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Chapter

Lag, Constant and Decay Release Characteristic of St-PVOH Encapsulated Urea as a Function of Coating Thickness Using Different Empirical Models

Chigozie Francolins Uzoh and Stone Raphael Odera

Abstract

Uncoated urea, when applied to crops is susceptible to losses from volatilization, leaching, nitrous emission and water eutrophication. Plants require varying quantities of nutrients during different stages of growth; they need smaller amounts during infancy and larger amounts during the development of roots, stalk and stem. In this research, controlled release coated urea (CRCU) was synthesized via encapsulation with starch- polyvinyl alcohol biocomposite (St-PVOH). Lag, constant and decay release characteristic of the CRCU were simulated using different empirical models as a function of coating thickness. Structural elucidation and morphology of the raw urea and CRCU were determined using FTIR and SEM analytical techniques, respectively. FTIR confirm esterification reaction for St-PVOH. The SEM image of the raw urea appears rough and have fine openings while that of CRCU possesses a seemingly decrease in membrane porosity, ordered and uniform layer. This characteristic qualifies the CRCU as a semi-permeable membrane. Simulation results revealed that coating thickness of 4.3 and 6.4 are best desirable in designing a CRCU for plant at infancy stage, root, and stalk and stem development. Overall, sigmoidal law shows best robust prediction to expanded varying coating thicknesses.

Keywords: release kinetics, controlled release coated urea, empirical model, process simulation, diffusion

1. Introduction

Fertilizers play a vital role to supplement the nutrients required for plant growth [1]. However, plants require varying amounts of nutrients during different phases of growth. They need lesser amounts at the infancy and higher quantities at the development of roots, stalk and stem. Fertilizer demands therefore change intermittently throughout the plant growth. However, uncoated fertilizers are susceptible to losses from volatilization, leaching and fixation, and researchers have found that only about 30% of the fertilizers are used by plants while the rest is lost [2]. Such losses have adverse environmental impacts due to the addition of excess nutrients to air

and water [1, 3]. Similarly, excess fertilizer spoils seedlings as only a small quantity of fertilizer is needed during sprout development [4–6].

Although coated urea provides a much longer release time and higher utility rate, it is mostly used in developed countries. It has not been popular in developing countries because of its higher cost [7]. It is noteworthy to say that developing countries, specifically Nigeria, consume more and more nitrogen fertilizer and yet have only 20–35% efficiency of nitrogen use.

Controlled release fertilizer (CRF) is a prominent green technology that helps to reduce the adverse effect of fertilizer on the environment. A controlled-release fertilizer (CRF) is a granulated fertilizer that releases nutrients gradually into the soil. The low solubility of the chemical compounds in the soil moisture determines the slowness of the release of the CRF. As conventional fertilizers dissolve in aqueous medium, the nutrients diffuse as quickly as the fertilizer dissolves. However, as controlled-release fertilizers are not readily water-soluble, their nutrients diffuse into the soil more slowly. The fertilizer granules may possess an insoluble substrate or a semi-permeable jacket that hindered the dissolution while allowing nutrients to flow out. Therefore, it is necessary to develop new types of fertilizers (CRF) that can improve nitrogen (N) use efficiency, sustain crop production, and protect the environment. Among newly developed commercial fertilizers, waterborne starch biopolymer-coated urea has great potential [8].

Starch is among the cheap, biodegradable, and abundantly available natural polysaccharide [9]. Starch alone is not realistic to be used as coating material due to its profound hydrophilic nature and poor mechanical properties [10]. Therefore, starch can be modified with some suitable additional agents to obtain coating materials devoid of these discrepancies. There is a plethora of studies for the use of starch as a coating material to produce controlled release devices [11, 12].

Coating film thickness plays a significant role for better controlled release properties [13]. The nutrient release time is a function of the diffusional path that the dissolved nutrient has to pass through and release from inside of the coating shell to the bulk water it is immersed in [14]. Critical review of literature reveals that viable controlled release properties of CRU are achieved mostly at the cost of non-biodegradability of coating material, process complexity, and elevated price [15].

