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Effect of Coating Thickness on Release Characteristics of Controlled Release Urea Produced in Fluidized Bed Using Waterborne Starch Biopolymer as Coating Material

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Abstract

Loss of granular urea through leaching, ammonia volatilization and denitrification can be overcome by the application of controlled release urea. Sulfur and organic polymers have been used as controlled-release coating materials but they have limitations of high cost, process complexity and environmental issues. Waterborne starch biopolymer modified with polyvinyl alcohol is a cheap, biodegradable and environmentally friendly coating material and is used for the production of controlled release urea in a fluidized bed. The effect of coating thickness is investigated on release time and diffusion coefficient of urea release in distilled water. Release time increases with increase in coating thickness. The diffusion coefficient of nutrient release decreases with increase in coating thickness. However, coating imperfections and porous coating in some cases produced the opposite results both for release time and diffusion coefficient. It is concluded that a significant coating thickness in addition to good uniformity of thickness and film integrity can produce promising controlled release characteristics.

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Keywords: Controlled release urea; coating thickness; starch biopolymer; fluidized bed coating; diffusion coefficient; release characteristics

1. Introduction

Common urea fertilizer is vulnerable to losses through nitrous emissions, leaching, denitrification and surface runoff when applied to the plants in bare form [1-2]. This loss results economic forfeit, low nutrient use efficiency of the plants and environmental pollution through water eutrophication and nitrous emissions into the stratosphere [3]. One of the abatement strategy is the production of controlled release urea (CRU) [4]. It is a manure that releases nitrogen in a controlled manner to supply nutrients to the plants in synchrony to their metabolic needs. It is produced by the physical intromission of urea granules with some appropriate coating material that can offer an effective barricade to the spontaneous release of nitrogen [5].

Initially sulfur had been employed to produce CRU [6] but the production of sulfur coated CRU has almost been abolished due to higher cost, process complexity and inconsistent results [1]. Synthetic polymers such as polyethylene [7], polystyrene [8],

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polyacrylamide [9], and polysulfone [10] offered promising results with respect to controlled release characteristics, batch to batch uniformity and water retention properties when used as coating materials to produce CRU [1, 11]. However, these materials could not be used to produce CRU on industrial scale due to augmented cost and non-biodegradability factors [4]. A paradigm shift has been observed on the research frontiers to use cost effective and environmentally friendly biomaterials to produce CRU. Starch is one of the cheap, biodegradable, and abundantly available natural polysaccharide [12]. However, starch alone is not feasible to be used as coating material due to its profound hydrophilic nature and poor mechanical properties [13]. Therefore, starch is modified with some appropriate additional agents to overcome these discrepancies. Several studies have been reported for the use of starch as a coating material to produce controlled release devices [14-15]. Number of methods including immersion technique, rotary pan coating and fluidized bed coating have been employed to produce CRU. The fluidized bed coater, however, is considered more appropriate equipment due to excellent heat and mass transfer characteristics, single unit operation and reduced processing time [1].

Coating film thickness plays an important role for better controlled release properties [16]. The nutrient release time depends on diffusional path the dissolved nutrient has to pass through and release from inside of the coating shell to the bulk water it is immersed in [17]. An extensive literature review reveals that promising controlled release properties of CRU are achieved mostly at the cost of non-biodegradability of coating material, process complexity, and elevated price [1]. In this study, starch is modified with polyvinyl alcohol using citric acid as a crosslinker. The literature on production of CRU using such a modified starch biopolymer and the study of release characteristics of CRU produced from such material is scarce. This paper covers the production of CRU using polyvinyl-modified starch biopolymer as coating material. The effect of coating thickness on nutrient release time and coefficient of diffusion of the nutrient release has been investigated.

