganic species leaving only relatively less volatile metal oxide. Zinc nitrate hexahydrate displayed two adjacent weight losses with a total loss of 73%. These indicated better thermal stability of nitrate and phosphate anions in ZLN and ZLP, respectively, which is presumably related to the electrostatic interaction between the negatively charged anions and the positively charged zinc-layered hydroxide.

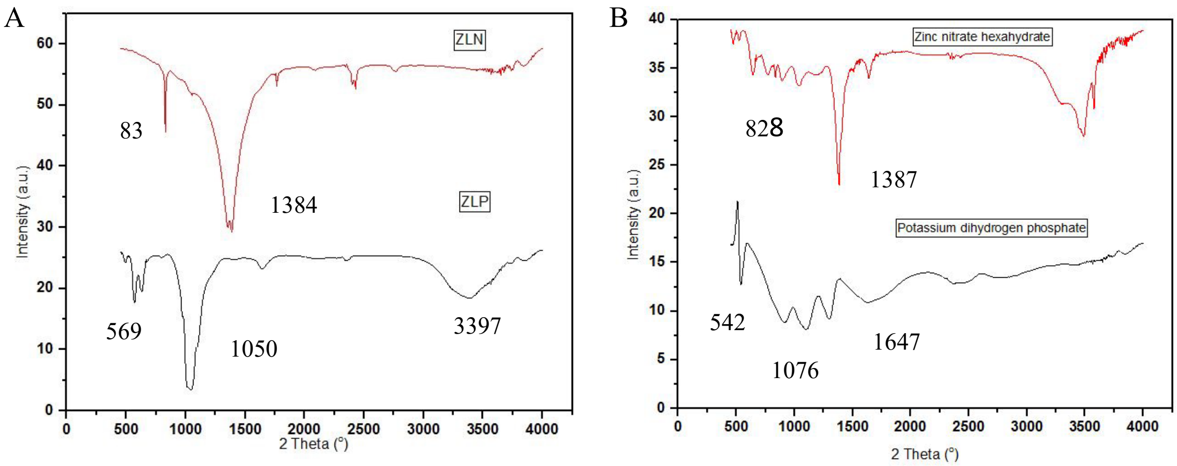


Figure 2. FTIR spectra of ZLN and ZLP (A), and zinc nitrate hexahydrate and potassium dihydrogen phosphate (B)

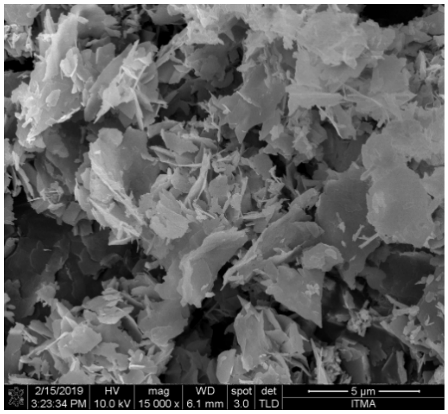
Table 1. The thermal properties of pure zinc nitrate hexahydrate, ZLN and ZLP nanohybrids

Sample	T_1–T_2	T_s (ºC)	Weight loss (%)
Zinc nitrate hexahydrate	50–250	105	42.50
	275–359	346	30.50
ZLN	75–130	125	3.75
	130–155	150	5.00
	155–200	175	3.75
	375–475	413	6.25
ZLP	50–110	92	2.50
	110–210	163	3.00
	210-325	248	0.50

Morphology

The scanning electron micrographs of ZLN and ZLP were examined to determine the nanostructure as shown in Figures 3A and 3B, respectively. The image of ZLN showed non-uniform and flake shape composition while ZLP recorded rod shape morphology of various sizes. The change in morphology that occurred from ZLN to ZLP may be due to the anion exchange process of nitrate to phosphate (Khadiran et al., 2021).