Nutrient release from coated CRFs is generally controlled by diffusion through the coated layer [1, 16] and numerous recent studies have focused on predicting nutrient release behaviour. The simplest approach is regression reported and used in [17–21]. Kochba et al. [17] employed a semi-empirical model where the release of CRF was found to be a first-order process. However, the effects from geometry and size were ignored. Moreover, they failed to account for the lag period. Gandeza et al. [18] developed a semi-empirical model to investigate the effect of soil temperature on nutrient release from CNR-polyolefin-coated urea using a quadric equation: $CNR = \alpha + \beta(CT) + \gamma(CT^2)$. Wang et al. [22] also studied the effect of temperature on the release rate by using a regression model that reduced experimental time from days to hours. However, each of these models only related to a specific coating material. Recently, Azeem et al. [7] studied the effect of coating thickness on waterborne starch biopolymer coated urea, the study did not account for the lag, constant and decay release characteristics, expressly. In another account, Lubkowski [23] established that sigmoidal equation best correlate constant and decay release kinetics of chitosan coated fertilizer. A model developed by Than et al. [24] only simulates the second stage of nitrogen release from a coated urea.

From the foregoing, a clear understanding of lag, constant and decay characteristics of coated urea is still lacking. **Figure 1** illustrates the dissolution model of a spherical urea particle surrounded by water defined as the fluid zone. Urea particles comprise two parts: the urea core and the coating layer.

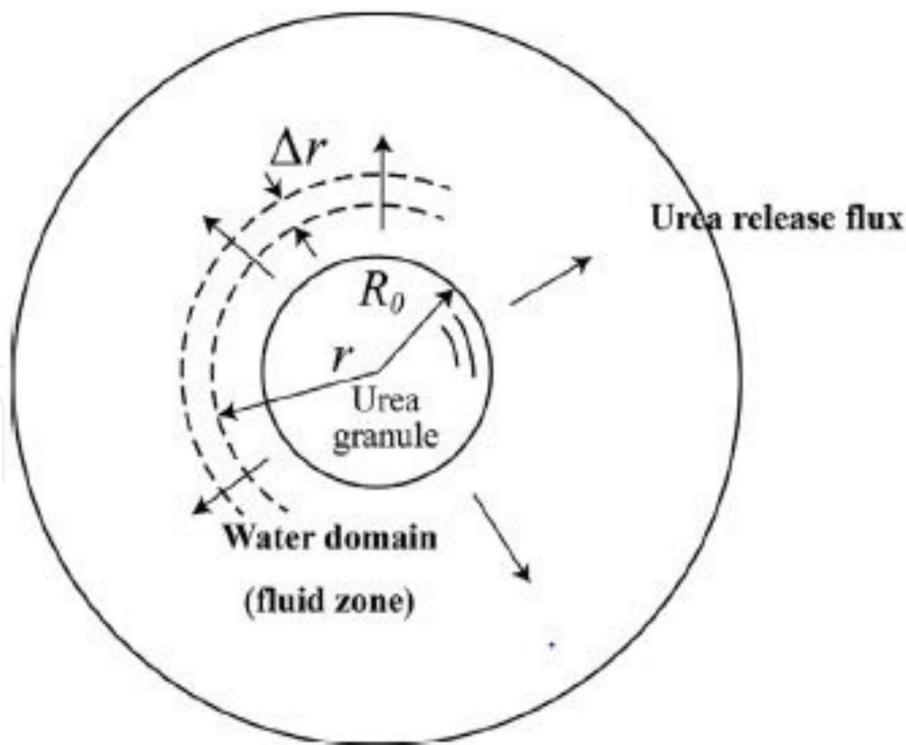


Figure 1.
Dissolution model of a spherical urea particle in water environment.

In this research, it is presumed that the coating layer was saturated with water at the time (t_0) of initial release i.e. lag period. Water inside the core initiates dissolving of the urea granules, where the concentration of the urea is kept constant at a saturated level provided that the solid urea is still inside the core. Nitrogen, from the urea, starts its release via the coating layer by diffusion at a constant rate and it is called “constant release” stage. When urea granule in the core is completely dissolved, urea concentration decreases, and a “decay release” stage starts and then proceeds to the end of the process. From on Raban’s experiments, Shaviv et al. [16] suggested that the release profile from a single polymer coated granule had a sigmoidal shape comprising of these three stages. The cost of the coated controlled release fertilizer has made its usage limited and a paradigm shift has been observed on the frontiers to; use cost effective, environmentally friendly material to produce CRF and their nutrient release characteristics (lag, constant and decay). This research, therefore, covers the production of CRU using polyvinyl alcohol modified starch biopolymer as encapsulation material. The effect of coating thickness on the nitrogen release time and characteristics using different empirical models (power, exponential and sigmoidal law) were also investigated.

