Research Article

Chitosan-Based Polyion Multilayer Coating on NPK Fertilizer as Controlled Released Fertilizer

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Low efficiency of conventional fertilizer (quick release fertilizer) application in agricultural sectors has caused environmental pollution and health problems. A method to overcome the drawback of the conventional fertilizer is by controlled release fertilizer (CRF) preparation. CRF is expected to be able to fulfil the nutrient demand of targeted plants. The objective of this research is to prepare CRF by coating NPK fertilizer with multilayer chitosan-polyanion using alginate, pectin, and sodium tripolyphosphate (TPP). In addition, the effect of the layer arrangement modification of material on the rate of nitrogen release was also studied. The mechanical strength of coated fertilizer was analysed by compressive stress test and the properties of the fertilizer coating was observed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The nitrogen release study shows that multilayer of chitosan-alginate $(CA)_5$, chitosan-pectin $(CP)_5$, and chitosan-TPP $(CT)_5$ as coating material was able to increase the compressive stress and decrease the nitrogen release of coated fertilizer. These results are supported by the FTIR analysis which exhibits the formation of ionic interaction between amine group of chitosan and carboxyl group of alginate in chitosan-alginate $(CA)_5$ layer, carboxyl group of pectin in chitosan-pectin $(CP)_5$ layer, and phosphate of TPP in chitosan-TPP $(CT)_5$ layer. On the other hand, the modification of the arrangement of chitosan-alginate layers showed that the fertilizer with the alternating layer arrangement $(CA)_5$ was able to optimally increase the compressive strength. The mathematical model for the nitrogen release of coated fertilizer is also prepared and simulated with the MATLAB software. The simulation results showed that the nitrogen release of coated fertilizer followed the proposed diffusion mechanism. The obtained diffusivity coefficient value in the layer of chitosan-alginate $(CA)_5$ is 2.0933×10^{-6} cm^2/s, 2.5606×10^{-6} cm^2/s in chitosan-TPP $(CT)_5$ layer, and 3.7256×10^{-6} cm^2/s in chitosan-pectin $(CP)_5$ layer.

1. Introduction

The wide use of conventional release fertilizer (quick release fertilizer, QRF) which has low nutrient uptake efficiency due to the high solubility has been a major challenge to the agriculture sector. The purpose of fertilizer application is to optimize nutrient intake of the plant and to increase crop yields. Unfortunately, the application of QRF is difficult to meet the target due to excessive nitrogen loss [1]. A research showed that only 20–30% of nitrogen-containing fertilizer is absorbed by plants, while the remaining percentage is lost through volatilization, nitrification, and leaching [2, 3]. The nitrogen losses due to volatilization and leaching will cause low efficiency, low crop production, less economic and cultivation and lead to environmental pollution [1]. In recent years, controlled release fertilizer (CRF) has been considered as the most suitable method to increase efficiency, reduce nutrient loss, and reduce the contamination effect to the environment. However, several types of manufactured polymer-coated CRF created other environmental

problems due to nondegradable polymer residues in the soil which could lead to the loss of agricultural land and reduce soil fertility [2, 3]. Thus, CRF with a degradable coating material should be developed to overcome this problem.

One of the potential materials that can be used as coating in CRF production is chitosan. Chitosan is available abundantly in nature and also has the ability to form film that does not soluble in water. With its biodegradability, chitosan tends to be an eco-friendly polymer [4]. In addition, the existing of cationic properties allowed chitosan to be modified with various polyanions from natural polymer to improve their physical and chemical properties [5]. Alginate, pectin, and sodium tripolyphosphate (TPP) are polyanions that can be combined with chitosan. Alginate as polyanion will interact with chitosan to form a polyion complex through ionic interaction between carboxyl group and amine group [6] that will enhance its mechanical properties [7, 8]. TPP is a nontoxic crosslinker which consists of three phosphate functional groups to form polyion or polyelectrolyte complex [9–12]. Pectin is composed of galacturonic acid chains with α-1,4 glyosidic bonds which some of the galacturonic acid is esterified as methyl ester. The carboxylic group of pectin will cause pectin to be anionic if it is dissolved in water. Thus, pectin is expected to create electrostatic bonding with chitosan as the result of carboxylic groups inside pectin interaction with amine groups in chitosan [13].

This study is aimed at preparing CRF coated by multilayer of chitosan-polyanion as a barrier film that can retain the fertilizer nutrients such as nitrogen, phosphorus, and potassium. The layer arrangement modification of chitosan-alginate will be carried out to obtain the best layer which can retain the nutrient longer. The coating process was conducted with layer by layer spray drying technique under continuous dry air flow. Also, the kinetics of nitrogen release was also studied by using the diffusion model approach.

