

Effect of Particle Size and Coating Thickness on the Release of Urea Using Multi-Diffusion Model

Thanh H. Trinh, Ku Zilati Ku Shaari, Abdul Basit, and Babar Azeem

Abstract—In the effort of getting a better understanding on urea release mechanism, a multi-diffusion model is used to simulate the diffusion of urea through coating layer and to environment. Based on the multi-diffusion model for "constant release" stage, the effect of particle size (R_0) and coating thickness (l) on diffusive flux, release rate and release time are investigated by using Finite Element Method (FEM) and 2D-geometry. Results show that an increase in particle size or coating thickness also leads to an increase in release time. However, adjusting on particle size is more economical than coating thickness. In addition, there is no relationship between the product $R_0 \times l$ with the diffusive flux or release rate. A linear relationship between the product $R_0^2 \times l^{-1}$ and release rate has been found instead.

Index Terms—Urea Release, urea diffusion, finite element method, multi-diffusion modeling.

I. INTRODUCTION

The aim of slow release or controlled release fertilizer (SRF/CRF) is to prevent nutrient loss and enhance nutrient utilization efficiency by plants [1]. Plant can only recover 30-50% of the nutrient in conventional fertilizer, while CRFs make least possible losses of the fertilizer through volatilization, leaching. Besides, CRFs help preventing the seedling damage and better protecting of the ecosystem in the case of biodegradable carriers [2].

Urea was selected as the material to be coated because of its high nitrogen content, low cost, and commercial availability [3]. The first study on the application of controlled release technology to fertilizers was conducted in 1962 by Ortil *et al.* [4]. The release of coated CRF is usually controlled by the diffusion through the coating layer. Many modeling efforts were based on the assumption that the release of nutrients from coated fertilizer is controlled by simple solute diffusion [2], [5]-[8]. Based on Raban's experiments, the release from a single granule of a polymer coated CRFs consists of three stages: an initial stage during which no release is observed (lag period), a stage of constant release, and finally a phase of gradual decay of the release rate [4]. In 2007, Lu proposed a mathematical model for the release of a scoop of polymer coated urea, which took into account the effect of sample population. This model was based on mass balance equation of pseudo-steady state of

Fick's law. However, the first stage of release process was neglected, and "trial and error" method was used to estimate diffusion coefficient [9]. Modeling has proved that it is the fast and cost effective way of predicting release of nutrients from CRFs.

There are many factors influencing nutrient release from CRFs, such as coating material, coating thickness, particle size, shape, coating surface irregularity, etc. [10]. The rate of nutrient release from a polymer coated product can be controlled not only by varying the type and the thickness of the coating but also by changing the ratio of different coating materials [10], [11]. Understanding the effect of these factors is very important to the longevity target (release profile) for crop application and quantity of coating material used for coated CRFs. A finite element based model has been used to study the effect of particle size and coating thickness on "constant release" stage using COMSOL Multiphysics 4.3a software.

II. METHODOLOGY

This study consists of two parts. The first part describes how to simulate the release of urea by mean of Finite Element Method (FEM) and its validation process. The second part investigates the effect of coating thickness, saturated concentration and effective diffusivity during the "constant release" stage.

A. Model Development

Model used for studying the effect of particle size and coating thickness is based on multi-diffusion model from our previous study [12], [13]. Fig. 1 shows the dissolution model of urea particle in water. Urea particle consist of a solid urea core and a coating layer on the surface of this core. Water surrounds the urea particle, and penetrates through the coating layer. An assumption is made that urea particle is spherical in shape. Urea is quickly dissolved in water so that the solute's concentration at the sphere's surface is saturated. Because the coated urea particle is immersed in a large fluid volume, the concentration far from the sphere is zero [14].

When coating layer is saturated with water, urea begins to release by mean of diffusion through the coating layer. Based on mass transport equation in porous medium, a transition state for urea diffusion through the coating could be written as below [9], [15]:

$$D_e \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] = \varepsilon \frac{\partial C}{\partial t} \quad (1)$$

where C is the concentration of urea in mol/m^3 , D_e is effective diffusivity (diffusion coefficient) of urea in porous medium

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in m^2/s , ε is porosity of the coating in percentage (%).

