Properties of slow release magnesium and calcium nitrate tablets composed of rice-husk-ash with chitosan coating, within water and in several types of soil

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Abstract. Preparation and characteristic of slow release tablet from environmental friendly material has been intensively studied. This current study focused on preparation of slow release tablet of magnesium and calcium nitrate. A mixture of sago starch, rice husk ash, hot water, magnesium and calcium nitrates gave compatible composite to prepare stable tablet. The higher sago starch in the composite gave the more stable tablet but with 20% sago content, tablets will survive at least 11 days in water. Magnesium and calcium release faster within distillate water than in soil. In media either water and soil, magnesium release rate was than rate of calcium release. Magnesium was found less available in RYP soil environment than in entisols and alluvial soil system.

1. Introduction

Slow release and control fertilizers has been studied intensively and most of which are on control-release coated-urea (CRCU). CRCU were coated either with sulphur, polyolefin, methacrylic acid copolymer, 4,4-diphenylmethane diisocyanate, triethanolamine, diethyleneglycol polyols or other synthetic polymeric materials [1-2]. The effect of additive chemical in the fertilizer has been concerned and it inspires to search friendly supported materials such as waste papers [3], wheat straws and attapulgite [4] but often additive chemicals were still used such as acrylic acid, polyvinyl alcohol or glutaraldehyde as the synthetic adhesive [5]. The synthetics adhesive in control release formula was replaced by chitosan and solidified by crosslinking methods [6]. Synthetic nano-zeolite containing plant nutrients was reported previously, but these are relatively complicated technique especially if it is applied in home industries [7]. CRCU was prepared by coating the granulated urea with gypsum and dolomite limestone [8]. Friendly environmental materials on preparation slow release urea tablets have been studied [9-10] but slow release magnesium and calcium using sago starch as additive has been not much explored.
Calcium and magnesium are essential mineral nutrients for plants. Without magnesium chlorophyll can not capture sun energy that requires for photosynthesis. It also has important role in carbohydrate metabolism and in the cell membrane stabilization. Naturally magnesium ions might come from the soil as calcitic or dolomite but often insufficient since many natural magnesium compounds including carbonates, phosphates, and silicates are hardly soluble in water, and they could not be absorbed by plants, whereas magnesium is found around 0.1 – 0.4% in dried plant for normal growth.

Magnesium fertilizer is usually MgSO₄·H₂O with commercial name as kieserite, it has 17% Mg and water soluble [11]. In some commercial fertilizer product, “kieserite” has been address to natural magnesium compounds with 28-30% MgO, but it often was found very insoluble in water and become ineffective magnesium source for large plantation industry [12]. Dolomite limestone contains very little of magnesium and calcium that are soluble in water and available for plant to be absorbed [13].

Calcium has important role in plant especially as regulator for building cell wall and plant root stability [14]. Calcium fertilizer is usually lime which is hardly insoluble in water and it causes soil become basic as the consequence of Ca(OH)₂ formation. The soluble calcium fertilizer is usually calcium nitrate that is highly soluble in water. Calcium is found 0.1 – 1.0% of dried plant depending of plant species.

Since both calcium and magnesium nitrate are highly soluble in water and they are easily leached and washed out by rain before all are adsorbed by plants. In environment of high concentration of phosphate ions, these metal ions will precipitate out. Plant will only absorb dissolved minerals but the rate of absorption is often slower than the precipitation and the water stream that leached out the mineral quickly. Therefore dissolved mineral that retained in soil is crucial information in fertilizing management. This phenomena inspires our work to prepare slow release calcium and magnesium fertilizer and study the leaching rate in water and in several type of soils.

Fertilizing using low solubility magnesium and calcium compound such MAP (magnesium ammonium phosphate) and calcium sulphate has been studied [15]. They reported these fertilizers have similarity effect with the commercial control release fertilizers on tomato plants. Although the control release fertilizers have been commercially available, finding the new material and methods are still important research agenda.

This study starts with finding appropriate ratio weight for tablet composition in order obtain stable tablet in water. Then the study continued with rate of leaching those mineral in water and several type of soils to predict the amount of mineral retained in each type of soil.

