Preparation and characterization natural rubber-urea-tablets coated by chitosan

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Abstract. Excessive urea leaching causes water pollution and fabricating slow release coated urea is usually performed at high temperature or using synthetic polymers and toxic solvent which might generate environmental pollution. This study aims to formulate “green process” of urea slow release tablets and characterize urea slow release tablets. The formula was composed of rice husk ash, urea, and liquid natural rubber (LNR). Several proportions were studied and characterized based on the stability in water and urea leaching. The immobilizing urea was carried in two models; core-shell and mixed model composite either coating or uncoated with chitosan. The slow release urea tablets were stable in water without decomposition at least 9 days of incubation times depending on LNR content but at least 15 mL of LNR was required to obtain stable tablets. Urea leaching from core-shell tablet was 0.045% and 0.75% for mixed model tablet in 10 days incubation times. Chitosan coating did not affect significantly on urea leaching for core-shell model but it caused urea release faster in mixed model after 12 days incubation times. Low LNR and chitosan coating retarded fungus growth on the urea slow release tablet.

1. Introduction
Plants absorb nutrients from the soil especially nitrate in form of water soluble ions. Nitrate as the source of nitrogen is often insufficient naturally for plant growth and urea fertilizer was used as nitrogen supply since it has high nitrogen content (~ 46 wt% in the molecules), affordable, widely available and compatible in uses. The urea was decomposed into ammonium ions and subsequently converted to nitrate catalysed by nitrosomonas and nitrobacter [1-3]. However, urea has low effectiveness, such as hygroscopic, easily denitrified, volatile, rapidly decomposing, leaching, and if accumulated in the ecosystem will adversely affect environmental health [4-5]. Several studies have shown that 40-70% of nitrogen in fertilizers released into the environment without being absorbed by plant roots [6-7].

One of promising alternatives to increasing fertilizer efficiency, reducing the soil toxicity, and minimizing potential negative effects such as overdose is using a slow release fertilizer (SRF) [8]. This type of urea fertilizer is usually fabricated by coating the composite SRF with a synthetic polymer. SRF can reduce the rate of fertilizer release in soil or in water. However, some slow release fertilizers were reported to have weaknesses such as complicated manufacturing, expensive production costs, non-biodegradable polymer matrices, and other less environmentally friendly mixtures [9].

Several studies on preparation slow release urea have been reviewed by several authors [3, 9]. Urea slow release was prepared either by polymer coating using a resin or thermoplastic materials or by inorganic coating such as melt sulphur. Several other coating alternatives are being intensively studied. Coating techniques was reported by using 26% gypsum–sulphur (20% total coating) or 3% paraffin wax [7]. Many other methods have been also introduced including blending urea with urea-
formaldehyde polymer [10] and by blending with leftover rice-urea-polyacrylic acid [11]. However, the fabrication using friendly material such as liquid natural rubber (LNR) was still very few in publication. Therefore this study aims to formulate the preparation of slow release urea fertilizer using LNR and rice husk ash (RHA) and the study of the characteristics of urea release and its stability in water.

2. Methods

2.1 Composition screening of slow release urea-Mg (SR-Urea-Mg) tablets

Liquid natural rubber latex (LNR) from *Havea bracileansis* (rubber plant grown in Aceh, Indonesia) was prepared by mixing 2 litre of field rubber latex with 50 mL of ammonium hydroxide solution (2.5%) as soon as after sapping, mixed homogeneously and kept it in a refrigerator before used [12]. Rice husk ash (RHA, 1 kg) was sun-dried, grinned and separated from larger particles by sieving with a 200 mesh sifter. Urea-Mg tablets were prepared from several composition of LNR, water, RHA, Urea and MgSO₄.7H₂O. Two tablet models were prepared that were a core-shell model (urea was inside of tablet) and a homogenous mixture model. The various compositions of LNR in tablet matrix were tested until we found the stable tablet in water. Finally the composition was kept constant where the RHA weight was kept at 60 gram, urea and MgSO₄.7H₂O were 20.8 g and 9.6 g respectively. The composition of LNR was reduced gradually and the water volume was increased accordingly. The mixture was stirred with a mixer to obtain relatively homogenously matrix. The mixture was inserted into a table dies and pressed with a hydraulic press at 100 Nm². Then, the urea-Mg tablets were dried at 105°C for 1 hour.

2.2 Decomposition test

At every combination of composite, 10 tablets of SR-Urea-Mg were randomly taken and placed in a 250 ml round bottom boiling flask. It was rotated using a rotary evaporator at 40 rpm for 30 minutes. The higher ratio between stable tablets and the decomposed ones was noted as the best composition formula. Similar to this test, at every combination of components, randomly take 3 tablets were soaked in 100 mL of water. Observation was conducted every day to record the number of tablets decomposed at certain time period. The tablets that lasted without decomposition more than 7 days were considered stable at given composition formula. Having obtained the rational formula, the SR-Urea-tablets was reproduced and coating with chitosan (type ~400000, Sigma) solution (0.6 gram of chitosan in 100 mL of 1.5% acetic acid). The SR-Urea tablet was compared with control that was neither urea, none Mg and without chitosan coating.