2. Materials and methods

2.1 Materials and pre-treatments

Fertilizer granules were procured from Eke Awka market in Awka, Anambra state. The granular fertilizer was subjected to sieve analysis to get a uniform range of the granules. For this study, granules of 2–2.8 mm were selected. The granules were carefully sealed to evade leaching on exposure to the atmosphere. Analytical grade polyvinyl Alcohol (PVOH) was obtained from CDH[®] and acetic acid were procured from JHD[®]. Refined starch was gotten from Burgoyne Burbidges & Co (India).

2.2 Preparation of starch-polyvinyl alcohol (St-PVOH) bio-polymer

Preparation of St-PVOH was done using two round bottom flasks. 10grams of polyvinyl alcohol was dissolved in 100 ml of deionized water at 90°C while aqueous solution of 10grams of starch dissolved in 100 ml of deionized water is added. A constant temperature of 90°C was maintained and stirred for 90 minutes to obtain a homogeneous hydrogel. The mixture was then allowed to cool to room temperature and an aqueous solution of acetic acid was added and stirred for another 90 minutes. A 25 grams by mass of starch was added to the resultant mixture to enhance its handling ability. The synthesized biopolymer was properly covered, kept at room temperature and consequently used for the coating of the granular urea.

2.3 Synthesis of St-PVOH encapsulated urea (St-PEU)

The St-PVOH coated urea was developed by creating balls of the synthesized biopolymer with the hands and fingers. Thereafter, the urea granule was encapsulated into each balls such that, the urea forms the core and the biopolymer, the sheath. These were repeated for five different coating thicknesses and then dry with the oven. A Constant diameter of the five different coating thicknesses was obtained by sieve analysis.

2.4 Determination of coating thickness of St-PEU granules

Vanier calipers were used to obtain the external diameter of the St-PVOH coated fertilizer. The average diameter of the urea granules were then subtracted from the measure diameter to obtain the thinking coating.

2.5 Determination of nutrient (nitrogen) release time from St-PEU granules

The dissolution of St-PEU in distilled water was studied by determining the time it took for the nitrogen present in the sample to be completely released (i.e. 100% release). As described in [7], two grams of each sample was immersed in a 200 ml of distilled water in a carefully sealed beaker. The period taken for the entire nitrogen released from the different coating thickness per time by using the Kjeldahl method was recorded. The experimental data related to release degree of mineral components from the starting fertilizer and from all prepared materials were described and interpreted with three kinetic equations: power, exponential and sigmoidal (Eqs. (1)–(3)):

$$\frac{M_t}{M_\infty} = k_p \cdot t^n \quad (1)$$

$$\frac{M_t}{M_\infty} = 1 - \exp(-k_e \cdot t) \quad (2)$$

$$\frac{M_t}{M_\infty} = \frac{a - b}{1 + \exp\left(\frac{t - d}{c}\right)} + b \quad (3)$$

where M_t/M_∞ is the fraction of nutrients released at time t , k_p and n are the power equation constants, k_e is the exponential equation constant, and a , b , c , d are the sigmoidal equation constants.

3. Results and discussion

3.1 Chemical formation of St-PVOH

Starch is hydrophilic in nature. The mechanical properties of starch are improved when it is blended with PVOH. Nevertheless, according to Izhar et al. [25], since both starch and PVOH are polar substances with hydroxyl group in their chemical structure, the blend of starch and PVOH exhibits poor water retaining properties. Therefore, acetic acid was introduced as a cross linker which enables the formation of intermolecular and intramolecular hydrogen bonds between hydroxyl groups of PVOH and starch to improve the integrity of St-PVOH blends. The chemical structure of St-PVOH blends can further be explained by the FTIR analysis as shown in **Figure 2**. The FTIR spectra of starch and PVOH were studied and compared with the spectra of the St-PVOH blend film. **Figure 2** shows the occurrence of -OH stretching vibration (3426 cm^{-1}), the intramolecular hydrogen bond (1646 cm^{-1}) and -CH₂OH stretching vibration (1260 cm^{-1}) as well as C-O-C ring vibration ($928, 858\text{ cm}^{-1}$) in the starch granules. For PVOH, a broad band at $3400\text{--}3100\text{ cm}^{-1}$ due to O-H stretching vibration and another band at 2936 cm^{-1} assigned as C-H stretching vibration were seen. The absorption points of 922 cm^{-1} denote C-C stretching. The $1200\text{--}1100\text{ cm}^{-1}$ region characterizes a number of modes, which have been shown to be sensitive to the degree of crystallinity in PVOH. The peak at 1147 cm^{-1} is crystallinity-dependent; this is in agreement with the work of Jayasekara et al. [26]. The FTIR spectra displays the following three sets of changes in the film: (a) the peak at $3300\text{--}3400\text{ cm}^{-1}$ of absorption bands weakened; (b) the crystallinity-dependent 1147 cm^{-1} peak of PVA weakened; and (c) the absorption peak of 922 cm^{-1} of PVA vanished and the peak of 854 cm^{-1} shifted.