2. Materials and Methods

2.1. Materials.
Multicomponent (nitrogen, phosphate, potassium) commercial fertilizer (NPK granules) obtained from Pupuk Indonesia Holding Company was used in this study. Local Indonesian chitosan powder (>90% degree of deacetylation, 10–500 cps viscosity, <1.5% ash content, <0.5% protein content) was purchased from PT Biotech Surindo (Cirebon, Indonesia). Glacial acetic acid (Merck, Germany) was used as the solvent, and alginate, citrus pectin, and sodium tripolyphosphate from Sigma-Aldrich (USA) were used as polyanion.

2.2. Methods.
The experiment was conducted based on the previous method with some modification [14, 15]. There are two coating solutions which are chitosan as the main coating material and the polyanion solution as support coating material, i.e., alginate, TPP, and pectin. The total volume of the coating solution is 50 mL where the concentration of each component is 3% (w/v). For CRF preparation, 10 g of NPK granule was placed in the rotary dryer (4.5 L capacity,

25 rpm) and sprayed with coating material using the layer-by-layer method in which every layer consists of 5 mL solution of coating material with pressure of 7-8 bar, coating process temperature of 80°C, and dry air flow rate at 1.7 L/s. Seven types of coated fertilizer samples were obtained and identified as listed in Table 1.

2.3. Analysis.
The mechanical strength of coated fertilizer was tested with LLOYD INSTRUMENTS LTD Version 4.0-LR Series Mark IV. The surface of coated fertilizer was analysed with scanning electron microscopy (SEM). The coating layer was characterized by SIMADZU Fourier transform infrared (FTIR) spectroscopy. Meanwhile, the nitrogen release was observed by placing 1 g of fertilizer in a beaker glass filled with 100 mL of demineralized water, and it was sealed with parafilm. The amount of coating agent which is attached in the fertilizer was determined by the gravimetric method. The amount of released nitrogen from CRF granule into the water was analyzed by the Kjehdahl method. The kinetics of fertilizer nutrient release was evaluated by using a diffusion model approach using MATLAB to obtain the diffusion coefficient of the formed layer.

3. Results and Discussion

3.1. Morphology of Chitosan-Polyanion Coating.
The SEM images of C_{10}, $(CA)_5$, $(CT)_5$, and $(CP)_5$ layers are shown in Figure 1. This analysis aims to observe the surface morphology of the formed coating. By comparing each image, it can be seen that the C_{10} layer is smoother than the other coating combination layers since it only contains a single coating agent. However, among the combination of chitosan-polyanion coating, $(CA)_5$ surface shows less surface texture than the $(CT)_5$ and $(CP)_5$ layers. With this evenly coated layer, it could increase the mechanical strength of pellets and reduce the nitrogen release that will be described later in Figures 2 and 3 respectively. The rough coating of $(CP)_5$ surface in Figure 1(d) is caused by a weak interaction between amine functional group of high molecular weight of chitosan and carboxyl functional group of low molecular weight of pectin.

3.2. Mechanical Strength.
Compressive stress analysis has been used for investigating the effect of multilayer coating to the mechanical strength of the coated fertilizer. Coated fertilizer that has a good mechanical strength will be more durable during bulk storage time and field application. Figure 2 shows that all coating methods that have been applied are able to increase the strength of untreated fertilizer granule significantly [15].

Meanwhile, the $(CA)_5$ sample has the highest value of compressive stress. It is supported by the image in Figure 1 that $(CA)_5$ coating has the most evenly distributed coating lead to high mechanical strength. This finding is in line with the reports of Baysal et al. [7] and Kumar et al. [8] which stated that combination of chitosan-alginate will be able to form polyelectrolyte which increases its mechanical properties. On

TABLE 1: Sample identifications.

Sample ID	Preparation method
TC	Uncoated fertilizer
C_{10}	10 layers of chitosan-coated fertilizer (CCCCCCCCCC)
$(CP)_5$	Coated fertilizer with 5 layers of chitosan and 5 layers of pectin with alternating arrangement (CPCPCPCPCP)
$(CT)_5$	Coated fertilizer with 5 layers of chitosan and 5 layers of TPP with alternating arrangement (CTCTCTCTCT)
$(CA)_5$	Coated fertilizer with 5 layers of chitosan and 5 layers of alginate with alternating arrangement (CACACACACA)
$(C_2A_2)_2C_2$	Coated fertilizer with 6 layers of chitosan and 4 layers of alginate with arrangement (CCAACCAACC)
$C_3A_4C_3$	Coated fertilizer with 6 layers of chitosan and 4 layers of alginate with arrangement (CCCAAAACCC)

the other hand, $(CT)_5$- and $(CP)_5$-coated fertilizers have lower compressive stress than $(CA)_5$ probably due to less homogenous coating formation on the fertilizer surface [7, 8].