2. Materials & Methods

2.1. Materials & Pre-treatment

Granular urea from PETRONAS Fertilizer (Kedah) Sdn. Bhd. was subjected to sieve analysis and granules of 1.5-2mm size range were used for all the coating runs. Ultra pure polyvinyl alcohol (PVOH) and citric acid were procured from Merck®. Citric acid is used as a crosslinker between starch and PVOH. The presence of citric acid facilitates starch and PVOH to have good affinity due to intermolecular and intramolecular hydrogen bonding effectuated by OH⁻ functional groups of both starch and PVOH [18]. Tapioca starch from Kapal ABC®, Malaysia, was obtained from the local market. To avoid any microbial attack, it was kept in a refrigerator at -20°C.

2.2. Preparation of polyvinyl alcohol modified starch biopolymer (St-PVOH)

The polyvinyl alcohol modified starch biopolymer solution was prepared by a method reported elsewhere [19]. PVOH was dissolved in deionized water at 90°C with continuous agitation for 45min. Separately prepared well mixed aqueous starch solution was added in PVOH solution and the agitation was continued for 1.5hrs at elevated temperature. Later on, temperature of this solution was lowered to 30°C followed by the addition of aqueous citric acid solution. Stirring was continued for another 1.5hrs and the resultant St-PVOH biopolymer hydrogel was allowed to cool at room temperature. The whole process was carried out in a two neck round bottom flask with a Teflon bar as agitator. Hot plate with magnetic stirring and temperature control system was employed as heating and mixing source.

2.3. Preparation of St-PVOH coated urea (St-PCU)

For each sample, 200g of urea was fed in the FLP-1.5 fluidized bed Coater provided by Wild Horse®, China. The schematic arrangement of the coating equipment is shown in Fig. 1. Filtered air is blown through the heater and the hot air passes through the annular space between the rotating plate and the equipment wall making the urea granules fluidize. A blower is installed for fluidizing air suction from top of the equipment. A peristaltic pump equipped with silicon tubing system transfers the coating solution in the fluidized bed through a two fluid nozzle. Thermocouples are used to monitor the temperature at inlet, outlet and throughout the fluidized bed. The process parameters are adjusted by a control panel. A set of different process variables gives rise to preferential coating which leads the granules to have different coating thickness. To avoid the granules' agglomeration and consequent bed collapse, intermittent coating was carried out instead of continuous one. The dried coated urea was re-coated for better results. This coating method has been reported elsewhere [20].

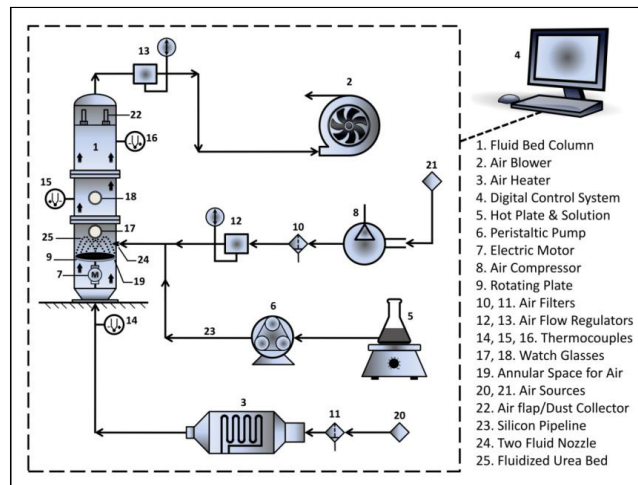


Fig. 1. Schematic arrangement of fluidized bed equipment for the production of CRU

2.4. Determination of coating film thickness of St-PCU granules

Five granules were randomly picked from each sample, each granule was cut with a sharp knife and the cross section was observed under Field Emission Scanning Electron Microscope (FESEM), Zeiss Supra 55 VP (Germany). For each cross section, coating thickness at 40 different positions along the perimeter was determined. For one sample, a mean of 200 data points is reported as mean coating thickness of the sample. Coating thickness was also verified using Dino Lite Digital Pro Microscope AM413T from Dutech Scientific (M) Sdn. Bhd. Malaysia.