A



B

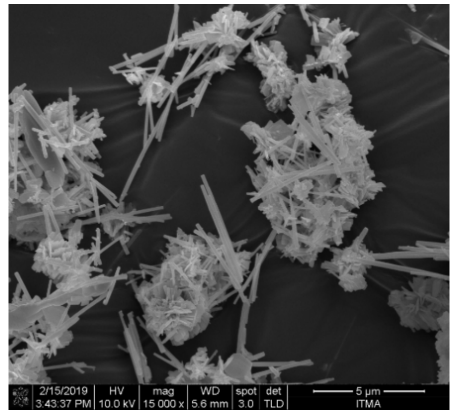


Figure 3. Field emission scanning electron micrographs of ZLN (A) and ZLP (B) at 15,000x magnifications

Controlled Release Pattern in Different pH Buffer

The release profile of nitrate anion from ZLN into carbonate buffer solution at pH 4 and 6.5 is presented in Figure 4A. In a period of 100 h of nanohybrid being placed in the media, the percentage of nitrate release was higher in the pH 4 solution (11.8%) than in pH 6.5 (3.4%). This observation may be associated with the dissolution of ZLH layers in acidic pH causing more nitrate anions to be released and exchanged with carbonate anions in the medium solution. This was further shown when ZLH layers were not stable in acidic pH and dissolved more easily causing the layered structure ZLH to collapse. On the contrary, at pH 6.5 fewer anions were released into the medium solution indicating that ZLH is more stable at higher pH, which agreed with the studies by Hashim et al. (2018) and Saifullah et al. (2013). A similar observation was also found in the release of phosphate anion from ZLP in pH 4 and pH 6.5 solution as illustrated in Figure 4B. The release of phosphate was 0.5% and 0.25% when ZLP was dispersed in pH 4 and 6.5 solutions, respectively, within 100 h. Despite pH levels, the nitrate anion was found to be higher than phosphate. This may be due to the molecule size of nitrate which is smaller than phosphate allowing more nitrate anions to be released and exchanged in the medium solution (Khadiran et al., 2021).

Controlled Release Profile in Different Concentrations of Medium Solutions

Controlled release of nitrate and phosphate anion from their respective nanohybrid into different media concentrations was performed using 0.005 and 0.1 M sodium carbonate solutions (Figures 5A and B). The increase in the release of anion in 0.1 M concentration was noted. The higher the concentration of the media, the percentage release of anions from the respective nanohybrid also increased. The release of nitrate anion from ZLN nanohybrid was slower in 0.005 M than 0.1 M concentration whereby it reached 12% at 100 h. While in 0.1 M solution, it recorded a higher release at 21% nitrate within the same period. A similar pattern was also observed for phosphate anions from ZLP. As expected, the phosphate release was faster in 0.1 M, recorded at 12% while 0.005 M solution gave a 0.5% reading. This situation can be associated with the CO_3^{2-} in the release media which acted as a driving force for the release of nitrate and phosphate. The CO_3^{2-} may have a high affinity towards the interlayer of nanohybrid compared to the presence of guest anions, resulting in the ion exchange occurring (Hussein et al., 2009). Furthermore, the strong electrostatic bond of phosphate anion in the ZLH interlayer may result in the slow release of anion leading to a lower percentage than nitrate anion.