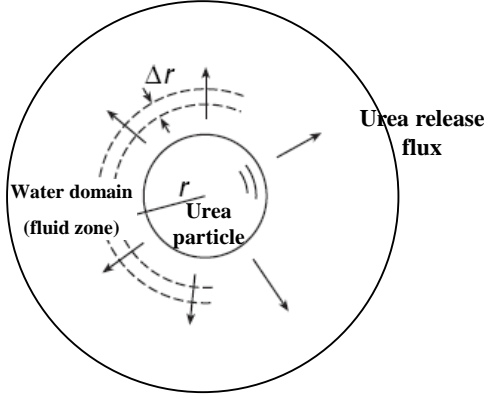


Fig. 1. Dissolution model of a spherical urea particle.

Since the urea pellet is motionless, it is assumed that urea flux from the interface of coating to the liquid is controlled by the diffusion of urea into the liquid, and calculated based on mass transport equation of urea in water. The equation for urea diffusion can be written as:

$$D_{urea} \frac{\partial^2 C}{\partial r^2} + \frac{2D_{urea}}{r} \frac{\partial C}{\partial r} = \frac{\partial C}{\partial t} \quad (2)$$

In this model, D_{urea} is a function of urea concentration [14]:

$$D_{urea} = (1.380 - 0.0782C + 0.00464C^2) \times 10^{-5} \quad \text{cm}^2/\text{s} \quad (3)$$

Three simulations are run following the input data summarized in Table I. These data are based on previous publication from Shaviv *et al.* [4]. Geometry and meshing steps are done for urea particles with radius and coating thickness as following

Table I and Fig. 2. Fluid zone which is defined as the distance from center of the urea particle to outer boundary of water domain is set to 22 times of the radius of urea core (see Fig. 1), [12]. Initial values and boundary conditions are specified for the model. At the time t_0 , urea concentration at the surface of urea core is saturated, and concentration is zero at the outer layer of fluid field. In these simulations, calculation time depends on the amount of urea (size and shape) and coating material (thickness and properties).

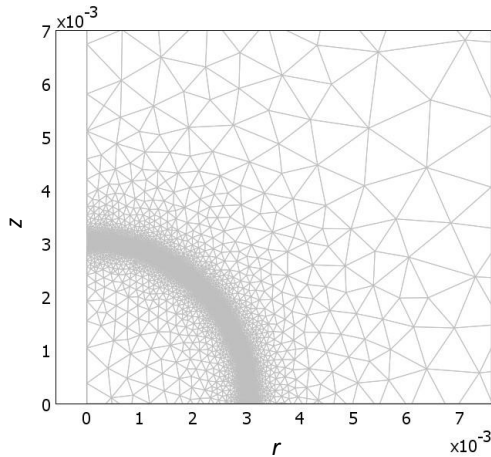


Fig. 2. Mesh generation for urea dissolution models for coated urea.

TABLE I: SIMULATION DATA

No.	Coating Material	Urea Radius (mm)	Coating Thickness (mm)	Lag time t_0 (days)
1	MPO ^a	1.2	0.0375	0.5
2	MPO ^a	1.2	0.0917	4
3	MPO ^a	1.2	0.1833	7

^a. Modified Polyolefin

Amount of urea released is defined as the integral of diffusive flux at the outer shell of urea particle.

$$m_{released} = M_{urea} A_{diff} \int_{t=0}^t J_{Urea} dt \quad (4)$$

where M_{urea} is molar mass of urea, g/mol

A_{diff} is diffusion surface area, m^2

J_{Urea} is the diffusive flux of urea at outer shell of urea particle, $\text{mol}/(\text{m}^2\text{s})$