From Figure 2, it can be observed that the alternating chitosan-alginate layer $(CA)_5$ has higher value of compressive stress than the nonalternating chitosan-alginate layer $(C_2A_2)_2C_2$ and $C_3A_4C_3$. This alternating arrangement opens wide possibility of amine groups in chitosan to interact with carboxyl groups in alginate; thus, the layer was stronger than the nonalternating arrangement as shown by an increase of compressive stress.

3.3. FTIR Analysis of the Coating Material.
FTIR analysis was used to confirm the existing functional groups from each layer composition. As shown in Figure 4, the characteristic of chitosan is shown by the peak at $1642\,cm^{-1}$ which caused by the vibrational stretch of carbonyl (C=O) in the amide group and other peak at $1560\,cm^{-1}$ which caused by bending vibration of N-H in the amine group [15], while the characteristic of alginate is shown by the peak at $1628\,cm^{-1}$ which represents the vibration of carbonyl in carboxylic functional group [16]. Figure 4 also shows that there are peak shifts in the $(CA)_5$ layer compared to the pure component of chitosan and alginate. The peak at $1642\,cm^{-1}$ in pure chitosan is shifted to $1647\,cm^{-1}$ in the $(CA)_5$ layer and the peak at $1560\,cm^{-1}$ is slightly shifted to $1562\,cm^{-1}$. This shift can be a hint of ionic interaction between negative charge of $-COO^-$ functional group from alginate and positive charge of $-NH_3^+$ from chitosan [7].

Pectin in FTIR spectra (Figure 4) can be represent by the peak at $1740\,cm^{-1}$ as an indication of the vibrational stretch of carbonyl in ester group and peak at $1614\,cm^{-1}$ as the vibrational stretch of carbonyl in the carboxylic group. The shift of the peaks also occurs in $(CP)_5$ spectra that suggest for ionic interactions between amine group of chitosan and carboxylic group of pectin. It is shown that the peak of carbonyl ester is shifted from $1740\,cm^{-1}$ to $1638\,cm^{-1}$ and merged with the peak at $1614\,cm^{-1}$ [17].

FTIR spectra shows peaks at $1218\,cm^{-1}$ and $1147\,cm^{-1}$ in chitosan-TPP $(CT)_5$ layer. Those peaks are caused by the stretch vibration of P=O, while the peak at $891\,cm^{-1}$ is caused by asymmetric stretching of P-OP vibration. The $1560\,cm^{-1}$ in pure chitosan which caused by the N-H bend vibration of amine group shifted to $1634\,cm^{-1}$ in $(CT)_5$ layer. This shifting shows that ionic interaction also occurs in chitosan-TPP layer which is caused by the interaction between phosphate group in TPP and amine functional group in chitosan [2, 18].

3.4. Release of Nitrogen.
The result of nitrogen release in water is shown in Figure 3. Both chitosan and chitosan-polyanion multilayer coating were able to decrease the nitrogen release compared to uncoated fertilizer [15]. The addition of polyanion such as alginate, pectin, and TPP demonstrated the electrostatic interaction between opposite charge of polyions and formed more stable complex to retain the releasing of nutrient better than chitosan coated only. The binding shows its strong dependency on the density and number of charged group from both polymers [19]. $(CA)_5$-coated fertilizer had the slowest rate of nitrogen release during five hours, while the $(CT)_5$- and $(CP)_5$-coated fertilizer could retain the nitrogen well only in the first two hours. The higher charge density owned by the molecules with higher molecular weight (chitosan and alginate) tends to form a more stable polyion complex. On the other hand, the rearrangement of polyions with lower molecular weight such as pectin has a tendency to create weaker bound of polyion complex. The $(CP)_5$- and $(CT)_5$-coated fertilizer may loss some pectin and TPP after being soaked for two hours in water due to the dissolution of pectin and TPP into the water. After soaking, the remaining coating materials in the fertilizer were chitosan and a little amount of pectin or TPP which still attach to chitosan. As a result, it formed uncoated spots in the surface of parent NPK granule allowing a fast nitrogen release.