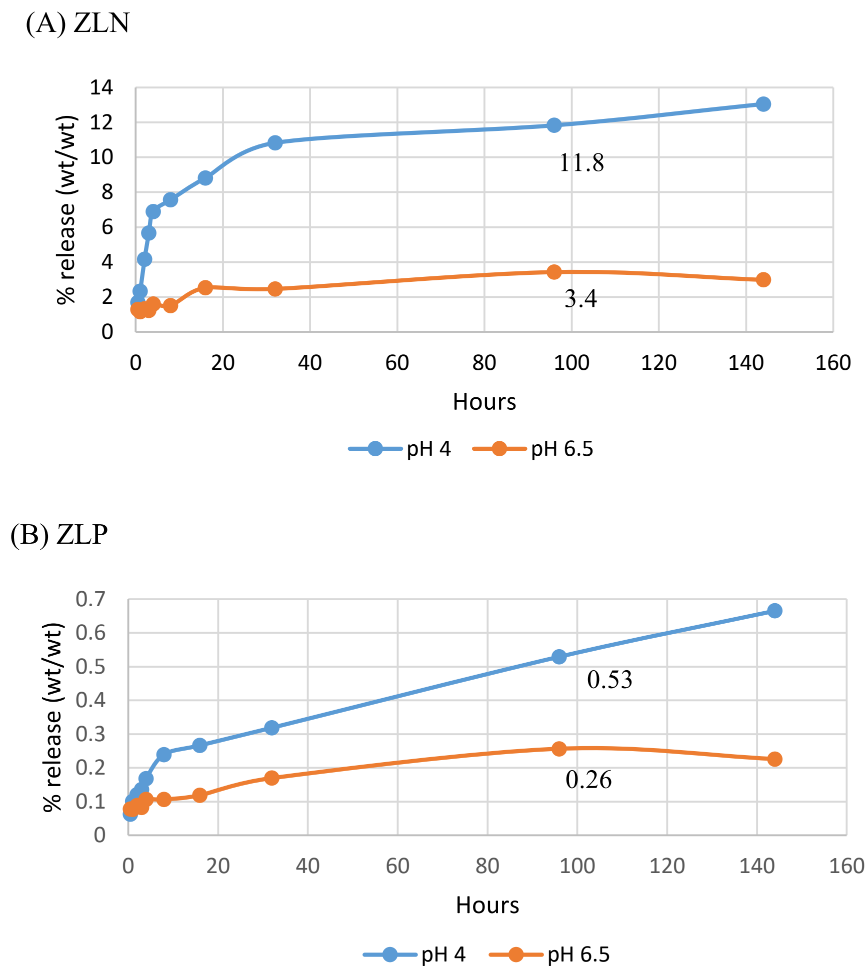


Figure 4. Percentage release of nitrate from ZLN (A) and phosphate from ZLP (B) into buffer solution pH 4 and 6.5

Biomass and Plant Nutrient Analysis

The biomass weight of Kelempayan seedlings after 4 months applied with ZLN and ZLP, commercial fertiliser and raw chemicals are displayed in Figure 6. In the control treatment, the lowest biomass weight with a value of 16.2 g was recorded. While T2 and T3 treatments with commercial fertiliser and raw chemicals recorded values of 20.3 and 29.5 g of biomass weight, respectively. The highest biomass weight recorded was obtained from treatments with ZLN and ZLP with reading reaching up to 33.6 g. This could be related to the controlled release properties of ZLN and ZLP, which improved the nutrient release and increased the biomass yield. The nitrogen, phosphorus and zinc content in Kelempayan leaf after treatment with various applications is presented in Figure 7. The concentration of N, P and Zn in leaf samples from treatment T4 with ZLN and ZLP application gave the highest readings of 2.14%, 0.22% and 96.8 ppm, accordingly. This pattern was consistent with the highest biomass weight observed in the same treatment. The control samples recorded the least amount with 1.41% N, 0.18% P and 25.9 ppm Zn. The commercial fertiliser and raw chemicals treatment recovered 1.55% and 1.58% for N, 0.19% for P and 55.9 and 57.2 ppm of Zn, respectively in leaf samples, which were less than the nanohybrid treatment. This supported the idea that controlled release properties of ZLH can improve nutrient uptake in plants and enhance the growth performance of Kelempayan with an increase in biomass yield. This may be due to ZLH acting as a zinc source that provided an important micronutrient for plant growth and a beneficial soil supplement (Ahmad et al., 2015).