Total urea of the urea particle is calculated as

$$m_{total\ urea} = V_{core} d_{urea} \quad (5)$$

where $m_{total\ urea}$ is total urea of the urea particle in g

V_{core} is volume of urea core, m^3

d_{urea} is urea density, g/m^3

At time t , amount of urea inside urea core is

$$m_{core} = m_{total\ urea} - M_{urea} \iiint_{V_{2+3}} C dV \quad (6)$$

where C is concentration of urea, mol/m^3

V_{2+3} is volume of coating layer and water domain

“Constant release” stage is considered from the time of beginning of the release to the time when solid urea is totally dissolved. At that time, the amount of urea in the core is

$$m_{core} = m_{sat} = M_{urea} C_{sat} V_{core} \quad (7)$$

where

m_{sat} is urea mass of the urea core when solid urea is totally dissolved,

C_{sat} is saturated urea concentration, mol/m^3

This is defined as the stop condition for “constant release” stage. This model focuses only on the “constant release” stage, and the lag time (t_0) is determined based on each experiments.

Validation process uses experiment data from Shaviv literature [4]. Data are extracted using Engauge Digitizer 4.1. Based on information from these papers and extracted data, simulation and experiment data are plotted to confirm our model results.

Validated model is then used to study the effect of particle sizes and coating thickness on the release of urea particle. In this model, diffusion coefficient of urea in liquid is defined as a function of urea concentration, and coupled in fluid field domain.

B. Effect of Particle Size (R_0) on the Release of Urea

Based on the model set up for urea diffusion model, simulations are done for five particle sizes such as 2.0, 2.5, 3.0, 3.5, and 4.0 mm with the same coating thickness. Diffusivity for these simulations is 10^{-14} m²/s. By defining different geometries which are different in particle radius, five simulations are set up and run. Diffusive fluxes are drawn from these simulations, and release times are based on the stop condition for constant release stage (Eq. 7).

C. Effect of Coating Thickness (l) on the Release of Urea

Based on the model set up for urea diffusion model, simulations are done for five coating thickness such as 0.050, 0.075, 0.100, 0.125, and 0.150 mm with the same particle radius (2 mm). Diffusivity for these simulations is 10^{-14} m²/s. Diffusive fluxes are drawn from these simulations, and release times are based on the stop condition for constant release stage (Eq. 7).

III. RESULTS AND DISCUSSION

A. Model Development and Validation

Simulations are conducted using information in Table I following experimental data from Shaviv *et al.* [4]. Their work was focused on MPO coating material, and experiments were conducted with three samples with the thickness as 0.0375, 0.0917, 0.1833 mm. Effective diffusivity, in all three simulations, is 1×10^{-5} cm²/day. In Fig. 3, simulation data correspond with experiments from Shaviv *et al.* This proves that model has well simulated the release of urea during “constant release” stage.

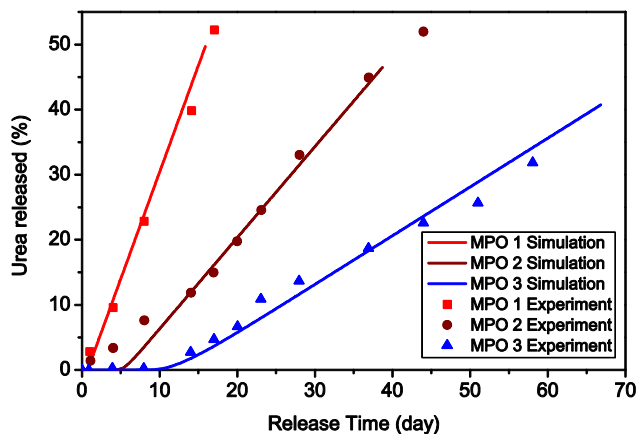


Fig. 3. Simulation released profile and validation based on Shaviv *et al.* experiments during “constant release” stage.