The result above is supported by the weight ratio data of coating mass and coated fertilizer mass in Figure 5, which was analysed after five hours of nitrogen release test [15]. The figure shows that $(CT)_5$ coating had the lowest mass as much as 50% of $(CA)_5$ coating and the mass of $(CP)_5$ coating is 72% of $(CA)_5$ coating. The data show that some of pectin and TPP redissolved during the nutrient release test. Indeed, $(CA)_5$ coating had the highest coating mass since the coating layer is able to be well preserved during the dilution process preventing a fast release of nitrogen content. The redissolution of pectin and TPP can be explained through the schematic interaction between the species and chitosan as shown in Figure 6.

Figure 6(a) shows that $(CA)_5$ polyelectrolyte is formed by the interaction between negative charge of carboxylic of alginate and positive charge of amine group of chitosan while Figure 6(b) shows that the $(CP)_5$ polyelectrolyte is formed by interaction between negative charge of carboxylic of pectin and positive charge of amine group of chitosan. From Figure 6(b), it can be seen that not of all amine group of chitosan interact with pectin. It is because in the same
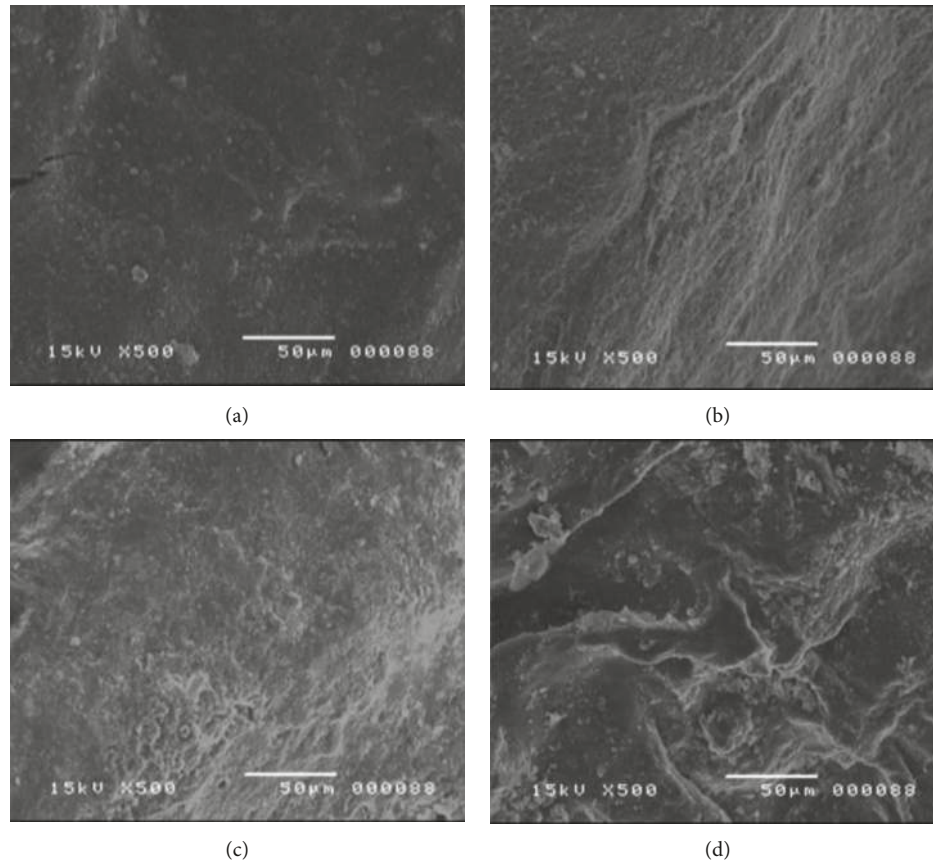
FIGURE 1: Scanning electron microscopic of coating layer: (a) C_{10}. (b) $(CA)_5$. (c) $(CT)_5$. (d) $(CP)_5$.
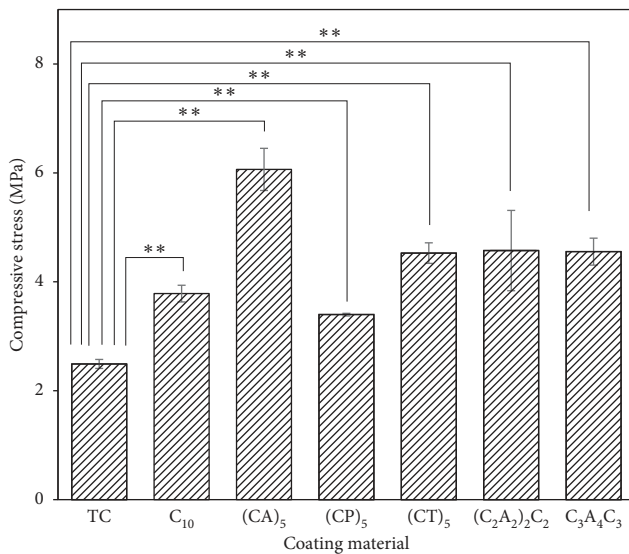