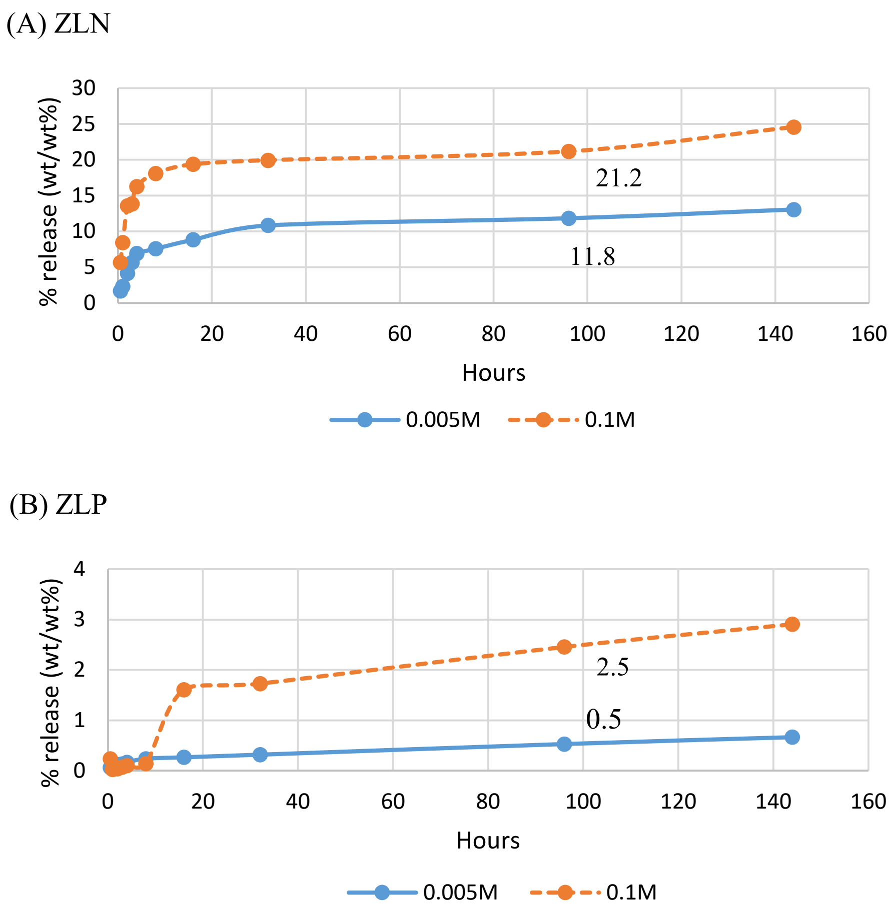


Figure 5. Percentage release of nitrate from ZLN (A) and phosphate from ZLP (B) into sodium carbonate solution at 0.005 and 0.1M concentrations

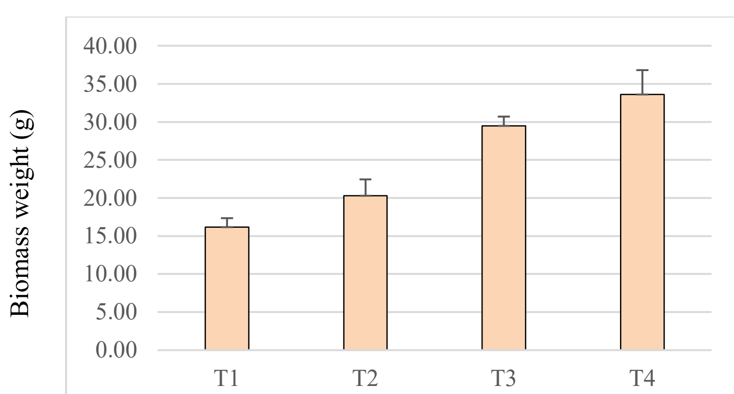


Figure 6. Mean value biomass weight of Kelempayan seedlings, g ± standard deviation after 4 months of application with different treatments. T1 = Control; T2 = commercial fertiliser; T3 = raw chemical, and T4 = ZLN and ZLP.