2. Material and Methods

Chitosan medium molecular weight (~400000, Fluke). (Ca(NO₃)₂·4H₂O, 98.5%; Merck) and Mg(NO₃)₂·6H₂O (p.a, 98%, Sigma-Alderich) were used as source of calcium, magnesium and nitrate ions. Rice husk ash (RHA) and sago powder that passed through 200 mesh sieve were used as filler and adhesive respectively. Spectrophotometer-UV-Vis, Shimadzu UV-1800 was used to determine of dissolved nitrate. Shimadzu AA-6300 equipped was used to determine calcium and magnesium respectively.

2.1 Preparation of RHA sago tablets composed of calcium nitrate (Ca-nitrate-Tablets) and magnesium nitrate (Mg-nitrate-Tablets).
Two type of RHA tablets were prepared, each was composed either 10 g of calcium nitrate or magnesium nitrate in small scale preparation. The total weight of other components was set constantly at 60 g and the volume of water was 20 mL. The component of weight ratio for sago:RHA were in combination of 5:45, 10:40, 15:35, 20:50 and 25:25. Typically, 45 gram of RHA and 5 sago powder were mixed and added slowly 20 mL of calcium nitrate solution (10 gram of Ca(NO₃)₂·4H₂O was dissolved in 20 mL of distilled water). While blending, the composite was placed in a water bath at 60°C until the composite coagulated and rigid. The composite was inserted on a tablet die with 9 holes. Each hole has dimension of 3 cm depth and 1 cm diameter. The composite was pressed with a hydraulic press at 1 tons pressure, dried at 50°C for 24 hours. The tablets were placed in plastic sifter and dipped 2 minutes in chitosan solution that made of 0.6 g chitosan in 100 mL of acetic acid 1.5%. The tablets were labelled as Ca-nitrate-Tablets. The procedure was repeated for other weight composition and for Mg(NO₃)₂·6H₂O content to prepare Mg-nitrate-Tablets. The experiment was repeated to fabricate tablets without chitosan coating and without calcium and magnesium nitrate contents as controls.

2.2 Stability test for Ca-nitrate-Tablets and for Mg-nitrate-Tablets
The stability of Ca-nitrate-Tablets and Mg-nitrate-Tablets in water was studied separately to find the decomposition of the tablets in water. For each weight combination, 5 tablets randomly taken were soaked in 250 mL of water for 30 days observation. Every day, it was observed the number of tablets decomposed in water. The decomposition indicated by the existence of crack on the tablets, the turbid solution or suspension formation. The most stable tablet was used as reference for finding the best weight composition for tablet preparation formula.

2.3 Determination of calcium in Ca-nitrate- Tablets and in Mg-nitrate-Tablets
Having found the stable composition of RHA-tablets, both Ca-nitrate-Tablet and Mg-nitrate-Tablets were fabricated in larger quantity by multiplication the weight ratio. Separately the tablet was dried in an oven for 4 hours at 105°C until constant weight. Randomly taken one of Ca-nitrate-Tablets was grinded and placed a porcelain crucible before calcinated at 700°C for 6 hours. The ash residue was weighted by using an analytical balance and was transferred in Beaker glass. A few drops of concentrated HNO₃ was added into the residue until all the surface were wet. The residue was diluted with 25 mL of distilled water, transferred and filtered through with a glass funnel into a 100 mL volumetric flask. The residue was washed in several times until the total volume of filtrate was 100 mL. The filtrate was analysed using AAS. Similar methods were repeated for Mg-nitrate-Tablets and for control-RHA-tablets. AAS standard solutions were prepared in range concentration of 1 – 8 ppm for each metal.