FIGURE 2: Effect of coating material to the compressive stress of the fertilizer.

concentration, pectin solution has less negative charge of carboxylic than alginate solution. All of alginate chain consists of carboxylic group while the pectin chain consists of ester and carboxylic groups; thus, pectin has less negative charge and causes the amount of interaction between carboxylic and amine in $(CP)_5$ to be less than $(CA)_5$. Therefore, the interaction between chitosan and pectin in $(CP)_5$ layer is weaker than the interaction of chitosan and alginate in $(CA)_5$. This weak interaction allows significant dissolution of pectin in $(CP)_5$ layer during the nitrogen release test as explained before.

From Figure 6(c), it can be seen that in the $(CT)_5$ layer, crosslinking ionic interaction is established between positive charge of chitosan amine group and negative charge of TPP phosphate group. Therefore, $(CT)_5$ will be better in retaining nitrogen than $(CA)_5$. However, the result shows the opposite. In Figure 3, it can be seen that for $(CT)_5$, after being soaked for two hours in demineralized water, the ability of chitosan-TPP coating to retain the nitrogen is decreased compared to chitosan-alginate pellets $(CA)_5$. It was reported that a polyelectrolyte complex that is composed of excess charge (whether positive or negative charge) is called a non-stoichiometric complex which is usually soluble [13, 20]. Thus, TPP in $(CT)_5$ polyelectrolyte complex has an excess of negative charge redissolved in demineralized water after two hours so that the nitrogen release suddenly increased after two hours. The redissolution of TPP caused the uncovered spots of $(CT)_5$ and became paths to nitrogen to release. It is different from the $(CA)_5$ layer which is likely to have a charge resultant near zero; this layer was not soluble in water and was able to survive well in holding nitrogen in fertilizers until the fifth hour.

Chitosan-alginate layer with a different arrangement will affect the layer formation. Consequently, it will also affect the nitrogen release profile. From Figure 7, it can be observed that alternating arrangement of chitosan-alginate layer $(CA)_5$ had
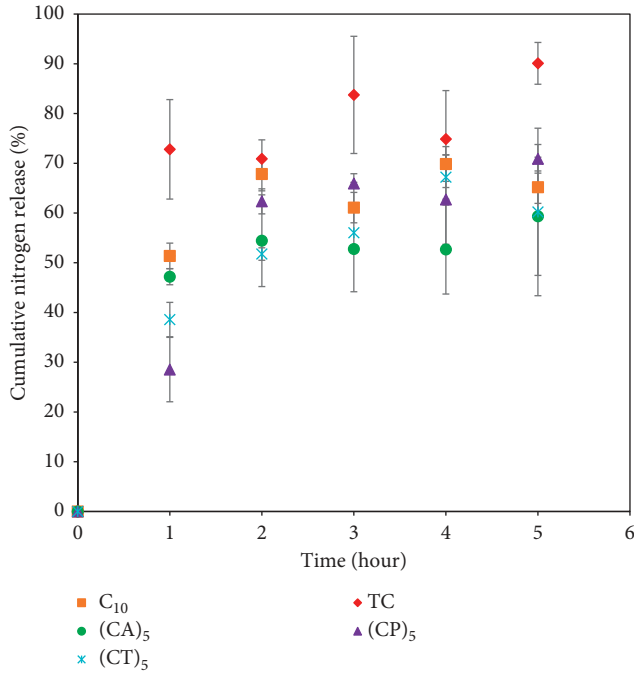
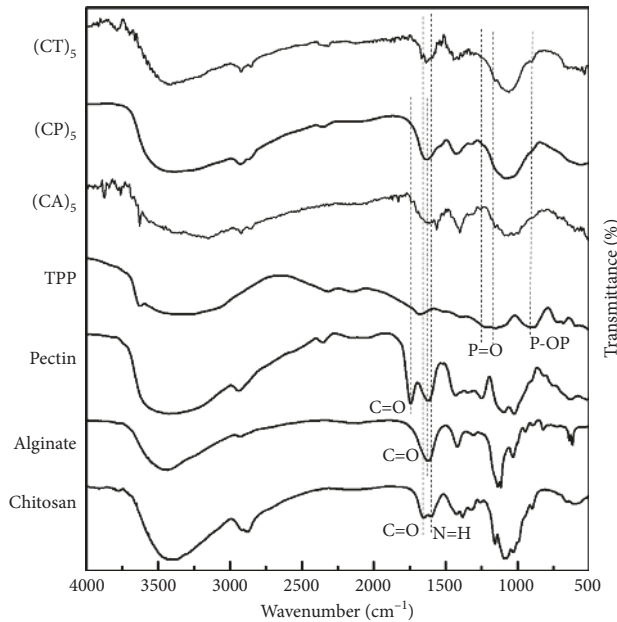FIGURE 3: Effect of chitosan-polyion multilayer coating on the release of nitrogen.