2.3 Determination of urea release

One tablet of chitosan-coated SR-urea was randomly taken from 100 dried tablets and soaked in 100 mL of distilled water. This procedure was done three replications and each solution was placed in a water bath to maintain the temperature at around 29°C and covered up with plastic film to avoid evaporation. The solution was stirred gently using a stirring rod and every 3 days, 5 mL of the aliquot was taken for urea determination using a spectrophotometric method. In a separate glass beaker; 0.2015 g of p-dimethylamino-benzaldehyde was dissolved in 0.25 mL of H₂SO₄ (36 N) and 70 mL of CH₃OH (labeled as DB solution). Three milliliters of aliquot were mixed with 2 mL of DB solution and the absorbance was recorded by using the spectrophotometer [13].

Urea standard solutions were made from urea solution at concentration of 1, 2, 3, 4, and 5 ppm. It was taken 3 mL aliquot from each solution was added 2 mL of DB solution, mixed truly and recorded the absorbance at 420 nm using a UV-Vis spectrophotometer model Spekol 2000. The absorbencies were plotted with the concentration to form a calibration curve.
3. Result and discussion

3.1 Composition screening of slow release urea-Mg (SR-Urea-Mg) tablets

Table 1 shows that stability of SR-Urea-Mg tablet increase with increasing of LNR content but it takes higher cost in production since LNR is relatively expensive. Increasing in LNR content let to better solidifying on the tablet matrix and protected urea from leaching into water. Urea tablet containing low LNR caused low adhesiveness toward RHA and not easily to shape the tablet. So the minimum amount of LNR required to obtain stable tablets for 9 days in water incubation was 15 mL. With this proportion, it caused the urea tablet slightly low durability in friction test. About 10% of the dried tablets mechanically decomposed during friction test that mimicking the tablet endurance level during packing and transportation (Table 2).

3.2 Urea release

In the first experiment, urea was placed inside the tablet and the tablets were either coated with or without chitosan. This formula was noted as a core-shell model tablet. It is found that there was no significant different in amount of urea release between coated and uncoated tablet with chitosan. The water content of coated tablet was 7.14% and the uncoated one was 3.76%. The total urea content inside the tablet was 0.633 g per tablet. After 10 days of incubation in water, the urea percentage of urea release was very low that was 0.044-0.045% as shown in Figure 1. The release retardation has correlation with tablet composite was made of LNR and RHA. When LNR-RHA became rigid, it inhibited water to enter the tablet and it made urea remained in solid form until water penetrated the composite. RHA inside the tablet also absorbed urea, it prevented urea to leach out from the tablet. The core model tablet preparation is still considered complicated because urea was inserted manually inside the tablet and an automatic insertion is being developed. Urea release from the tablet model was also too slow since only 0.0027 g urea per day in 0.04 m² or 6.75 x 10⁻¹² g.m⁻².day⁻¹ in water. As comparison, urea uptake rate by potato plant was 3.7 x 10⁻¹² g.m⁻².day⁻¹ which is very close to urea release core-shell model tablet [14]. The polymer coated urea (PCU) and the epoxy resin coating of sulphur coated urea (PSCU) has N release rate of 22.4% and 17.2% respectively in 30 days during cotton planting [15].

Table 1. Comparison of the composist formula and the stability (RHA = 60 g; Urea = 20 g; Mg = 9.6 g)

| No | LNR (mL) | Water (mL) | Texture       | Dried test (# stable tablet, %) | Wet test (# day standing) |
|----|----------|------------|---------------|---------------------------------|---------------------------|
| 1. | 60       | 0          | easy to shape | 100                             | > 9                       |
| 2. | 40       | 20         | easy to shape | 100                             | > 9                       |
| 3. | 20       | 40         | easy to shape | 100                             | > 9                       |
| 4. | 15       | 45         | easy to shape | 90                              | 9                         |
| 5. | 10       | 50         | not easy to shape | 10                             | 6                         |

The second formula, urea was mixed truly tablet with RHA and LNR in tablet formation. This is named as mixed model tablet. The LNR proportion was gradually reduced up to 15 mL in 60 gram of RHA as shown in Table 1 & 2. The amount of urea per tablet was 0.625 g. The mean water content of coated urea tablet was 36%.

It can be deduced from Figure 2 that percentage of urea release from the mixed model tablet was much higher than from the core-shell model tablet (Figure 1). There was not much different on urea release between coated and uncoated tablet except after 12 days of water incubation times as shown in Figure 2. Obviously, urea release was higher in coated tablet than the uncoated one. This is different from hypothesis that coating was expected to reduce urea release from the tablet. The explanation might be referred from chitosan properties that it absorbed urea and accumulated into the surface then subsequently brought urea to leach out into water.
Table 2. Data on durability test

| No | LNR content (mL) in composite | Physically appearance during shaking times |
|----|------------------------------|------------------------------------------|
|    |                              | First 30 minutes | Last 30 minutes |
| 1  | 60                           | Intact           | Intact          |
| 2  | 40                           | Intact           | Intact          |
| 3  | 20                           | Intact           | partially crushed |
| 4  | 15                           | Intact           | partially crushed |
| 5  | 10                           | Shattered        | shattered       |

The amount of urea release from core-shell and mixed model tablet was 3.5% (or 1.61% N) in 12 days for chitosan coated tablet and only 0.25% (or 0.11% N) in 12 days for uncoated tablet. This is considered slow since the standardize slow release urea was less than 15% in 24 h or < 75% release in 28 days [9]. Therefore this composite was categorized as slow release urea.