2.4 Determination total nitrate ion in Ca-nitrate-Tablets and Mg-nitrate-Tablets
Randomly taken two of Ca-nitrate-Tablets were grinded and placed a porcelain crucible, stored 24 h in a dedicator equipped with dried silica before dried carefully in oven at 40°C until constant weight. It was sampled 4.000 gram of the dried powder and dissolved in 50 mL of distilled water. The slurry was filtered through with a glass funnel and transferred into a 100 mL volumetric flask. The residue was washed in several times until the total volume of filtrate was 100 mL. The filtrate was analysed using UV-Vis method at 220-275 nm. The standard solution were prepared from KNO₃ in various concentrations.
2.5. Determination release rate of calcium, magnesium and nitrate ions from the RHA-Tablet composite in water

Randomly taken 3 of Ca-nitrate-Tablets were dried in a desiccator equipped with dried silica gel before they were stored in oven at 40°C for 30 minutes. Randomly taken one of the dried tablets and soaked into 500 mL of distillate water for 30 days observation. Every two days, the solution was carefully stirred using a glass rod before pipetting 2 mL of the supernatant solution for calcium release determination. The sample was stored in closed vial and placed in a refrigerator before analysing by using AAS. Sampling was repeated for several times at different period. Parallel to this experiment, in separated Beaker, similar experiment was carried out for nitrate release sampling and for Mg-nitrate-tablets.

2.6. Determination release rate of calcium, magnesium and nitrate ions from the RHA-Tablet composite in different type of soil

Three types of identified soils that were alluvial, entisols and Red-Yellow-Podsolik(RYP) were obtained from soil laboratory of Syiah Kuala University. 1000 gram of each type of soil was air dried, then each was ground with a porcelain mortar and sieved with 200 mesh sifter. For each type of soil was sampled 150 gram and transferred into a Beaker glass, then 500 mL of distilled water was added and mixed truly. Randomly taken one of Ca-nitrate-Tablets, then it was immersed into the each water-soil mixture. The incubation time was up to 20 days and every four days the mixture was mixed and 5 mL of the supernatant was pipetted and analysed with AAS method. The procedure was repeated for Mg-nitrate-Tablets. The characteristics of soil is tabulated in Table 1.

![Soil types](image)

Figure 1. Soil types used; (a) Entisols (b) Alluvial (c) Red-Yellow-Podsolik (RYP)

| Parameters                | Entisols | Alluvial | Red-Yellow-Podsolik (RYP) |
|---------------------------|----------|----------|---------------------------|
| pH                        | 7.62     | 6.02     | 5.53                      |
| CEC (me /100 g)           | 16.860   | 8.60     | 10.8                      |
| Dissolved magnesium (%)   | 0.03     | 0.017    | 0.003                     |

Table 1. Soil sample characteristics
3. Result and Discussion

3.1 Screening tablet mineral slow release formula

This research was started by finding the optimum composition of calcium and magnesium slow release tablets by analyzing the survival times of the tablets in water. Table 2 show that the more sago content, the more stable tablet. Sago function as adhesive for RHA in which calcium salt was immobilized. However high content of sago gave consequence on cost production. Therefore 20 g sago in composite is considered enough for calcium slow release tablet since it was only 20% of the solid composite and it was stable for 29 days without decomposition. The shorter time survival in water was observed for Mg-RHA tablet that is only 11 days stand in water for composite with 20% sago content. This differences might have correlation with different of the metal ions on gelatinization of sago starch. Apparently magnesium stimulated lower sago gelatinization since the previous study found that sago gelatinization was affected by type of salt and ion calcium and magnesium in rice starch [16-17].

| Treated tablets for each mineral | Tablet composition | Survival each tablet in water immersion (days) |
|---------------------------------|-------------------|---------------------------------------------|
|                                 | Sago starch (g)   | RHA (g) | Ca-nitrate-Tablet | Mg-nitrate-Tablet |
| CT1 & MT1                       | 10                | 90      | 7±1                | 7±1                |
| CT2 & MT2                       | 20                | 80      | 29±1               | 11±1               |
| CT3 & MT3                       | 30                | 70      | 29±1               | 23±1               |
| CT4 & MT4                       | 40                | 60      | 31±1               | 30±1               |
| CT5 & MT5                       | 50                | 50      | 34±1               | 37±1               |