TABLE II: EFFECT OF PARTICLE SIZE ON THE RELEASE OF UREA

Particle size (mm)	Product $R_0 \times l$ (mm ²)	Diffusive flux (mol/(m ² .s))	Release time (days)	Release rate (mol/s)
1.0	0.10	9.52E-7	34.84	1.45E-11
1.5	0.15	9.82E-7	55.79	3.16E-11
2.0	0.20	9.98E-7	76.85	5.53E-11
2.5	0.25	1.00E-6	97.92	8.56E-11
3.0	0.30	1.01E-6	118.98	1.22E-10

B. Effect of Particle Size on the Release of Urea

Table II summarizes simulation results for different

particle sizes. Diffusive fluxes in these cases are around 1.0×10^{-6} mol/(m².s). Release time ranges from 34.84 days to 118.98 days as the particle size increases from 1 to 3 mm. Hence it can be deduced that the release time proportionally depends on the particle size. This relationship is a linear relationship as in Fig. 4 ($R^2 = 1$). Release rate is from 1.04×10^{-10} mol/s to 4.07×10^{-10} mol/s as particle size changes from 2 to 4 mm.

As shown in Fig. 4 and Fig. 5, although the diffusive fluxes are almost the same (1.0×10^{-6}) in these cases with a specific coating thickness, release time increases as particle size increases. The reason of this phenomenon comes from the change in overall mass of the urea particle. Moreover, the time for urea diffusing through coating layer depends on the amount of total urea inside the core. Therefore, the bigger the urea particle, the more release time it gains. So, urea particle needs more time for urea release. From this point, if one would like to increase the release time, changing in particle size is an easier way to adjust the release time within a small range. This conclusion was also mentioned by Shaviv *et al.* that increasing in the radius is more economical and technically feasible [4].

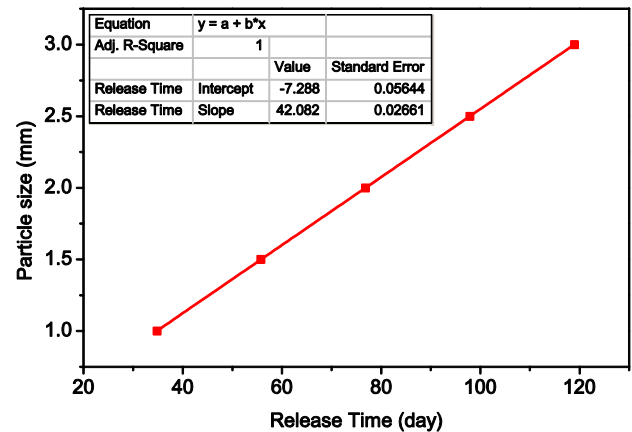


Fig. 4. Effect of particle size on urea release time when coating thickness is 0.1mm.

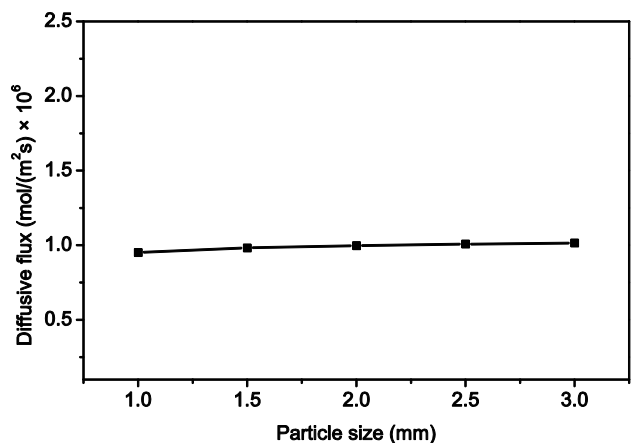


Fig. 5. Effect of particle size on diffusive flux when coating thickness is 0.1mm.

C. Effect of Coating Thickness on the Release of Urea

Simulation results are summarized as in Table III. As coating thickness increases, release time also increases. It causes by the increase in diffusion resistant. As shown in Fig. 7, coating thickness play an important role in the diffusion of

urea. Diffusive flux is 2.04×10^{-6} mol/(m².s) as coating thickness is 0.050 mm, and it decreases to 0.65×10^{-6} mol/(m².s) with a 0.150 mm of coating thickness. Release rate also decreases due to an increase on coating thickness.

Effect of coating thickness on the release time is plotted in Fig. 6. Release time changes from 76.85 days to 93.75 days when thickness changes from 0.1 mm to 0.125 mm. The difference between two thicknesses is 0.025 mm but release time increases 22%.