Figure 1. Urea release core-shell model tablet, the comparison of urea release between coated tablet and uncoated tablet during incubation time.

Figure 2. Urea release from mixture model tablet, comparison coated and uncoated chitosan

Chitosan coating prevent the fungi growth in tablet as describe Table 3. Tablet without chitosan coating, cause the tablet surface was covered by fungus hive and less fungus was observed in chitosan coated tablet. This is due to chitosan coating that has antimicrobial properties [16]. The amount of LNR in composition affected the stability and the decomposition times. More stable tablet in water can be achieved by increasing LNR proportion in the formula but it generated more fungi and finally shortened the long life storage. Dried tablet with water content less than 10% extended the long life but drying too long, it caused urea evaporation.

Table 3. The fungi growth observation and decomposition time

| LNR content | Chitosan Coating | Fungus growth (F) observed & physically decomposed (D) (in weeks) |
|-------------|-----------------|------------------------------------------------------|
|             |                 | 1 2 3 4 5 6 7 8 9 10 1 2 3 4 5 6 7 8                               |
| 60 g (50%)  | Yes             | - - F D                                               |
| 15 g (12.5%)| No              | - - F F F D                                           |
|             | Yes             | - - - - - - - - - - - - - - - - - - - - - - - - - - - F F F D D D D D D D D D |
With amount of mean water content of 36%, tablet containing high LNR (50%) would have lasted in two weeks before attacked by fungus and subsequently decomposed into powder. Less LNR in composite caused survival longer up to 12 weeks before decompose and it would last up to 16 weeks if it is coated by chitosan film.

4. Conclusion
Two models of stable SL-urea tablets were fabricated from LNR, RHA and chitosan in which minimum 15 mL LNR was required for 60 gram RHA. The more LNR content in the tablet matrix gave the more stable composite but hosted more fungi. With the optimum LNR, the SL-Urea tablet was survive in water for 9 days without decomposing the matrix and the composite also lasted in friction test. Core-shell model SL-urea tablets gave very slow urea release, the rate was slower than the rate nitrate uptake by several plants. Mixed SL-urea tablets performed moderate urea leaching after 12 days in water incubation. Urea release was 0.992%wt per day which is much slower than the existing commercial slow release coated urea (SCU). Low LNR and water content and coating the tablet with chitosan retarded the growth of fungi on the SL-urea tablets. Nutrient releases from these SL-urea tablets into soil shall be studied prior to the fertilizing test performance on the plant. Production cost was also need to be considered.

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6. References
[1] Ghaly AE and Ramakrishnan VV 2013 Am. J. Agri. Biol. Sci. 8 330.
[2] Lubkowski K 2014 Environ. Eng. Manage. J. 13 2573.
[3] Azeem B, KuShaari K, Man ZB, Basit A, and Thanh TH 2014 Control Release 181 11.
[4] Rai N, Ashiya P and Rathore, DS 2014 Inter. J Innov. Res. Sci. Eng. Technol. 3 12991.
[5] Guo M, Liu M, Liang R and Aizhen N 2006 Journal of Applied Polymer Science 99 3230
[6] Hekmat AA, Barati B, Zendehdel M, Norouzi HR and Afraz A 2008 12th National Chem. Eng. Congress (Iran: Tbriz).
[7] Ibrahim KRM, Babadi FE and Yunus R 2014 Particuology 17 165.
[8] Xiang Y, Ji-Yun J, Ping H and Ming-Zao, L 2008 Agriculture Saince China 7 469.
[9] Naz MY and Sulaiman SA 2016 J. Control. Release 225 109.
[10] Yamamoto CF, Pereira EI, Mattoso LHC, Matsunaka T and Ribeiro C (2016). Chem. Eng. J. 287 390
[11] Zhou T, Wang Y, Huang S and Zhao Y 2018 Sci. Total Environ. 615 422.
[12] Santipanusopon S and Riyajan S -A 2009 Physics Procedia 2 127.
[13] Husain I, Mahmood Z, Yasmin, R, Jahangir M, Hammed R and Nasir R 2002 J. Chem. Soc. Pakistan, 24, 122.
[14] Zotarella L, Rens LR, Cantiliffe DJ, Stoffella PJ, Gergela D and Burhans D 2015 Field Crops Res. 183 246.
[15] Tian X, Li C, Zhang M, Li T, Lu Y and Liu L 2018 Soil Tillage Res. 175 158.
[16] Goy RC, de Britto D and Assis OBG 2009 Polímeros: Ciência e Tecnologia 19 241.