An Advanced Synthetic Technique of Nitrate Fertilizer supported by a Clay Material shows a Remarkable Controlled Release behavior into soils

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Abstract
Here, we offer an advanced technique of supporting nitrogen into soil in a controlled release process. Mg-Al-layered double hydroxide (LDH) material was used as a carrier for nitrogen which was loaded into LDH in a nitrate form by using a reconstruction-incorporation process. The prepared materials were characterized by different spectroscopic techniques including; elemental analysis, X-ray powder spectroscopy, Infrared spectroscopy, scanning electron microscopy, transmittance electron microscopy, and thermal gravimetric analysis. The release process of nitrate was conducted in different soil types at different climate conditions, showing a remarkable controlled release of nitrate from LDH. Hence, our technique can support as a new nitrogen fertilizer source into soils.

Keywords: Soil Nitrate; layered double hydroxide; controlled release; reconstruction-incorporation process

1. Introduction

The technology development in the field of soil nitrogen fixation is receiving a great deal of attention where leaching of soil nitrogen is still representing an important issue in the field of horticultural and agricultural productions. Looking more closely, nitrate as an anion is not easily adsorbed on soil particles and therefore moves within the soil profile with draining water.(Cameron et al., 2013) Accordingly, from health, environmental, and financial points of views, leaching of nitrate is an issue of high concern.

Layered double hydroxides is a type of natural clay materials with the empirical formula (M^{II}_{1-x} M^{III}_x $(OH)_2.A_{x/n}.mH_2O$), where M^{II} is a divalent metal ion, M^{III} is a trivalent metal ion, and A is an exchangeable interlayer anion. This variable chemical structure provided LDH specific properties for different applications, e.g. anion exchangers, adsorbents, anion scavengers, and supports. In particular, in the agriculture filed, it has been used for the incorporation and the exchange of nutrients, pesticides, plant hormones and different soil fertilizers. Hence, it has promising future for different agriculture applications.(Hafez et al., 2010)
In the sector of improving the use-efficiency of nitrogen-based soil fertilizers, different techniques have been introduced, e.g. the irrigation system applied, multiple applications of nitrogen-based soil fertilizers, and urease/nitrification inhibitors(Neilsen et al., 1992; Zaman et al., 2013). Additionally, one of the most effect method of controlling the nitrate leaching is the use of adsorbents e.g. clays (Zhou et al., 2015). Bigelow et al., has showed the ability of using the cationic clay clinoptilolite-zeolite to keep high levels of nitrates into soils during the irrigation process. Thus, applying new types of clays may result in controlling the nitrates release into the soils (Bigelow et al., 2001).
Here, we synthesize the nitrate form of Mg-Al-LDH by using the calcination-reconstruction process (using the memory effect of LDH) which provide a high loading ratio of the target anion supported in the reconstruction medium, as in our case the nitrate anion. Purpose of this study is to offer a potential formulation technique of soil-nitrate fertilizer with a high loading amount of Nitrogen that can be released in a controlled process through the nitrate-form of the layered double hydroxide material.

2. Experimental work

2.1. Materials

Magnesium chloride hexahydrates, and aluminum chloride hexahydrates, were purchased from alfa easer chemical Co. Ltd. Sodium nitrate, potassium hydroxides, calcium chloride, potassium chloride, and

nitric acid were purchased from El-Gomhouria Co. for Trading chemicals and medical supplies. These materials were used without further purification. All solutions are prepared by using deionized water (18.2 MΩ/cm).

2.2. Mg-Al-LDH preparation

A 60 mL aqueous solution of 3.387 g Magnesium chloride hexahydrates, and 2.01 g of Aluminum chloride hexahydrates with the metals (Mg^{2+}/ Al^{3+}) molar ratio of 2 was prepared with magnetic stirring at room temperature. A solution of 2M potassium hydroxides was added dropwise to the metal solution in irder to precipitate the LDH material, keeping the pH of the precipitation medium at 8. The solution volume was completed to 100 ml by using deionized water. Then, the resultant suspension was stirred at 100 °C for 24 hrs under nitrogen atmosphere. The obtained LDH was filtered, washed with deionized water till a negative test for chloride ion, and finally oven dried at 110 °C.