This change leads to a difficulty in coating technology when producing controlled release urea. If coating technique is not good, the release time of CRF will be varied and cannot be controlled because of the variation of the coating layer. From the above discussion, to get a well-controlled release urea, one not only concentrate on the material but also on the coating techniques. As a result, in design coating application, coating thickness must be identified for crop application, and particle size is used to obtain a release time suitable for crop period.

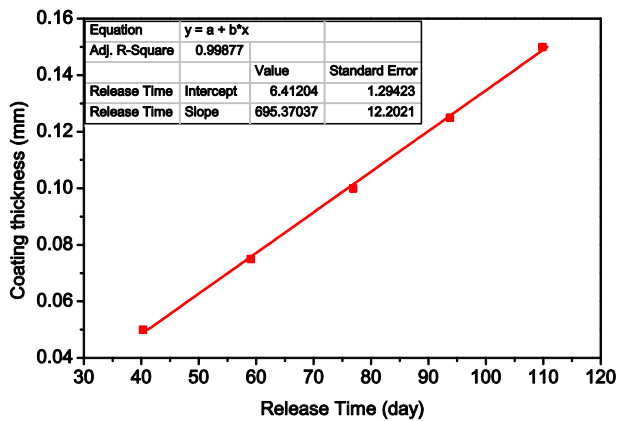


Fig. 6. Effect of coating thickness on urea release time when the particle size is 2 mm.

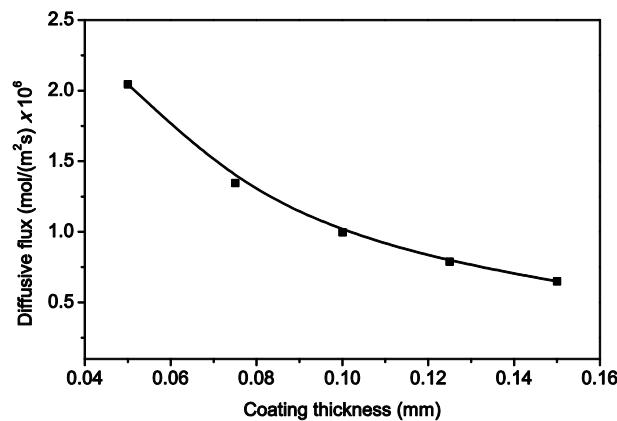


Fig. 7. Effect of coating thickness on diffusive flux when the particle size is 2 mm.

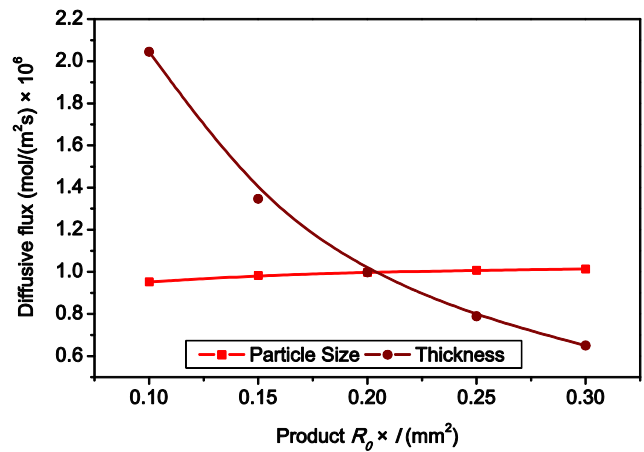
TABLE III: EFFECT OF COATING THICKNESS ON THE RELEASE OF UREA

Thickness mm	Product $R_0 \times l$	Diffusive flux mol/(m ² .s) $\times 10^6$	Release time days	Release rate mol/s $\times 10^{10}$
0.050	0.1	2.04	40.28	1.08
0.075	0.15	1.35	59.03	0.73
0.100	0.2	1.00	76.85	0.55
0.125	0.25	0.79	93.75	0.45
0.150	0.3	0.65	109.84	0.38