2.5. Determination of release time of nutrient from St-PCU granules

Jasco V-630 UV-Vis spectrophotometer (Japan) was used to study the dissolution of St-PCU in distilled water. Two grams of each sample was immersed in 200ml of distilled water in a properly sealed beaker. After a defined interval, the aliquots were stirred gently with glass rod and 3.5ml of sample was taken out for the absorbance measurement in the UV-Vis spectrophotometer. To maintain the volume, equal volume of the distilled water was added in the aliquots. Triplicates were performed and the mean time for 100% release of the nutrients is reported. The product samples were classified into two categories (A & B) based on the apparent quality of the coating evaluated by the visual inspection.

2.6. Determination of diffusion coefficient of nutrient release from St-PCU granules

The coefficient of diffusion of nutrient release from the coating layer is determined using a mathematical model proposed by Du [21] for the population of granules. The model is represented as follows;

$$D = \frac{l}{C_s(t-t')} \left\{ \left(\frac{1}{3} r g_t \rho_s \right) + \frac{l}{6} \right\} \quad (1)$$

Where D is the diffusion coefficient ($cm^2/min.$), l is the coating thickness (cm), C_s is the saturation concentration of urea (g/cm^3), t is the release time ($min.$), t' is the lag period ($min.$), r is the diffusion radius (cm), g_t is the release rate ($g/min.$) and ρ_s is density of the nutrient. The term r , called as the diffusion radius, is the radius of the granule in the swelled condition. Since it is difficult to measure r , so it is assumed that 20% swelling takes place in the starch based coating layer. Hence, r can be calculated multiplying the radius of coated granules by 1.2. It has also been experienced in the release experiments that the lag period is very low, hence the term t' is ignored for the calculation of the diffusion coefficient. The product samples were classified into two categories (A & B) based on the apparent quality of the coating evaluated by the visual inspection. The classification of the coated product based on visual inspection was comfortably done keeping in view the results of several trial runs.

3. Results & Discussion

3.1. Effect of coating thickness on release time

The investigation of coating thickness is critical for the determination of nutrient release rate [16]. The data for release time for different coating thicknesses are given in Table 1 against certain process conditions of the fluidized bed. Different process conditions of the fluidized bed gave rise to a distribution of coating thickness for different samples. In Table 1, X_1 , X_2 , X_3 , X_4 , and X_5 represent atomizing air pressure, fluidizing gas temperature, spray rate, spray temperature and coating time respectively.

Table 1: Data on coating thickness and release time against different process conditions

| Run | X_1 (Bar) | X_2 (°C) | X_3 (RPM) | X_4 (°C) | X_5 (hrs.) | Coating Thickness l (μm) | Release Time t (hrs.) |
|-----|----------------|---------------|----------------|---------------|-----------------|--|----------------------------|
| 1 | 0.225 | 85 | 2.75 | 85 | 150 | 523.47 | 22.50 |
| 2 | 0.05 | 50 | 5.00 | 70 | 30 | 125.00 | 2.50 |
| 3 | 0.225 | 85 | 2.75 | 85 | 90 | 475.68 | 17.50 |
| 4 | 0.4 | 120 | 0.50 | 100 | 150 | 205.92 | 1.08 |
| 5 | 0.225 | 85 | 2.75 | 85 | 90 | 459.63 | 16.50 |
| 6 | 0.05 | 50 | 0.50 | 70 | 150 | 309.15 | 4.67 |
| 7 | 0.225 | 85 | 2.75 | 85 | 90 | 442.52 | 16.00 |
| 8 | 0.4 | 50 | 5.00 | 70 | 150 | 281.06 | 2.83 |
| 9 | 0.225 | 85 | 2.75 | 85 | 90 | 421.78 | 15.50 |
| 10 | 0.4 | 85 | 2.75 | 85 | 90 | 228.03 | 12.50 |
| 11 | 0.225 | 85 | 2.75 | 85 | 30 | 168.30 | 5.33 |
| 12 | 0.05 | 120 | 0.50 | 70 | 30 | 91.66 | 1.00 |
| 13 | 0.05 | 120 | 0.50 | 100 | 30 | 85.43 | 0.58 |
| 14 | 0.4 | 120 | 5.00 | 100 | 30 | 226.93 | 1.67 |
| 15 | 0.05 | 120 | 5.00 | 70 | 150 | 235.07 | 1.83 |
| 16 | 0.05 | 50 | 5.00 | 70 | 150 | 298.54 | 3.33 |
| 17 | 0.05 | 50 | 5.00 | 100 | 150 | 312.95 | 6.33 |
| 18 | 0.225 | 85 | 5.00 | 85 | 90 | 328.39 | 11.50 |
| 19 | 0.225 | 85 | 2.75 | 70 | 90 | 389.74 | 14.00 |
| 20 | 0.225 | 85 | 2.75 | 85 | 90 | 408.15 | 15.00 |