2.3. Calcination of Mg-Al-LDH

Typically, the prepared Mg-Al-LDH was calcined at 400 °C for 6 hrs in nitrogen atmosphere. After cooling down the calcination furnace, the calcined LDH material was kept under nitrogen for further experiments.

2.4. Preparation of nitrate form of Mg-Al-LDH

1 g of the calcined LDH was dispersed into a 100 mL aqueous solution of 1M Sodium nitrate. The pH of the reaction medium was kept at 10 by using drops of 0.1M nitric acid. The resultant suspension was stirred at 100 °C for 4 days under nitrogen atmosphere. The formed nitrate–LDH sample was filtered, washed with deionized water, and finally oven dried at 110 °C.

2.5. Characterization process of the prepared materials

The electron microscope micrographs (Scanning electron micrographs; SEM, and Transmittance electron micrographs; TEM) were captured by a SEM S-4700 and a JEOL JEM-2010 microscopes, respectively. Infrared spectra were measured on a Bio-Rad FTS 3000MX FT-IR spectrophotometer with a TGS detector by accumulating 16 scans at 4 cm^{-1} resolutions. X-ray powder diffraction patterns (XRD) were measured on a Rigaku X-ray diffractometer by using CuKα radiation at λ = 1.5405 Å. The measurements were performed with a 2θ scanning step of 0.02°, a scanning step time of 5 s, a filament intensity of 40 mA, and a voltage of 30 kV. Thermogravimetric analysis (TGA) was recorded with a Shimadzu thermogravimetric analyzer (TGA-50, TA-60WS) with a heating rate of 10 °C/min.

2.6. The release experiment of NO_3 from LDH

In order to draw a clear picture about the new formulated nitrate fertilizer and in order to meet the real application of nitrate fertilizer in the agriculture field, the release experiments of nitrate were conducted at different climate conditions in different soil solutions as follows. Typically, two different buffers were used at different temperatures. Buffer A that mimics the acidic agriculture soils. It consists of a 100-mL solution mixture of the same volumes of 5.0 mM calcium chloride, 1.0 mM magnesium chloride, and 0.25 mM potassium chloride, plus few drops of 10.0 mM hydrochloric acid to adjust the solution pH at 4.0. Buffer B that mimics the normal agriculture soils. It consists of a 100-mL solution mixture of the same volumes of 5.0 mM calcium chloride, 1.0 mM magnesium chloride, and 0.25 mM potassium chloride, plus few drops of 10.0 mM sodium hydroxide to adjust the solution pH at 7.0. These buffer solutions were defined based on literature data (Álvarez Rogel et al., 2001).

The release experiments were conducted as follows. In different conical flasks of same size, a 200-mg of nitrate-LDH fertilizer was dispersed in 100 mL of soil solution. Each conical flask was then incubated at 20.0 ± 1.0 °C. Then, at different time intervals, the conical flask content was withdrawn and get filtered. The recovered precipitate was then dried and assayed for analysis to determine the amount of nitrate left inside LDH. The release experiments were repeated at another two different temperatures (30.0 ± 1.0 °C and 40.0 ± 1.0 °C) to mimic different soil climates. All the release experiments were performed in duplicates.

3. Results and discussions

The SEM image of the freshly prepared LDH has showed the Nano-flakes of LDH (**Figure 1**).
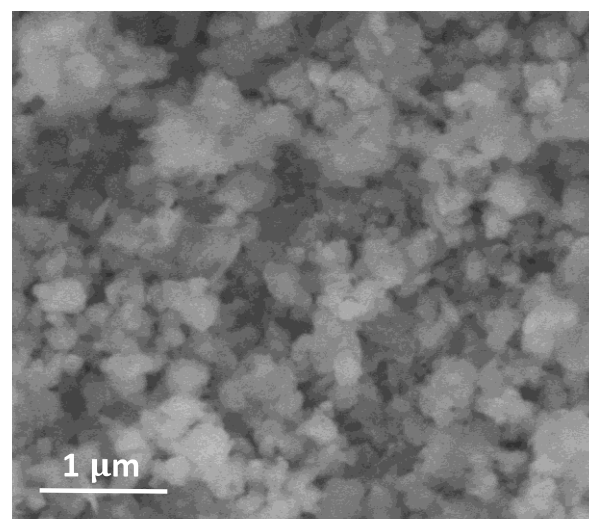
Figure 1. SEM micrograph of freshly prepared Mg-Al-LDH.