FIGURE 4: FTIR (Fourier transform infrared spectroscopy) of coating layer.

the best ability to retain nitrogen compared to the $(C_2A_2)_2C_2$ and $C_3A_4C_3$ arrangement layer [15]. This was caused by the redissolution of some alginate from the $(C_2A_2)_2C_2$ and $C_3A_4C_3$ layer, thus leaving an uncovered spot (bare spot) for the fast release of nitrogen to the water. It is shown in Figure 5 that the measured $(C_2A_2)_2C_2$ and $C_3A_4C_3$ coating mass after five hours nutrient release test was less than the coating mass of $(CA)_5$ layer. The partial dissolution of alginate in the $(C_2A_2)_2C_2$ and $C_3A_4C_3$ layer was caused by formation of
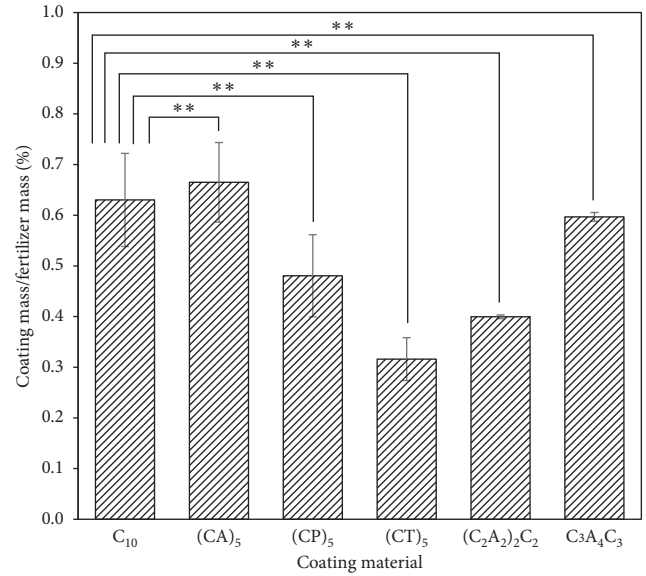

FIGURE 5: Coating mass after five hours nitrogen release test.

nonstoichiometric complex; thus, some components from coating material dissolved when soaked in aquadest [20]. The formation of the nonstoichiometric complex was because the change of chitosan arrangement was not directly intermitted with alginate, so that amine group of chitosan was difficult to interact with carboxylate group of alginate.

The coated fertilizer applied to the field is surrounded by water as a diluting agent. It is generally assumed that the water will penetrate through the coated fertilizer and then dissolve the content of nitrogen inside the coating as described by previous research work [14]. The release of nutrient fertilizer can be approached using diffusion mechanism which follows Fick's law [21]. The assumptions that have been taken are the coated fertilizer is small enough (4 mm in diameter); thus, the nitrogen concentration inside the fertilizer granule is homogen, and the time which needed by the water to enter the fertilizer and to dissolve the nutrient is neglected. The diffusion rate (D_{ab}) of nutrient is assumed much lower than the convection rate (k_c) from the outside surface of coated fertilizer to bulk liquid; thus, the value of k_c is neglected. Then, the mathematical model was obtained by the mass balance of nitrogen content in coating layer and in water as shown in equation (1) by considering all the assumptions:

$$\frac{AD_{ab}N_b}{V\delta}\left(HC_{Aso} - \frac{HVC_{AL}}{N_bV_b} - \frac{C_{AL}}{H}\right) = \frac{dC_{AL}}{dt}, \quad (1)$$

