Slow Release Fertilizer from Treated Rice Straw/Urea Beads Coated With Natural Rubber: FTIR and UV-Vis Analysis

Aini A K¹, R Hamzah¹, N Z Noriman¹, Awad A. Al-rashdi², I. Johari³, Z M Razlan⁴, Shahriman A B⁴, I Zunaidi⁵ and Wan Khairunizam⁴

¹Center of Excellence Geopolymer and Green Technology (CEGeoGTech), Faculty of Engineering Technology (FETech), Universiti Malaysia Perlis (UniMAP), UniCITI Alam Campus, 02100, Perlis, Malaysia.
²Chemistry Department, Umm Al-Qura University, Al-qunfudah University College, Al-qunfudah Center for Scientific Research (QCSR), Saudi Arabia
³School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia
⁴School of Mechatronic Engineering, Universiti Malaysia Perlis (UniMAP), Pauh Putra Campus, 02600 Arau, Perlis, Malaysia
⁵Faculty of Technology, University of Sunderland, St Peter's Campus, Sunderland, SR6 0DD, United Kingdom

Abstract. Slow release fertilizer (SRF) that consist of rice straw (RS) and urea coated with natural rubber (NR) and salt abbreviated as RS/Urea beads coated with NR/salt composites were prepared. RS was sieved in two different sizes which were 500 μm and 1 mm. Both of the RS sizes were treated with sodium hydroxide to expand the fibre capacity in order to store more urea. The RS/urea beads were then coated with NR/salt composite. Two concentrations of the salts prepared which were 5 % and 10 % towards the weight of the NR while 0 % salt act as a control. The role of salt is to introduce pore to the NR which allow urea to pass through its coating when soaked in the water. All SRF samples were analysed using FTIR and UV-Vis technique.

1. Introduction
Nowadays, food demand keeps increasing from all over the world [1] [2] and there are increment in population growth per year from all over the world. However, continuous reduction in cultivated land per capita to provide food supply and steady intensification of fertilizer application will accelerate fast increase in food production of land per hectare. Then, increasing in population growth will burden the agronomic production which need to be enhanced with same limited resources of land and water.

In order to fulfil food supply in limited working land, the sufficient and targeted delivery fertilizer is required [3][4]. Uncontrolled intensification of fertilizer application will lead to decline in land quality due to high solubility of fertilizers. Normally, about 40 – 75 % of fertilizers are leached out and affects loss towards environmental issues, plant growth and health problems. A normal fertilizer contains 80 – 90 % of phosphorus, 50 – 70 % of potassium and 40 – 70 % of nitrogen. Since this fertilizer is lost to environment and cannot be absorbed by plants, it will cause a huge wastage of fertilizers as well as economic implication [5].

All of the above issues must be take seriously and a challenge to change the agronomic practices by designing a new green technology fertilizer. Recently, the usage of slow release fertilizers (SRF) is a potential approach to save minimize environmental problems and fertilizer consumption. The conventional fertilizer releases fertilizer without any control rate will cause high solubility of fertilizer
inside the water while SRF also used to release fertilizer over stimulated period of time. This can be achieved by coating with biodegradable polymer [6]. So, fertilizer releases gradually and permits the maximum uptake of the nutrient to the plant. At the same time, this minimized fertilizer losses due to leaching, volatilization, or excessive growth to the plant [7].

SRF defined as releasing active fertilizer nutrients in a control and delayed manner that synchronize with the requirement of plant. These fertilizers can be made physically by coating granules of conventional fertilizers with various material that reduce dissolution rate [5]. The release and dissolution rates of water-soluble fertilizers depend on the coating materials. Chitosan is one of the suitable coating material and been classified as carbohydrate polymer. Chitosan-coated NPK compound is one of the product that use slow release fertilizer concept. The product not only has slow release property but also can absorb water and preserve the soil moisture at the same time.

2. Experimental

2.1. Materials

Rice straw as the raw material that used to store the urea as its structure was obtained at paddy field from Ninamaju Sdn. Bhd. at Jitra, Kedah. The natural rubber as coating material for urea fertilizer was supplied by Tiang Huat Rubber Factory, Sungai Petani, Kedah. Urea fertilizer was supplied by Petronas Fertilizer (Kedah) Sdn. Bhd. while sodium hydroxide supplied by Shama Fertilizer Chemical Company, Kulim, Kedah. Others chemical which is sodium chloride, acetone, methanol, chloroform and tetrahydrofuran were supplied by Kumpulan Saintific F. E. Sdn. Bhd., Selangor.