The weakness, vanishing, and shifting of the characteristic absorption bands may be as a consequence of the interaction of different -OH groups in the starch and PVA molecular chains. It can be concluded therefore from these results that the starch was linked with PVA by chemical bonding introduced by acetic acid. This type of linkage has significant effect on the enhancement of compatibility.

3.2 Scanning electron microscope (SEM)

The coated urea was characterized using SEM to compare their morphologies to the original urea obtained. Morphology refers to the study of form and structure of a material and in this case, CRCU. SEM images were taken from the samples to present the morphology. As stated earlier, it must be noted that the starch is hydrophilic in nature due to the structure and composition. The SEM image of uncoated and coated urea (CRCU) is shown in **Figure 3** (a and b, respectively). The optical image for the uncoated urea is observed to appear rough and have fine openings where water can penetrate so as to dissolve the urea granule. An asymmetric structure and porosity are clearly seen at the magnification of $\times 1000$. A seemingly decrease in membrane porosity, ordered and uniform layer, however, were noticed in **Figure 3**. This may be as a result of encapsulation with the biopolymer (St-PVOH). The slower the penetration time, the longer it will take for the urea to dissolve and consequently escape to the outer surface of the sample. This characteristic is needed for increasing the encapsulation efficacy of the released material, which in this research is urea. The elementary nanolayers of the bio-composite can be observed in the SEM image of **Figure 3a**. Using the image, it is difficult to determine the actual interlayer spacing of the biopolymer. In order to determine the d-spacing, high-resolution transmission electron microscopy would be needed. From **Figure 3b**,

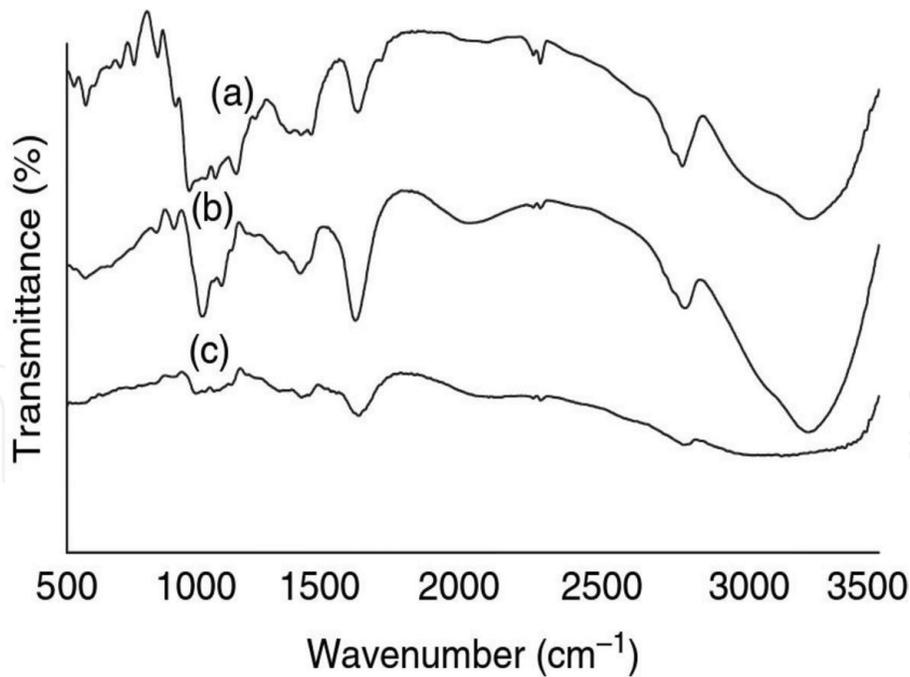


Figure 2. FT-IR spectra of (a) PVOH, (b) starch, and (c) blend films (St-PVOH) cross-linked with acetic acid content.