where D_{ab} is the diffusivity coefficient (mm^2/s), H is the equilibrium constant, V is the volume demineralized water for nutrients release test (mL), C_{Aso} is the initial nitrogen concentration in fertilizer (g/mL), C_{AL} is the concentration of nitrogen release in demineralized water (g/mL), N_b is the amount of the fertilizer granule in demineralized water, V_b is the volume of a granule of fertilizer (mm^3), A is the outer surface area of coated fertilizer (mm^2), t is the time (hour), and δ is the thickness of the chitosan coating film (mm).
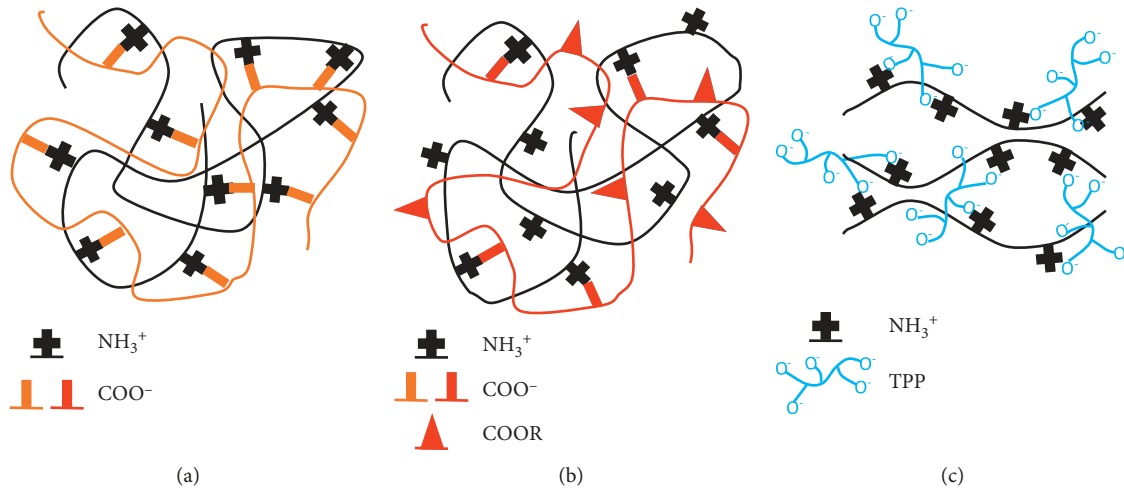
FIGURE 6: Schematic interaction of (a) chitosan-alginate (CA)$_5$, (b) chitosan-pectin (CP)$_5$, and (c) chitosan-TPP (CT)$_5$.
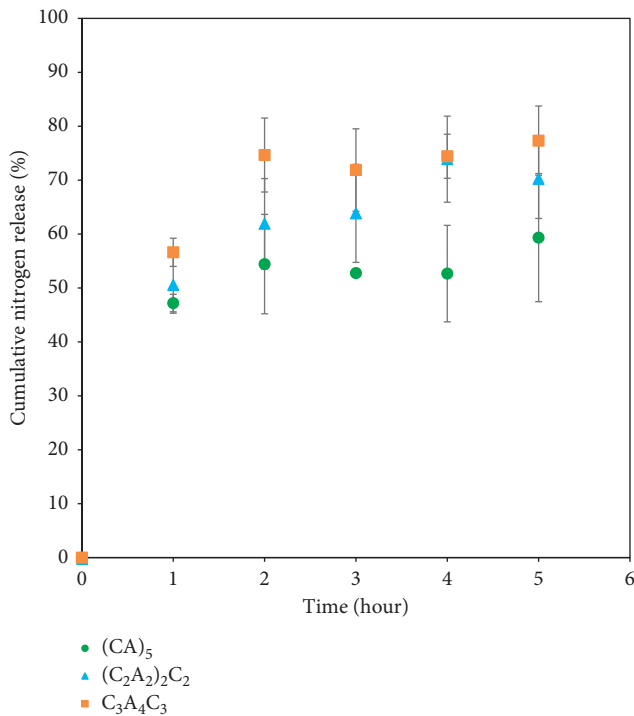

FIGURE 7: Effect of arrangement chitosan-alginate layer to the release of nitrogen.

FIGURE 8: MATLAB simulation of nitrogen release.