2.2. Rice Straw Preparation

Firstly, rice straw (RS) was collected about 500 g and washed with tap water, followed by distilled water to remove impurities like dust. The clean RS was dried by using air dryer to remove moisture. RS was sieved at two different size, 500 µm and 1 mm. Hermatic plastic containers was used to put the sieved RS to avoid microbial attack like fungi before it was use in subsequent treatment. RS was undergo with alkaline treatment by using sodium hydroxide (NaOH) solution to improve it performance and wettability. It was soaked in 1 % of NaOH solution for 24 hours at room temperature. Then, treated RS was washed using distilled water several times until it become neutral at pH 7. Apart from that, centrifuge was used during washing process at 2000 rpm. Finally, RS was dried in oven to remove excessive moisture. Another sample of RS was prepared simultaneously without treatment process as a control.

2.3. Preparation of RS / Urea Beads

RS / urea beads was prepared about 100 g of concentration urea being dissolved in 100 ml of water. Urea was poured into the beaker until it saturated and concentration was calculate using formula weight / volume. Both of treated and untreated RS was immered in urea solution for 24 hours. Once the immersion process complete, RS been recoverd by centrifugation or filtration and try it in oven. The same step was repeated for untreated RS and from this process, product of RS / Urea beads will be obtain.

2.4. Purification of Natural Rubber

Natural rubber (NR) was prepared by immersed 20 g of it for 2 days in 400 ml chloroform and continuously stirred for 24 hours at room temperature. Then, NR was filtered through filter cloth to separate low and high molecular weight of NR. Low molecular weight of NR will passed through the filter while high molecular NR remained at filter cloth. To coat RS / Urea beads, NR with low molecular weight was used because it is easy to coat and mold. High molecular weight of NR was more sticky and difficult to used as coating agent. Low molecular weight NR was poured into petri dish and dried for two days in fume hood and form a thin layer.

2.5. Preparation of NR / Salt Composite

Two different beaker was used to mix 0.1 g sodium chloride (NaCl) dissolved in 20 ml of methanol and about 2 g of purified natural rubber dissolve back in 30 ml of chloroform. So, 12 beakers was prepared
for different parameter. NR / Salt Composites was produced when both of the prepared solvent was completely mixed. Then, another NR without salt as control was prepared.

2.6. Preparation of RS/Urea Beads coated with NR / Salt Composites

RS / Urea beads was poured into petri dish with NR / Salt Composite. Next, 2 g of RS / Urea beads was poured into NR/ salt composite which is known as solvent casting process where NR / Salt Composite coat RS / Urea beads. Ratio for NR : RS was 1 : 1 used and the product was dried in fume cupboard for 2 days until all parts were fully dried. Then, continue dried in vacuum oven for 48 hours at 50 °C.

2.7. Release Study

All product was soaked in known volume of H₂O. 10 g of dry product with different salt loading was added into conical flask that contain 250 ml distilled water. This experiment was carried out for 40 days by take out 3 ml of product solution and 3 ml of distilled water was refill again to maintain constant amount of solvent. Then, product was tested using UV-vis in term of time period of release.

3. Results And Discussion

3.1. Characterization of Untreated Rice Straw and Treated Rice Straw

The size of RS does not influence its alkaline pre-treatment because both sizes undergoes similar breakage of lignin and provides space for use in the fibrous structure of RS [8]. FTIR analysis in Figure 1 shows changes in treated and untreated RS when peaks range 3000 - 3500 cm⁻¹ from the FTIR expressed to hydroxyl group (— OH). For untreated RS, both size (c) and (d), the peak 3400.22 cm⁻¹ and 3400.18 cm⁻¹ were broad as compared to treated RS for both size (a) and (b). The peaks for treated RS seems to be more stretched. This shows that there was reduction in hydroxyl group when RS being treated because the hydroxyl group involve in hydrogen bonding [9].