A plot between coating thickness and nutrient release time for both A and B categories of the samples is shown in Fig. 2. The error bars represent standard deviation of the triplicates performed. From curve A in Fig. 2, it is observed that the release time of the nutrient from St-PCU granules increases with an increase in the coating thickness. To understand this phenomenon, it is imperative to understand the mechanism of nutrient release from a polymer coated film. When a hydrophilic polymer is subjected to dissolution in water, the polymer matrix starts to swell due to imbibement of water into the coating film [22]. Water migrates through dynamic spaces between the macromolecules of the polymer film and dissolves the core nutrient as soon as it comes in contact with it [1]. This osmotic imbibement 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 deformation and the active nutrient starts to release from the micropores developed at the weakest sites on the coating film [23]. At this point, coating thickness plays an important role to control the release rate of the nutrient. Higher coating thickness results higher release time because it takes longer for the nutrient molecules to diffuse through thick coating film and reach the outer reservoir [17]. In addition the augmented diffusion resistant for higher coating thickness also increases the release time [24]. According to Ko [23], a critical value of the coating thickness is necessary for promising release properties. However, coating thickness less than the critical value may cause the nutrient to immediately release when subjected to dissolution test in water. This spontaneous release is attributed to the presence of holes or microscopic pores in the coating film.

For the results of effect of coating thickness on release time as represented in Fig. 2 (category A), it can be explained 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 St-PVOH coating film bears the hydrostatic pressure of the dissolved nutrient for longer time in case of higher 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 [25-26]. 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. For example, sample 13 have a release time of only 0.58 hrs. In such cases, the release of the nutrient is spontaneous which is due to the poor coating quality and low

coating thickness. These results are in synchrony to the ones reported in literature [27-29]. The FESEM micrograph and microscopic images of coated urea granule are shown in Fig. 3 as a reference.