As it can be seen from the TEM image (**Figure 2**), the flakes possess a roughly hexagonal nanomaterial with less sharp edges (Li et al., 2016). The Mg and Al content was confirmed by the energy-dispersive analysis of the X-ray spectrum. The Mg/Al ratio was determined to be 1.8.
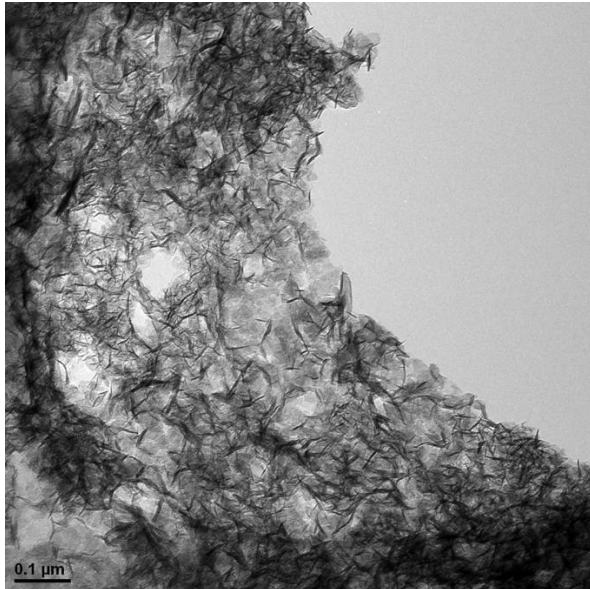

**Figure 2.** TEM micrograph of freshly prepared Mg-Al-LDH.

The X-ray pattern of **Figure 3a**, has showed the typical reflections of carbonate-form of LDH. The peaks were indexed as the (003), (006), (012), (015), (018), (110), and (113) reflections of a carbonate-LDH (Yokoi et al., 2015). **Figure 3b**, shows the X-ray pattern of calcined LDH. As it can be seen, the specific reflection peaks of LDH were disappeared as a result of the calcination process, and instead a peak at around 2θ of 30 has been emerged, indicating the formation of metal oxides of the calcined LDH (Teixeira et al., 2014). On the other side, **Figure 3c**, has showed the characteristic reflections peaks of Nitrate-form of LDH (Mahjoubi et al., 2017), indicating a successful reconstruction process of LDH and a successful incorporation of the nitrate anions.