Apart from that, the band at 2800 - 3000 cm⁻¹ is attributed to C — H stretching vibrations of CH₂ and CH₃. For untreated RS, C — H stretching vibration was broader compared to treated RS due to the characteristic bands of the C — H usually present in the hemicellulose and cellulose [10]. So, reduction of C — H group can be seen for treated RS due to NaOH treatment [11]. For untreated RS, the peaks at 1320 cm⁻¹ that corresponds to lignin can be seen clearly as compared to treated RS which almost disappeared. These results proved that alkali pre-treatment can removes the lignin content. The range of peak 1000 - 1100 cm⁻¹ linked with C — O, C = O, C — O band stretching present in untreated RS as well as the treated RS indicates the band of cellulose [8].
3.2. Characterization of Treated and Untreated RS/Urea Beads

The FTIR result in Figure 2 illustrated about treated and untreated RS/Urea Beads. Treated RS with size (a) 1 mm and (b) 500μm, hydroxyl group can be seen at range 3000 - 3500 cm\(^{-1}\) with stretching vibration while for untreated with size (c) 1 mm and (d) 500μm, broader peak can be observed due to the treatment with NaOH which the hydroxyl group form hydrogen bonds. For treated fibre, pores were created by dissolution of hemicellulose and lignin content which will provide surface area for the urea to retain in the fibrous structure of RS [8]. Therefore, the peaks of C = O (amide I) can be observed at 1634 cm\(^{-1}\) and 1637 cm\(^{-1}\) for both sizes respectively. However, urea peaks for untreated RS for both size can be observed but the intensity of peaks was lower than treated RS which were 1575 cm\(^{-1}\) and 1571 cm\(^{-1}\) respectively. This shows that treated urea can store more urea compared untreated RS especially for size 500 μm compared 1 mm. Other researcher reported, when diameter of fibre being reduced, there will be increase in surface area. Surface area of fibres will clearly have an effect on the ability of particle to diffuse and adsorb [12].

![Figure 1. FTIR spectra of treated and untreated Rice Straw with size for treated Rice Straw (a) 500μm (b) 1 mm and untreated Rice Straw with size (c) 500μm (d) 1 mm](image-url)
3.3. Release Study

Figure 3 shows the result of slow release for two different size which is Figure 3a is the concentration of urea release for untreated RS with size 1 mm and Figure 3b Concentration of urea release for untreated RS with size 500 μm. Based on trend shows in Figure 3a, 10 % salt has higher concentration of urea release compared to 5 % salt. This is due to 10 % salt introduce more pore to the coating surface thus allow the urea from the core to diffuse out. This is due to the release path of the urea through the coating is totally depend on natural voids and holes of the polymer chain in NR. While Figure 3b represent the untreated RS with size 500 μm had similar trend with untreated RS with size 1 mm. 10 % salt loadings had higher concentration of urea release as compared to 0 % and 5 %.
Figure 4 shows the concentration of urea release for treated RS (a) size 1 mm and (b) size 500 μm. It can be observed that 10 % salt release more urea as compared to 5% salt. For untreated RS, the concentration of urea release from day 1 until 6 decreased whereas for treated the concentration of urea increased constantly because treated RS undergoes treatment with NaOH where the lignin of fibrous structure RS was broken thus allowing urea to be occupied at the expand structure. For Figure 4b, 10 % salt loading has higher concentration of urea release than 5 %. So, treated RS can hold up more urea compared to untreated as the releasing rate of urea increases constantly and does not stop at day 30.

Figure 4. (a) Concentration of urea release for treated RS with size 1 mm and (b) Concentration of urea release for treated RS with size 500 μm

4. Conclusion
In conclusion, RS / Urea result shows that treated RS can retain more urea compared with untreated RS. However in term of sizes, 500 μm is more preferable due to 500 μm occupies larger surface area than 1mm. Then, RS / Urea beads was successfully coated by NR / salt composite and percentage of 10 % give broader peak for untreated RS for both sizes whereas for treated RS, 5% salt give broader peak. The performance of the finished product which is RS / Urea beads coated with NR / salt composites determined by using UV-Vis analysis shows untreated RS with size 500 μm has higher concentration of urea release as compared to 1 mm for the two salt loadings.

5. References
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