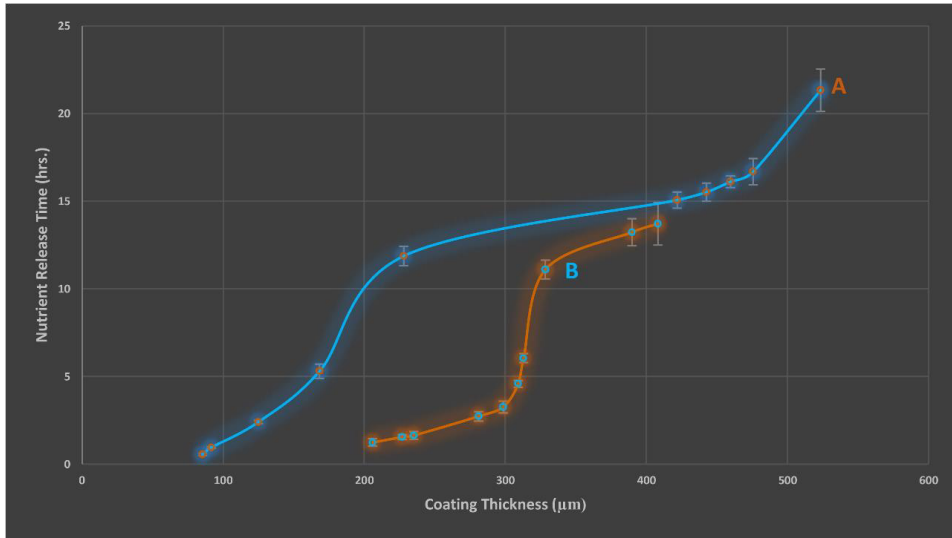


Fig. 2. Effect of coating thickness on nutrient release time

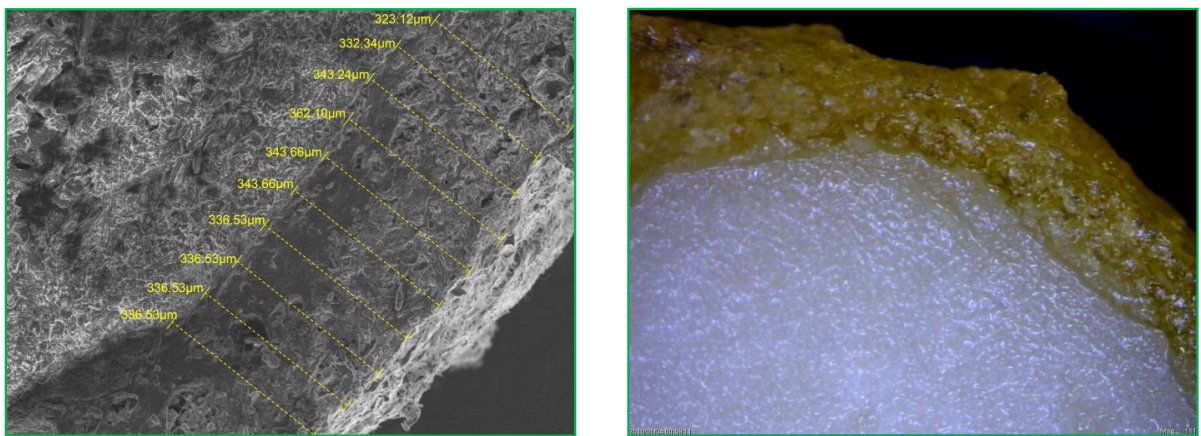


Fig. 3. FESEM micrograph and optical microscopic image of a St-PCU granule cross-section

For the samples included in category B too, it is seen in Fig. 2 that the release time increases with increase in coating thickness. However, a comparison of the release results of both categories reveals some interesting situations. For example, for a coating thickness of 228.03µm in curve A, the release time is 12.50 hrs. whereas, for a coating thickness of 235.07µm in curve B, a little higher than its counterpart in curve A, the release time is only 1.83 hrs. which is much less than 12.50 hrs. This may be attributed to the coating imperfections resulted because of the preferential coating of the granules. In such cases, it was observed that part of a granule received a very thick coating while the other fraction of the same granule received a very thin encapsulating film during coating in the fluidized bed. As a consequence, in spite of the fact that such granules get significant mean coating thickness but the point of least coating thickness of the same granule cannot withstand the hydrostatic pressure of the dissolved nutrient for long and the complete dissolution of the nutrient is observed in a short period of time. In addition to the coating imperfections, another

discrepancy also caused the inferior release characteristics. In some samples of category B, in spite of significant coating thickness and negligible coating imperfections due to least coefficient of variance of the coating thickness, low release time was observed. This was because of the highly porous coating film. For such a coating film, not only the water penetration into the coating film and the core nutrient, but also, the diffusion of dissolved solute from inside the core to the interface and into the external reservoir is very quick. Hence it can be concluded that solely a momentous coating thickness is not enough for the promising controlled release characteristics but a strong, steady and integrated coating film along with uniformity of thickness over the granule surface is equally important.

3.2. Effect of coating thickness on diffusion coefficient of nutrient release

The knowledge of diffusion coefficient of the nutrient release can be used as a design tool for the development of new controlled release fertilizers with known and desired release characteristics [30]. In addition, the accurate understanding of the diffusion coefficient is needed for the prediction of transport phenomenon involving molecular diffusion [31]. The data on diffusion coefficients of the nutrient release from different St-PCU samples for different coating thicknesses is given in Table 2. In Table 2, X_1 , X_2 , X_3 , X_4 , and X_5 represent atomizing air pressure, fluidizing gas temperature, spray rate, spray temperature and coating time respectively.