The Infrared spectra of the measured samples are displayed in **Figure 4**. **Figure 4a**, has revealed the characteristic peaks of the carbonate-LDH, in particular, the carbonate peak at 1352 cm^{-1}, the Metal-oxide peaks at 779 and 682 cm^{-1}, and the layered hydroxide groups at 3470 cm^{-1}(Tanaka et al., 2012). As a result of the calcination-reconstruction process, the carbonate peak is disapeared, and on the other hand, the nitrate peak is emerged at 1371 cm^{-1} (Mahjoubi et al., 2017) (**Figure 4b)**, confirming the sucessfull incorporation process of nitrate into the interlayers-gallary of LDH (Abellan et al., 2010). The magnification of the interlayer anion region (**Figure 4c)** has showed a positive shift to a higher wavelength in the case of nitrate-LDH, indicating
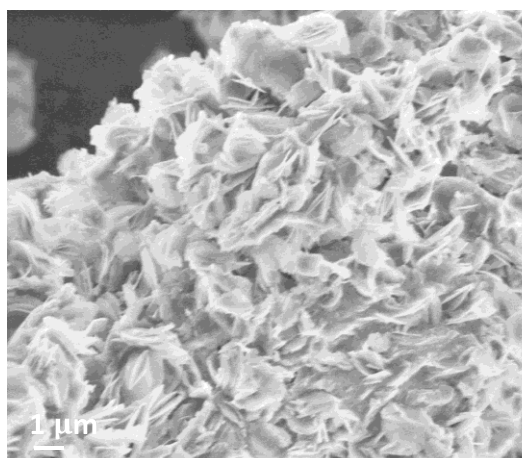
a weak interaction of nitrate anion with the LDH layers compared to carbonate-LDH.
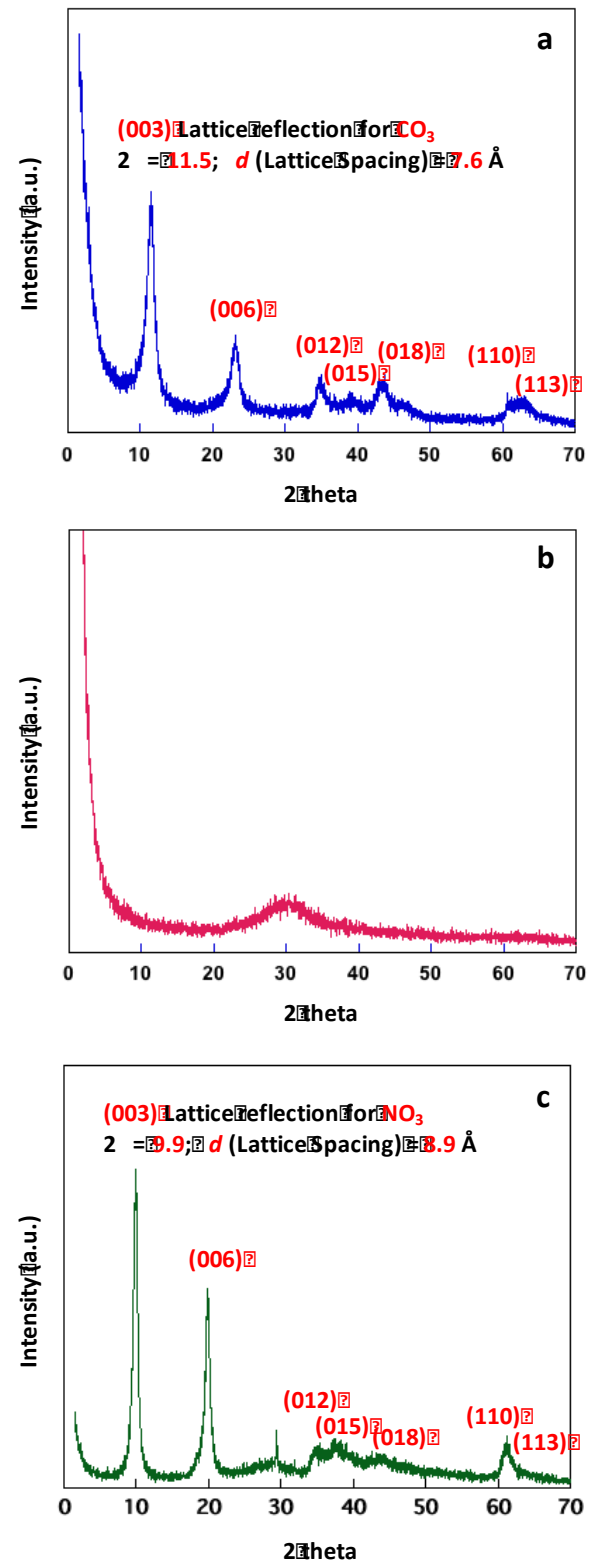
Figure 3. XRD pattern of: (a) carbonate-LDH, (b) calcined-LDH, and (c) Nitrate-LDH.
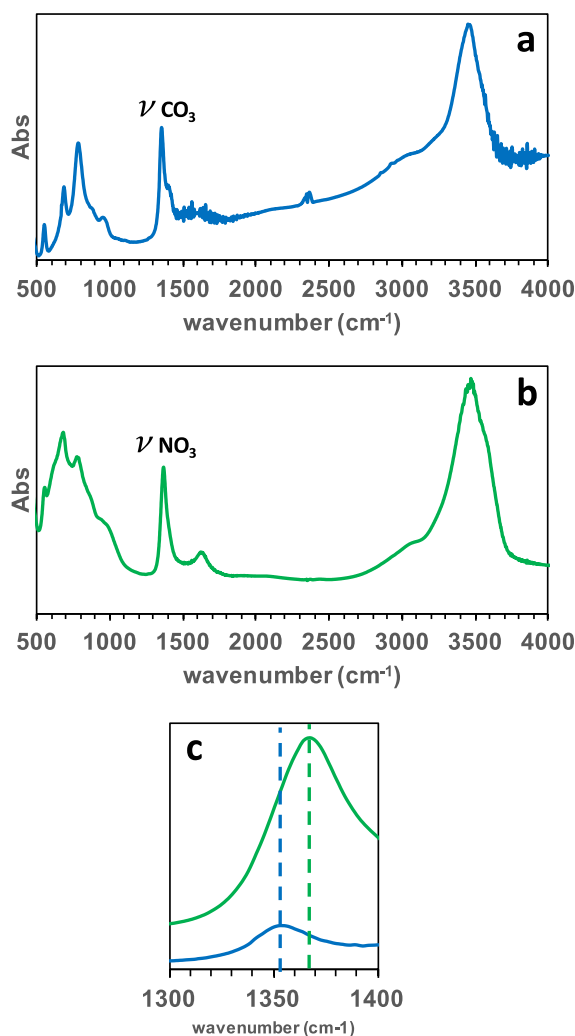
Figure 4. Infrared spectra of: (a) carbonate-LDH, (b) Nitrate-LDH, (c) Magnification region of the interlayer anion of carbonate-LDH (a) and Nitrate-LDH (b). Additionally, the SEM image of the reconstructed LDH has confirmed