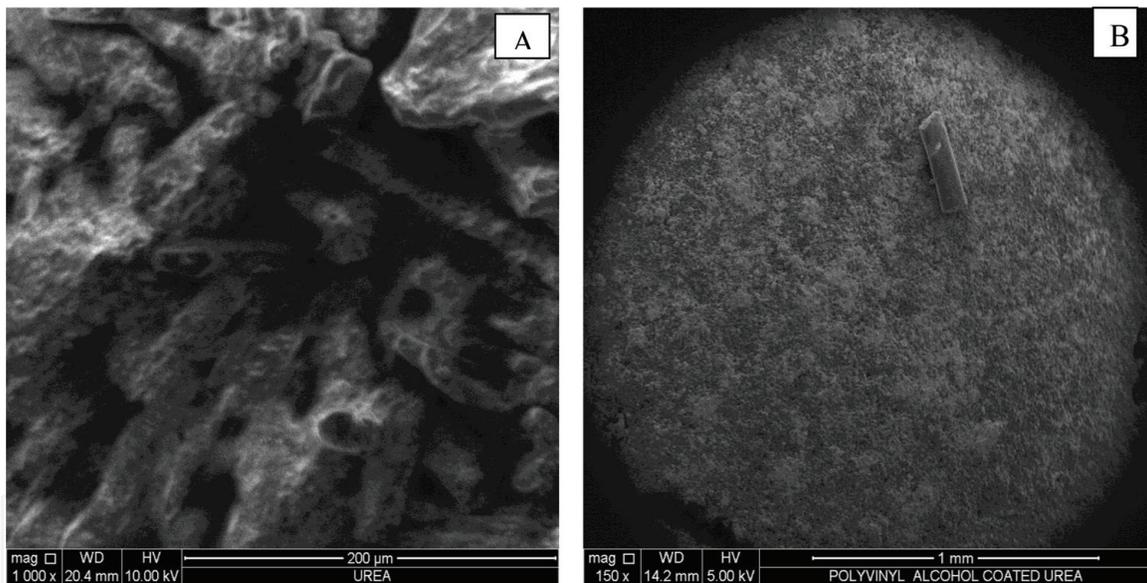


Figure 3. SEM images of (a) uncoated urea (b) St-PVOH coated urea.

it can be concluded that the membrane can withstand the hydrostatic pressure of the dissolved nitrogen for long due to the tiny pore diameter. Thus St-PVOH biocomposite is an effective coating material for coated urea as it provides a semi permeable membrane and do not impede complete hindrance to nutrient release.

3.3 Effect of coating thickness on nutrient release time

The investigation of coating thickness is critical for the determination of nutrient release rate [13]. The result of the cumulative nitrogen release rate (wt%) for a monitored period of 30 days is given in **Figure 4**. **Figure 4** indicates that increase in thickness reduces the release rate. From **Figure 4**, the coated urea with 0.1 mm thickness released up to 19.82% nitrogen, that of 2.2 mm released 14.32% nitrogen, that of 4.3 mm thickness released 3.16% nitrogen, that of 6.4 mm thickness released

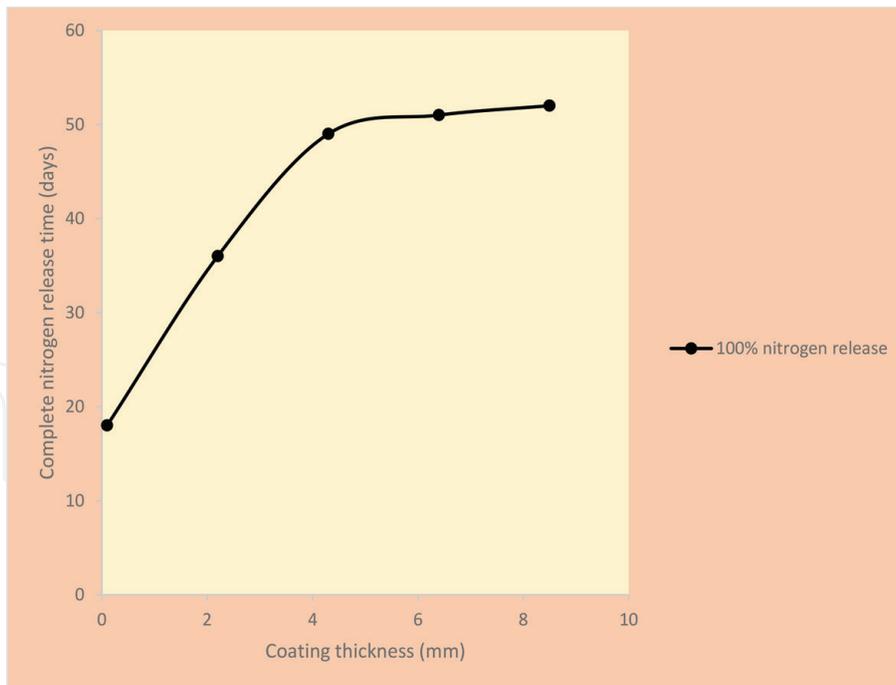


Figure 4.
Graph of complete nitrogen release time against coating thickness.