With the initial condition ($t = 0$), the concentration of nitrogen in water is equal to zero ($C_{AL} = 0$). Using MATLAB programming, the value of both diffusivity coefficient (D_{ab}) and equilibrium constant (H) could be obtained by guessing the initial value and minimizing the error with sum of square error (SSE) method. The profile of nitrogen release is shown in Figure 8. In general, diffusivity coefficient in gas phase is close to 1×10^{-1} cm^2/s, while the diffusivity coefficient in liquid phase is approximately 1×10^{-5} cm^2/s and typically 1×10^{-7} cm^2/s or lower in solid phase. The diffusion coefficient in C$_{10}$, (CA)$_5$, (CT)$_5$, and (CP)$_5$ film should be smaller than 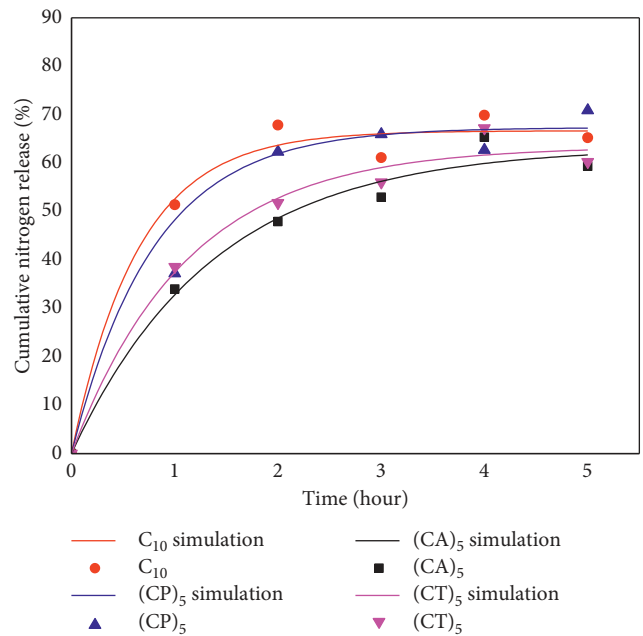1×10^{-7} cm^2/s; however, Table 2 shows that the obtained value of diffusion coefficient in the film was in the range of 2.0933×10^{-6}–4.5747×10^{-6} cm^2/s with the equilibrium constant was 0.8132–0.8397. This unexpected result might be caused by uneven formation of film; thus, the granule surface was not perfectly coated. The uncoated spots became the paths of nitrogen release from fertilizer so that the obtained diffusivity coefficient in chitosan film was still in between the range of diffusion coefficient in gas phase and in liquid phase. In line with the nitrogen release, lower diffusion coefficient of coating represents its ability to retain nitrogen longer inside the granules.

4. Conclusions

Chitosan-polyanion multilayer such as chitosan-alginate (CA)$_5$, chitosan-pectin (CP)$_5$, and chitosan-TPP (CT)$_5$

Table 2: Calculated diffusion coefficient.

ID	Diffusion coefficient (cm^2/s)	Equilibrium constant (H)	SSE (sum of square error)
C$_{10}$	4.5747×10^{-6}	0.8350	1.5×10^{-3}
(CA)$_5$	2.0933×10^{-6}	0.8132	1.3×10^{-3}
(CT)$_5$	2.5606×10^{-6}	0.8139	1.3×10^{-3}
(CP)$_5$	3.7256×10^{-6}	0.8397	8.4×10^{-4}

was able to form layer as fertilizer granule coating which could increase the mechanical strength and decrease the nitrogen release of coated fertilizer. In addition, the modification of chitosan-alginate arrangement layers such as (CA)$_5$, (C$_2$A$_2$)$_2$C$_2$, and C$_3$A$_4$C$_3$ are also able to reduce the nitrogen release but still inferior than the previous multilayer. The alternating layer (CA)$_5$ exhibits the highest mechanical strength and lowest nitrogen release rate compared to others. Meanwhile, the mechanism of nitrogen release of the coated fertilizer follows the proposed diffusion mechanism. It also complies with the mathematical model with the effective diffusivity values for (CA)$_5$, (CP)$_5$, and (CT)$_5$ layer in the range of 2.0933×10^{-6}–4.5747×10^{-6} cm^2/s.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

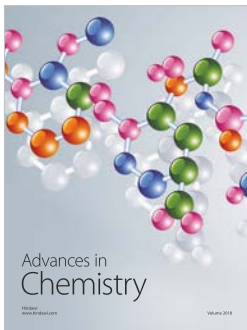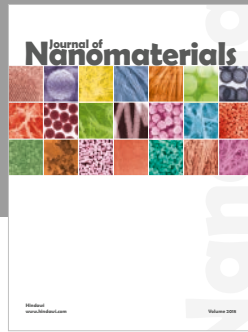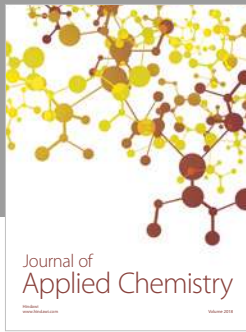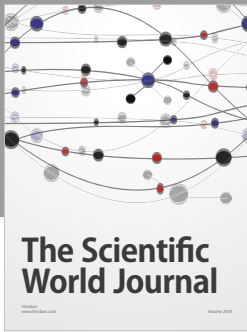The authors declare no conflicts of interest.

Acknowledgments

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