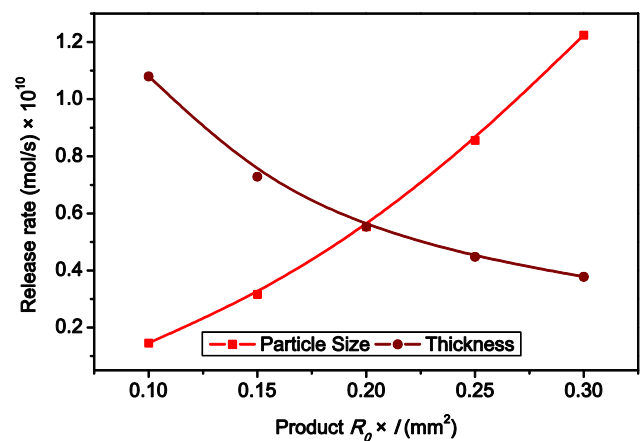
D. Relationship Between Product $R_0 \times l$ with Diffusive Flux, Release Rate

The effect of particle size and coating thickness on release rate also mentioned by Shaviv on modified polyolefin (MPO) and polyurethane-like coating (PULC) [4] but they act on difference ways as in our discussion. They stated: "Release rate inversely depends on the product of granule radius R_0 and coating thickness l " [4]. It means that release rate increases when particle size or coating thickness decreases. From our results (Fig. 8), release rate increases due to a decrease of product $R_0 \times l$ when changing the thickness (l), while the change in radius (R_0) leads to an increase in release rate as the product $R_0 \times l$ increases. There is no relationship between the product $R_0 \times l$ with diffusive flux or release rate. However, a linear relationship between the product $R_0^2 \times l^2$ and release rate has been found as in Eq. 8 and Fig. 9.

$$\text{Release rate} = \left(1.6 + 1.33 \left(\frac{R_0^2}{l} \right) \right) 10^{-12} \text{ mol/s} \quad (8)$$



(a)



(b)

Fig. 8. Relationship between product $R_0 \times l$ with diffusive flux (a) and release rate (b) when changing radius or thickness.

This relationship is in good agreement with theory of diffusion for mass transport. It shows that release rate inversely depends on coating thickness and directly proportional to square of urea particle size. Because diffusive flux inversely depends on the coating thickness l ,

release rate also inversely depends on this thickness. Besides, release rate depends on diffusion surface area which equivalents to square of particle size R_0 . So, Eq. 8 can be used to estimate the effect of particle size and coating thickness of coated urea during constant release stage when effective diffusivity is $10^{-14} \text{ m}^2/\text{s}$.

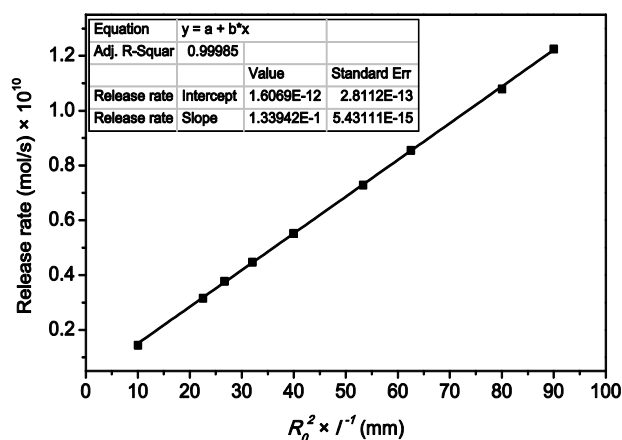


Fig. 9. Relationship between product $R_0^2 \times l^{-1}$ and release rate.

IV. CONCLUSION

By using multi-diffusion model and 2D-FEM method, the effect of urea particle radius and coating thickness on urea release time are investigated. Release time is proportional to coating thickness and particle size but their mechanisms are different. Results also show that an adjustment in particle size is easier and more economical than coating thickness. Moreover, there is no relationship between product $R_0 \times l$ with diffusive flux or release rate. However, a linear relationship between product $R_0^2 \times l^{-1}$ and release rate has been found, and is in good agreement with diffusion theory.

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