up to 2.93% nitrogen, and that of 8.5 mm thickness released 0.86% of nitrogen; all in 3 days. According to the Comité Européen de Normalization (CEN), a fertilizer can be described as having controlled release properties if the nutrient release is not more than 15% after 1 day or not more than 75% after 28 days [27]. From the above postulation, the coated urea with 2.2, 4.3, 6.4 and 8.5 mm can be considered controlled release fertilizer. A further look at the graph shows that the 8.5 mm coating gave the slowest controlled release rate followed by that of 6.4 mm.

The time required for each coating thickness to have released 100% nitrogen was also ascertained and the results are represented in **Figure 4**, which shows that the time required for 100% nitrogen release time increases with increase in coating thickness. Thus, the more the coating thickness, the slower the release rate and the longer the fertilizer will last on the farm. To further elucidate this phenomenon, it is important to understand the process of nutrient release from a polymer coated film. When a hydrophilic polymer is exposed to dissolution in water, the polymer matrix begins to swell due to uptake of water into the coating film [7]. Water moves through dynamic void between the macromolecules of the polymer film and dissolves the core nutrient as soon as it comes in contact with it [15]. This Osmotic uptake of water into the nutrient core is followed by the creation of hydrostatic pressure inside the coating shell. At a certain threshold value of the hydrostatic pressure, the swelled polymer matrix experiences deformation and the active nutrient starts to release from the microspores developed at the weakest sites on the coating film [28]. At that instant, the coating thickness plays an important role to control the release rate of the nutrient. Larger coating thickness results in higher release time as it takes longer time for the nutrient molecules to diffuse through thick coating film and reach the outer reservoir. Thus, the result obtained shows that the coating thickness of 8.5 mm have the highest release time and will last longer in the farm.

3.4 Release characteristic of the St-PVOH

As expected for a typical controlled release process, the nitrogen release of the CRCU generally decreases readily with increasing coating thickness, approaching

60% (for 8.5 mm thickness) in all the models indicating sufficient retardation of nitrogen. Such observations conform to a large extent with the results of literature [29]. In order elucidate this phenomenon, it is very important to understand the mechanism of nutrient release from a bio-composite or polymer coated film. When a hydrophilic polymer is subjected to dissolution in water, the polymer matrix begins to swell due to diffusion of water into the coating film [30]. Water moves through dynamic spaces between the macromolecules of the polymer film and dissolves the core nutrient as soon as it comes in contact with it [15]. This osmotic diffusion of water into the nutrient core is followed by the development of hydrostatic pressure inside the coating shell. At a threshold value of the hydrostatic pressure, the swelled network of the polymer experiences distortion and some active nutrient starts to release from the micropores developed at the weakest sites on the coating film [28]. At this point, coating thickness plays an important role to control the release rate of the nutrient. Larger coating thickness results in higher release time because it takes longer time for the nutrient molecules to diffuse through thick coating film and reach the outer reservoir [31]. In addition the augmented diffusion resistant for higher coating thickness also increases the release time [32]. Ko et al. [28], opined that a dire value of the coating thickness is essential for viable release properties. Nevertheless, coating thickness less than some critical threshold can cause immediate release of nutrient when subjected to dissolution test in water. This spontaneous release is due to the presence of void or microscopic pores in the coating film.

From the results of effect of coating thickness on release time as represented in **Figures 5–8**, it may be elucidated that when water comes in contact with the coated granule, it takes longer for water to completely wet thicker coating layer and reach the core nutrient. Once the core nutrient is dissolved, the swelled macromolecular hydrogel structure of encapsulated urea coating film bears the hydrostatic pressure of the dissolved nutrient for longer time in case of larger coating thickness. Once the dissolved nutrient reaches the interface, it again takes longer for its escape from thicker coating layer to the outer reservoir. Hence, thicker coating films result higher release time and better controlled release characteristics [24, 32]. This principle can only be attributed to those samples which resulted higher release time. On the contrary, there are samples which have very low release time. Shaviv et al. [16] reported that the release behavior of a single polymer coated granule had a sigmoidal shape comprising three stages: an initial stage during which no release is