Figure 5. SEM micrograph of Mg-Al-LDH reconstructed with Nitrate anion.

Additionally, the SEM image of the reconstructed LDH has showed a hexagonal morphology of the nitrate-LDH particles, indicating a successful preparation of a highly crystalline material. The size of the particles in the case of nitrate-LDH was slightly bigger due to the improvement of the rate of nucleation during the reconstruction process.

The elemental analysis of nitrate–LDH has showed a nitrate loading ratio of approximately 21%.

The thermal gravimetric analysis was measured to show the thermal behavior and stability of the nitrate–LDH material. **Figure 6** shows the temperature-dependence of the weight loss of nitrate–LDH.
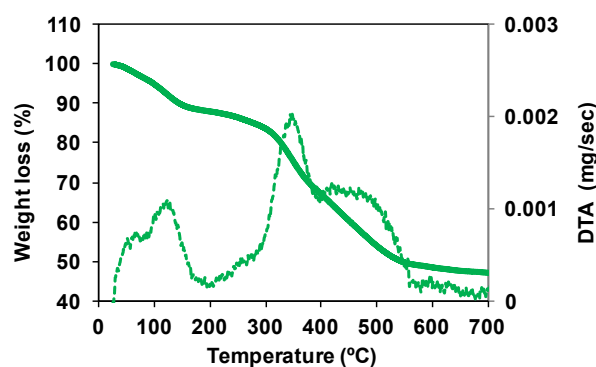
Figure 6. Temperature-dependence of the weight loss of nitrate–LDH.

As it can be seen, the thermal behavior of nitrate–LDH (solid green line) proceed mainly through two weight loss processes. The physically and interlayer water molecules was removed between 30-200 °C. The removal of the structural water was recorded between 200-300 °C. The temperature range 300-600 °C, has showed a weight loss of ~38%, which was attributed to the loss of nitrate anions and the dehydroxylation of the brucite-like layers, respectively. DTA profile of nitrate–LDH (dashed green line) has displayed two mail endothermic peaks. The endothermic peak between 300-600 °C was used to calculate and confirm the mass loss of nitrate. As calculated, the nitrate weight into LDH was recorded to be 19%, in a good agreement with the elemental analysis results.

The newly formulated nitrate LDH fertilizer has showed a remarkable release of the nitrate anion into the release mediums of the different soil solutions. In Buffer A that mimics the acidic agriculture soils, around 30% of the intercalated nitrate was released in a sustained process during 6 days (rate, ~5% of the intercalated nitrate was released per day). Then, during the next 3 days, around 40% of the intercalated nitrate was released with the rate of ~13% per day. Finally, the rest of the intercalated nitrate was release during 1 day. This behavior is probably due to an exchange process with the medium carbonate, followed by a slow and a fast collapsing

processes of the brucite layers, respectively, which may result under the effect of the acidic medium. The same release behavior was observed at the two other temperatures; 30 °C and 40 °C. The only difference was the total time consumed for the release, where at it took 8 days and 7 days at 30 °C and 40 °C, respectively. On the other side, in Buffer B, the release was more sustained, probably due to the effect of the basic medium that cannot easily destroy the brucite layers. In general, the release was observed to proceed very slowly during the first days. Around 60% of the intercalated nitrate was released during 16 days. Then, 40% was release during the next 8 days. The same slow release was also observed at the other two temperatures where it took 22 days and 19 days at 30 °C and 40 °C, respectively.