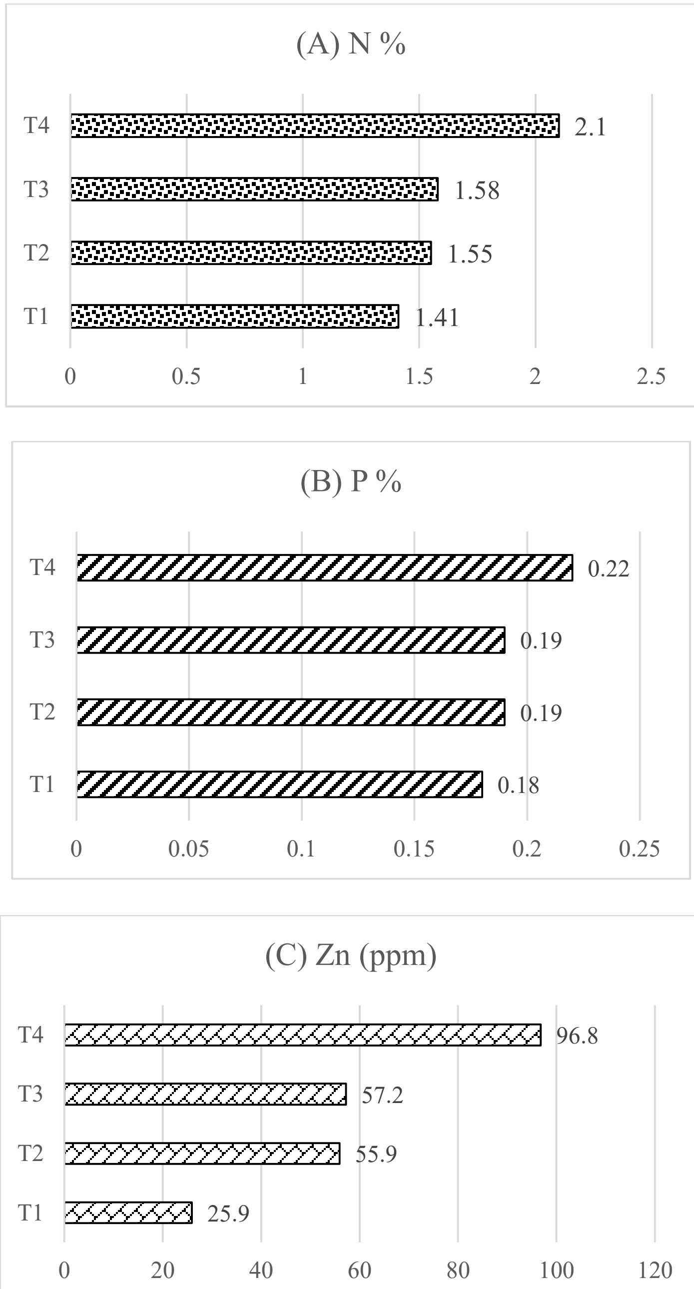


Figure 7. The concentration of (A) N, (B) P and (C) Zn in Kelempayan leaves after 4 months of application at different treatments. T1 = Control; T2 = commercial fertilizer; T3 = raw chemical and T4 = ZLN and ZLP.

CONCLUSIONS

Two nanohybrids of zinc-layered hydroxide nitrate and zinc-layered hydroxide phosphate were obtained using the co-precipitation and anion exchange methods. The synthesised materials had basal spacing at 9.57Å (ZLN) and 6.78 Å (ZLP) from the PXRD analysis. The presence of nitrate and phosphate was proven in the FTIR study. The thermal stability of nanohybrids obtained was enhanced compared to its starting material, zinc nitrate hexahydrate whose percentage weight loss was higher with two steps of decomposition. Investigation on the controlled release study showed that the percentage of guest anion released from ZLH depended on the pH and concentration of the release medium. The release of anion at pH 4 was higher than pH 6.5 indicating the instability of ZLH layers in acidic pH. The more concentrated a medium solution, the anion increased correspondingly. Despite the type of release media, the weight percentage release of nitrate from ZLN was higher than phosphate from ZLP. The plant growth study indicated that treatment with ZLN and ZLP would enhance the growth of Kelempayan seedlings which recorded the highest biomass yield and had the highest concentration of N, P and Zn in leaf samples after 4 months. Treatment with commercial fertiliser and raw chemicals was unable to compete with the phase shown by ZLH. This study showed that layered zinc hydroxide can be a potential candidate as a host for plant nutrient storage and delivery. The incorporation of nitrate and phosphate in ZLH improved the growth performance of Kelempayan seedlings with better plant nutrient uptake under nursery trials. Further work should be carried out to determine the effect of ZLH nanohybrid on different soil properties.