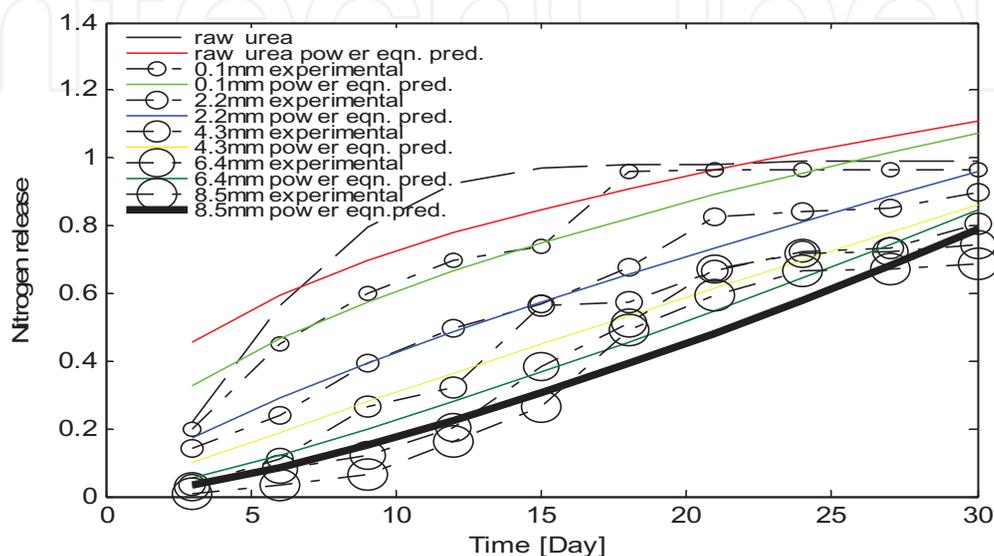


Figure 5. Nitrogen release prediction of St-PVOH with power model.

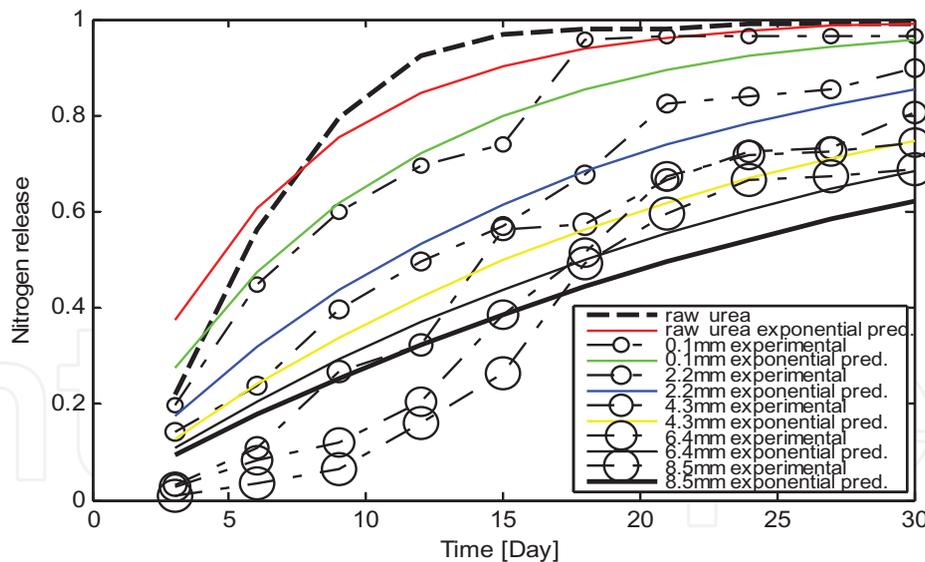


Figure 6.
 Nitrogen release prediction with exponential model.