4. Conclusion

This study has showed a controlled release process of a newly functionalized soil nitrate fertilizer using an environmentally friendly material;LDH. The release was very slow in the basic soil compared to the acidic soils. The increase of the soil temperature has accelerated the nitrate release.

References

Abellan, G., Coronado, E., Marti-Gastaldo, C., Pinilla-Cienfuegos, E., and Ribera, A. (2010). Hexagonal nanosheets from the exfoliation of Ni2+-Fe3+ LDHs: a route towards layered multifunctional materials. *Journal of Materials Chemistry* **20**, 7451-7455.

Álvarez Rogel, J., Ortiz Silla, R., and Alcaraz Ariza, F. (2001). Edaphic characterization and soil ionic composition influencing plant zonation in a semiarid Mediterranean salt marsh. *Geoderma* **99**, 81-98.

Bigelow, C. A., Bowman, D. C., and Cassel, D. K. (2001). Nitrogen Leaching in Sand-based Rootzones Amended with Inorganic Soil Amendments and Sphagnum Peat. *Journal of the American Society for Horticultural Science* **126**, 151-156.

Cameron, K. C., Di, H. J., and Moir, J. L. (2013). Nitrogen losses from the soil/plant system: a review. *Annals of Applied Biology* **162**, 145-173.

Hafez, I. H., Berber, M. R., Minagawa, K., Mori, T., and Tanaka, M. (2010). Design of a Multifunctional Nanohybrid System of the Phytohormone Gibberellic Acid Using an Inorganic Layered Double-Hydroxide Material. *Journal of Agricultural and Food Chemistry* **58**, 10118-10123.

Li, J., Fan, Q., Wu, Y., Wang, X., Chen, C., Tang, Z., and Wang, X. (2016). Magnetic polydopamine decorated with Mg-Al LDH nanoflakes as a novel bio-based adsorbent for simultaneous removal of potentially toxic metals and anionic dyes. *Journal of Materials Chemistry A* **4**, 1737-1746.

Mahjoubi, F. Z., Khalidi, A., Abdennouri, M., and Barka, N. (2017). Zn–Al layered double hydroxides intercalated with carbonate, nitrate, chloride and sulphate ions: Synthesis, characterisation and dye removal properties. *Journal of Taibah University for Science* **11**, 90-100.

Neilsen, W. A., Pataczek, W., Lynch, T., and Pyrke, R. (1992). Growth response of Pinus radiata to multiple applications of nitrogen fertilizer and evaluation of the quantity of added nitrogen remaining in the forest system. *Plant and Soil* **144**, 207-217.

Tanaka, T., Kameshima, Y., Nishimoto, S., and Miyake, M. (2012). Determination of carbonate ion contents in layered double hydroxides by FTIR spectrometry. *Analytical Methods* **4**, 3925-3927.

Teixeira, T. P. F., Aquino, S. F., Pereira, S. I., and Dias, A. (2014). Use of calcined layered double hydroxides for the removal of color and organic matter from textile effluents: kinetic, equilibrium and recycling studies. *Brazilian Journal of Chemical Engineering* **31**, 19-26.

Yokoi, T., Tsukada, K., Terasaka, S., Kamitakahara, M., and Matsubara, H. (2015). Morphological control of layered double hydroxide through a biomimetic approach using carboxylic and sulfonic acids. *Journal of Asian Ceramic Societies* **3**, 230-233.

Zaman, M., Zaman, S., Adhinarayanan, C., Nguyen, M. L., Nawaz, S., and Dawar, K. M. (2013). Effects of urease and nitrification inhibitors on the efficient use of urea for pastoral systems. *Soil Science and Plant Nutrition* **59**, 649-659.

Zhou, L., Cai, D., He, L., Zhong, N., Yu, M., Zhang, X., and Wu, Z. (2015). Fabrication of a High-Performance Fertilizer To Control the Loss of Water and Nutrient Using Micro/Nano Networks. *ACS Sustainable Chemistry & Engineering* **3**, 645-653.