Table 2: Data on coating thickness and diffusion coefficient against different process conditions

| Run | X_1 (Bar) | X_2 (°C) | X_3 (RPM) | X_4 (°C) | X_5 (hrs.) | Coating Thickness l (μm) | Diffusion Coefficient D ($\text{cm}^2/\text{min.}$) |
|-----|----------------|---------------|----------------|---------------|-----------------|--|--|
| 1 | 0.05 | 120 | 5.00 | 70 | 0.5 | 286.46 | 6.26×10^{-4} |
| 2 | 0.40 | 50 | 5.00 | 70 | 0.5 | 117.61 | 0.778×10^{-4} |
| 3 | 0.40 | 50 | 0.50 | 100 | 0.5 | 154.91 | 1.26×10^{-4} |
| 4 | 0.225 | 85 | 2.75 | 85 | 1.5 | 475.68 | 0.976×10^{-4} |
| 5 | 0.40 | 50 | 5.00 | 100 | 0.5 | 93.87 | 0.77×10^{-4} |
| 6 | 0.225 | 85 | 2.75 | 85 | 1.5 | 459.63 | 0.976×10^{-4} |
| 7 | 0.225 | 85 | 2.75 | 85 | 2.5 | 523.47 | 0.924×10^{-4} |
| 8 | 0.225 | 85 | 2.75 | 85 | 1.5 | 462.82 | 0.963×10^{-4} |
| 9 | 0.40 | 50 | 0.50 | 100 | 2.5 | 370.50 | 1.26×10^{-4} |
| 10 | 0.05 | 50 | 0.50 | 70 | 2.5 | 309.15 | 1.8×10^{-4} |
| 11 | 0.05 | 120 | 0.50 | 70 | 2.5 | 228.40 | 8.77×10^{-4} |
| 12 | 0.05 | 50 | 5.00 | 70 | 2.5 | 298.54 | 2.4×10^{-4} |
| 13 | 0.40 | 120 | 5.00 | 70 | 0.5 | 265.25 | 4.63×10^{-4} |
| 14 | 0.40 | 50 | 5.00 | 70 | 0.5 | 300.00 | 6.0×10^{-4} |
| 15 | 0.05 | 50 | 0.50 | 70 | 2.5 | 350.00 | 6.5×10^{-4} |
| 16 | 0.225 | 85 | 2.75 | 85 | 2.5 | 400.00 | 6.5×10^{-4} |

A plot between coating thickness and diffusion coefficient for both A and B categories of the samples is shown in Fig. 4. The error bars represent standard deviation of the triplicates performed. The curve A in Fig. 4 shows that the diffusion coefficient of nutrient release decreases with an increase in coating thickness. This is in agreement to the literature results reported in different papers [16-17, 28, 32]. With the increase in coating thickness, diffusion length increases which leads to the increase in diffusion coefficient of the nutrient release and vice versa. The diffusion behaviour of dissolved nutrient inside the macromolecular polymer chains is quite complex. If the nutrient transport is governed only by the concentration gradient as the driving force for the nutrient diffusion from granule core across the swelled polymer coating layer, the transport is said to obey the Fickian diffusion [33]. For the Fickian transport, it is believed that the nutrient release is much slower than the polymer chains' relaxation. The polymer chain relaxation involves large scale motion or changes in the polymer chain structure. In another case, the nutrient transport is governed by the dynamic swelling and macromolecular chain relaxation. In this case, the nutrient diffusion in or out of the swollen polymer chains is comparable to the relaxation rate, that is, the nutrient release is governed by the combination of diffusion and polymer relaxation. The solute diffusion in the polymer wall and solute dissolution into the main water body takes place simultaneously [34]. It is reported that the nutrient transport in most of the superabsorbent hydrogels follows this transport phenomenon that is also termed as non-Fickian or anomalous diffusion. For the Case-II transport, solely the molecular relaxation is responsible for nutrient transport [35].