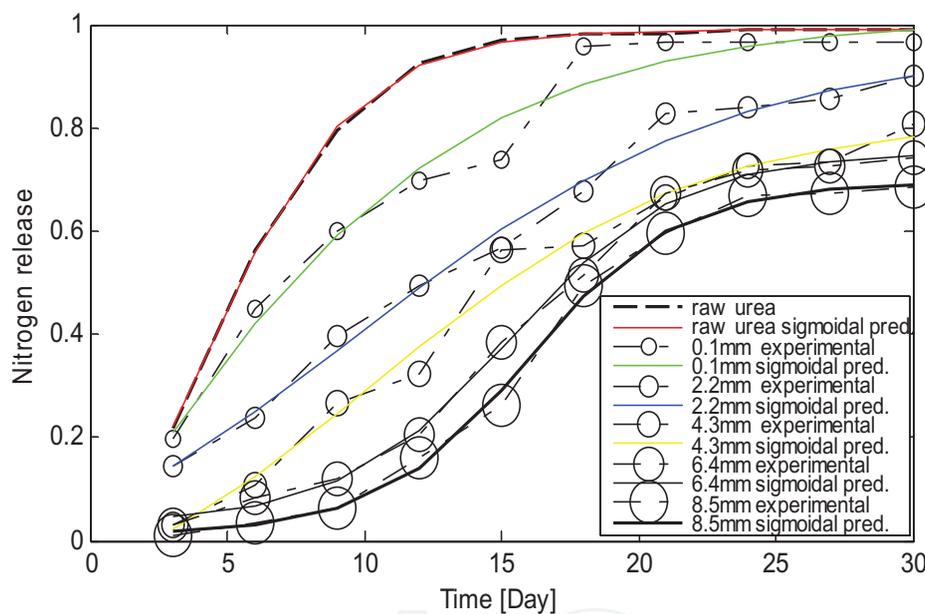


Figure 7.
 Nitrogen release prediction with sigmoidal model.

seen (lag period); a stage of constant or steady state release; and finally, a stage of gradual decay of release. An interesting observation is recorded where the power and exponential model show intrinsic similarities in nitrogen release characteristics. One noticeable unusual result is the apparent lack of lag period for coating thicknesses of 0.1 and 2.2 mm. This type of nitrogen release profile cannot explicitly support plants infancy stage. However, it is noticeable that coating thickness of 4.3 and 6.4 mm resulted in desirable release rate throughout the incubation time for all the models. The release degree of nitrogen from St-PVOH encapsulated urea were not more than 18% within 6 days incubation time and 62% after 30 days (see **Figures 5–8**).

A fertilizer is considered a controlled-release fertilizer (CRF) if these conditions are fulfilled: no more than 15% of nutrients are released within 24 hours, no more than 75% of nutrients are released within 28 days [27]. Specifically, a lag period of 2.5 days was observed with the sigmoidal model. The prediction ability of the sigmoidal model was further confirmed to be most robust from the observed



Figure 8.
Coated urea of various coating thickness.

	Power			Exponential		Sigmoidal				
	k_p	n	r	k_e	r	a	b	c	D	r
Raw Urea	0.2994	0.3847	0.888	0.1562	0.986	-0.3146	0.9900	2.7864	4.0190	1
0.1 mm	0.1838	0.5187	0.957	0.1066	0.987	-1.1582	1.0154	6.7805	-0.6027	0.988
2.2 mm	0.0769	0.7416	0.987	0.0638	0.991	-0.1634	0.9581	6.9069	9.7049	0.996
4.3 mm	0.0354	0.9381	0.976	0.0460	0.989	-0.1962	0.8166	5.8552	10.5014	0.993
6.4 mm	0.0143	1.1990	0.969	0.0385	0.972	0.0317	0.7519	3.1002	15.3357	0.999
8.5 mm	0.0075	1.3685	0.963	0.0325	0.965	0.0147	0.6912	2.6945	15.9864	0.999

Table 1.
Correlation coefficients of the empirical equations.

correlation coefficients established with the expanded varying coating thicknesses. Therefore knowledge of plant metabolic requirement is a prerequisite in the design of CRFs. The sigmoidal model has also proved its usefulness in the description of the controlled release. The constants and correlation coefficients of the sigmoidal model equations were determined and recorded in **Table 1**. k_p and n are the power equation constants, k_e is the exponential equation constant, and a , b , c , d are the sigmoidal equation constants.

4. Conclusion

The effect of coating thickness on lag, constant and decay release characteristic of CRCU has been investigated. It observed that the release time increases with increase in coating thickness. Starch-polyvinyl alcohol (St-PVOH) biocomposite as materials of biodegradable and regenerative resource was found to provide a semi

permeable membrane suitable for the coating. Structural and morphology elucidation of the raw urea and encapsulated urea were established using FTIR and SEM instrumental analysis, respectively. There exist blend between the hydroxyl groups of starch and PVOH, where acetic acid served as a crosslinker to the bonding. Thus, the mechanical properties of the biocomposite are improved. SEM on the other hand, confirmed the porosity of the coating material, hence, validating its ability to absorb water. Observing the release rate, encapsulated urea with thicknesses of (2.2, 4.3, 6.4, and 8.5) mm is controlled release fertilizer, for they agree with Comité Européen de Normalization (CEN) descriptions of CRF. The result of the mathematical model shows that sigmoidal model satisfactorily fit the experimental data obtained. Conclusively, St-PVOH biocomposite is a feasible coating material in the production of controlled release fertilizer.

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