AUTHORS CONTRIBUTION

RA and NH conceived and designed the analysis. RA, NFK, TK, SSH and WRK collected the data and performed the analysis. RA wrote the paper, and MZH, ZZ and NH checked and approved the submission.

CONFLICT OF INTEREST

The authors declare no conflict of interests.

FUNDING

This research was funded by the Malaysian Ministry of Higher Education (MOHE) through the Fundamental Research Grant Scheme, FRGS/1/2017/STG01/NRE/03/1.

ACKNOWLEDGEMENTS

The authors would like to thank the staff from the Soil Chemistry Laboratory, FRIM for assisting in the laboratory analysis.

REFERENCES

Ahmad, R., Hussein, M. Z., Kadir, W. A. W. R., Sarijo, S. H. and Yun, H. T. -Y. (2018). Phytotoxicity performance and controlled release behaviour of insect pheromone delivery system based on valeric acid-zinc layered hydroxide nanohybrid. *International Journal of Agriculture, Forestry and Plantation*, 6, 50-65.

Ahmad, R., Hussein, M. Z., Kadir, W. A. W. R., Sarijo, S. H. and Yun, H. T. -Y. (2015). Evaluation of controlled release property and phytotoxicity effect of insect pheromone zinc-layered hydroxide nanohybrid intercalated with hexenoic acid. *Journal of Agriculture and Food Chemistry*, 63, 10893-10902.

Berber, M. R., Hafez, I. H., Minagawa, K. and Mori, T. (2014). A sustained controlled release formulation of soil nitrogen based on nitrate-layered double hydroxide nanoparticle material. *Journal of Soils Sediments*, 14, 60-66.

Biswick, T. T., Park, D. W., Sul, Y. G. and Choy, J. H. (2010). P-coumaric acid-zinc basic salt nanohybrid for controlled release and sustained antioxidant activity. *Journal of Physics and Chemistry of Solids*, 71, 647-649.

Cursino, A. C., Rives, V., Carlos, L. D., Rocha, J. and Wypych, F. (2015). Layered zinc hydroxide salts intercalated with anion surfactants and solubilized with UV-absorbing organic molecules. *Journal Brazilian Chemistry Society*, 26, 1769-1780.

Hashim, N., Sharif, S. N. M., Muda, Z., Isa, I. M., Ali, N. M., Bakar, S, A., Sidik, S. M. and Hussein, M. H. (2018). Preparation of zinc layered hydroxide-ferulate and coated zinc layered hydroxide ferulate nanocomposites for controlled release of ferulic acid. *Materials Research Innovations*, 23(4), 1-13.

Hashim, N, Hussein, M. Z., Isa, I. M., Kumari, A., Mohamed, A., Jaafar, A. M. and Taha, H. (2014a). Synthesis and controlled release of cloprop herbicides from cloprop-layered double hydroxide and cloprop-zinc layered hydroxide nanocomposites. *Journal of Inorganic Chemistry*, 4, 1-9.

Hashim, N., Muda, Z., Abdul Hamid, S., Md Isa, I., Kamari, A., Mohamed, A., Hussein, M. Z. and Abdul Ghani, S. (2014b). Characterization and controlled release formulation of agrochemical herbicides based on zinc-layered hydroxide-3-(4-Methoxyphenyl) propionate nanocomposite. *Journal of Physical and Chemical Sciences*, 1(4), 1-6.

Hussein, M. Z., Hashim, N., Yahaya, A. H. and Zainal, Z. (2009). Controlled release formulation of pesticide agrochemical based on 4-(2,4-dichloro phenoxy) butyrate nanohybrid. *Journal of Nanoscience and Nanotechnology*, 9, 2140-2147.

Isa, I. M., Dahlan, S. N. A., Hashim, N., Ahmad, M. and Ghani, S. A. (2012). Electrochemical sensor for cobalt (II) by modified carbon paste electrode with Zn/Al-2(3-chlorophenoxy) propionate nanocomposite. *International Journal of Electrochemical Sensor*, 7, 7797-7808.