CT = calcium tablet slow release; MT = magnesium tablet slow release

3.2 Leaching rate of minerals within water

Each of Ca-nitrate-Tablet and Mg-nitrate-Tablet was immersed into water in separated glass. Each mineral leached into water after penetrated the chitosan coating as shown in Figure 2. The chitosan coating inhibit the fungi grew during the tablet storage. It also retarded the mineral leaching as demonstrated in previous study [9-10]. The chitosan coating swelled in water and let the minerals pulled out into the water and some also absorbed in chitosan film since chitosan has amino group that acts as Lewis base to host the mineral ions. During tablet immersion in water calcium and magnesium ions leached from the tablets constantly increase along with immersion time (Figure 2). The mean of leaching rate was 6.07 wt%, 6.25 wt% per day (Ca\(^{2+},\) NO\(_3\)^-) and 8.17 wt%, 4.38 wt% per day (Mg\(^{2+},\) NO\(_3\)^-) as shown Figure 2. The leaching rate of magnesium ions within tablets was considered slow compare to Mg(NO\(_3\))\(_2\) and MgSO\(_4\).H\(_2\)O which dissolve almost immediately in water. However it is still considered fast leaching compared to magnesium uptake of maize in fertilizing with kieserite (MgSO\(_4\).H\(_2\)O) in ultisol soil as reported previously [18].They reported the magnesium lost after 12 weeks was between 8.7%-22.3% and assuming maize uptake 1.09% magnesium per day. Calcium slower release than magnesium but higher content especially after 20 days of immersion. Nitrate leached is considered fast compared to nitrogen uptake by typical plant like Corylus avellana, C. americana and C. cornuta, which is nitrogen uptake from ammonium nitrate was 12% in five months [19]. However this is considered slow compared to urea slow release as source of nitrate in fertilizing system that is 47% per day and common urea rate is 75% in < 0.5 h [20]. Nitrate as the calcium conjugate base slightly release higher than nitrate from conjugated base of magnesium. Difference leaching rate of mineral from different tablets might be affected by different interaction with rice husk ash as the supporting material in tablets. Naturally, the content of calcium is higher than magnesium within rice husk ash. This consistently found in many reports [21].
3.3 Effect of soil on dissolved minerals

The amount of dissolved magnesium ions was found different in various types of soil, the least amount of magnesium was in RYP soil environment. Mean magnesium release rate in 20 days of incubation; in entisols soil was 6.73±3.5 wt% per day; in alluvial was 6.95±3.7 wt% per day; in RYP was 3.72±0.9 wt% per day. Slower magnesium release in ion RYP soil might have correlation with the soil pH which is acidic (pH 5.53) that was different from two other type soils (pH of 6.02-7.6) [22]. RYP provides more positive site of proton (H\(^+\)) whereas in equilibrium of magnesium preferred less proton ions or slightly basic condition. The magnesium release increased along with incubation time and slower when reaching the equilibrium as shown in Figure 3.

Calcium rate in several type of soil was generally slower in several types of soil. The rate in entisols was 5.34±2.1 wt% per day, 3.68±0.7 per day in alluvial and 3.84±0.7 in RYP. The comparison trend is presented in Figure 2 (b). The different rate between magnesium and calcium found in soil might be due to their difference in the solubility. Magnesium and calcium ions interacted with sulfate and carbonate ions in soil and precipitated out. Generally magnesium sulfate and carbonate have higher solubility than the calcium compounds. This is also the argument that the release rate in distilled water is faster than in soil.

![Figure 2. Ion release in water during incubation time](image)

![Figure 3. Magnesium (a) and calcium ion release from tablet into soil during incubation times](image)
4. Conclusion
In the preparation of magnesium and calcium slow release tablets, sago starch, rice husk ash, magnesium or calcium nitrate formed a compatible mixture to produce slow release mineral tablets. The higher proportion of sago starch in the composite the longer survival tablet in water. However due to cost consequence, a sable tablet containing at least 20% of sago starch was sufficient to form stable tablets that survive at least 11 days in water. Mineral released from tablet was faster in water than in soil because soil absorb mineral and some precipitated out with ion sulfate and carbonates from the soil. Magnesium release in water and in the soil was faster than calcium release. Magnesium release much slower in RYP soil compare to the release in entisols and in alluvial soil.

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