In this study, the transport of nutrient through the swollen network of macromolecular polymer chains for samples in curve A is expected to follow the non-Fickian or anomalous diffusional transport. In curve A, the diffusion coefficient decreases with increase in coating thickness. On the contrary, the increase in coating thickness increases the diffusion coefficient for the samples in curve B.

This is because of coating imperfections and highly porous structure of the coating film. In some cases, the mean thickness of the coating layer was quite significant but the fraction of granule had very thin coating thickness. In such cases, the coating layer is highly vulnerable to rupture when the hydrostatic pressure inside the coating layer increases beyond the immunity of the coating layer at the imperfection site of coating film. In this case, the ruptured film caused the nutrient to release spontaneously. Diffusion coefficient has a direct relationship with release rate as represented in equation 1.

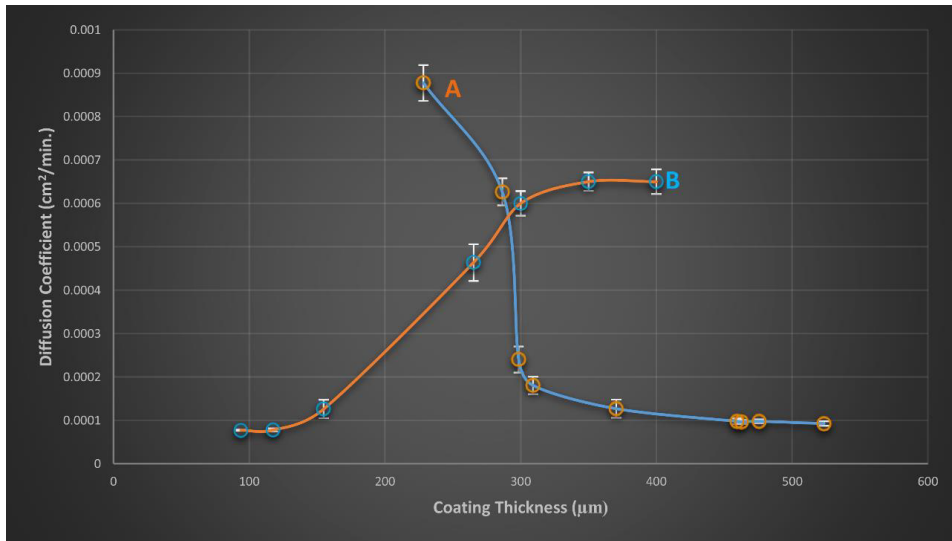


Fig. 4. Effect of coating thickness on coefficient of diffusion of nutrient release

For cases when the coating imperfections cause spontaneous release, the release rate appears to have higher value and consequently, the diffusion coefficient also increases. In another case of increase of diffusion coefficient with increase of coating thickness, it is seen that significantly thick but highly porous coating film causes the nutrient to diffuse through the large voids of the film quickly. Hence the release rate is higher in this case too, and that leads to higher diffusion coefficient. In both of such cases, that is, the coating imperfections and highly porous coating film, the nutrient transport is believed to follow the Case-II transport which is governed solely by the chain relaxation of the macromolecules of the polymer network.

4. Conclusion

PVOH-modified waterborne starch biopolymer has been used as coating material to produce controlled release coated urea in a fluidized bed equipment. The effect of coating thickness on release time and diffusion coefficient of the nutrient release has been investigated. It has been observed that the release time increases with increase in coating thickness. However, in case of coating imperfections and porous coating film, even thicker coating films could not produce promising results. The diffusion coefficient decreases with increase in coating thickness. However, the increase in coating thickness also resulted increase of diffusion coefficient for samples having coating imperfections and highly porous coating film in spite of significant mean coating thickness and least coefficient of variance of coating thickness. It can be concluded that merely a good coating thickness is not enough for promising release characteristics of the controlled release urea. A combination of good coating thickness along with least heterogeneity and film integrity is also important.

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