Khadiran, N. F., Hussein, M. Z., Ahmad, R., Khadiran, T., Zainal, Z., Wan Abdul Kadir, W. R. and Hashim, S. S. (2021). Preparation and properties of zinc layered hydroxide with nitrate and phosphate as the counter anion, a novel control release fertilizer formulation. *Journal of Porous Materials*, 28, 1797-1811.

Li, P., Xu, Z. P., Hampton, M. A., Vu, D. T., Huang, L., Rudolph, V. and Nguyen, A. V. (2012) Control preparation of zinc hydroxide nitrate nanocrystals and examination of the chemical and structure stability. *Journal Physical Chemistry C: Nanomaterials, Interfaces and Hard Matter*, 116(18), 10325-10332.

Machado, G. S., Arizaga, G. G. C., Wypych, F. and Nakagaki, S. (2010). Immobilization of anionic metalloporphyrins on zinc hydroxide nitrate and study of unusual catalytic activity. *Journal of Catalysts*, 274, 130-141

Madzokere, T. C., Murombo, L. T. and Chiririwa, H. (2021). Nano-based slow-releasing fertilizers for enhanced agricultural productivity. *Materials Today: Proceedings*, 45(3), 3709-3715.

Muda, Z., Hashim, N., Isa, M. I., Ali, N. M., Bakar, S. A., Mamat, M., Hussein, M. Z., Bakar, N. A. and Mahamod, W. R. W. (2018). Synthesis and characterization of carbamate insecticide intercalated zinc layered hydroxide modified with sodium dodecyl sulphate. *IOP Conf. Series: Materials Science and Engineering*, 440, 012003.

Nabipour, H., Hosaini Sadr, M. and Thomas, N. (2015). Synthesis, characterisation and sustained release properties of layered zinc hydroxide intercalated with amoxicillin trihydrate. *Journal of Experimental Nanoscience*, 10(16), 1269-1284.

Najem Abed, N. A. R, Abudoleh, S. M, Alshawabkeh, I. D., Najem Abed, A. R., Abuthawabeh, R. K. A., Hussein-Al-Ali, S. H. (2017). Aspirin drug intercalated into zinc-layered hydroxides as nanolayers: structure and *in vitro* release. *Nano Hybrids and Composites*, 18, 42-52.

Preetha, P. S. and Balakrishnan, M. (2017). A review of nano fertilizers and their use and functions in soil. *International Journal of Current Microbiology and Applied Science*, 6(12), 3117-3133.

Ruiz, C. V., Rodríguez-Castellón, E. and Giraldo, O. (2019). Hybrid materials based on a layered zinc hydroxide solid and gallic acid: Structural characterization and evaluation of the controlled release behaviour as a function of the gallic acid content. *Applied Clay Science*, 181, 105228.

Saifullah, B., Hussein, M. Z., Hussein-Al-Ali, S. H., Arulselvan, P. and Fakurazi, S. (2013). Sustained release formulation of an anti-tuberculosis drug based on para-amino salicylic acid-zinc layered hydroxide nanocomposite. *Chemistry Central Journal*, 7, 72-82.

Sarijo, S. H., Hussein, M. Z., Yahya, A., Zainal, Z. and Yarmo, M. A. (2010). Synthesis of phenoxy herbicides-intercalated layered double hydroxide nanohybrids and their controlled release property. *Current Nanoscience*, 6, 199-205.

Woo, M. A., Kim, T. W., Paek, M., Ha, H., Choy, J. and Hwang, S. (2011). Phosphate-intercalated Ca–Fe layered double hydroxides: Crystal structure, bonding character, and release kinetics of phosphate. *Journal of State Chemistry*, 184, 171-176.

Zobir, S. A. M., Ali, A., Adzmi, F., Sulaiman, M. R. and Ahmad, K. (2021). A review on nano pesticides for plant protection synthesized using the supramolecular chemistry of layered hydroxide host. *Biology*, 10(11), 1077.