

Modeling of Urea Release from Coated Urea for Prediction of Coating Material Diffusivity

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Abstract

This study investigates the diffusion of urea from the surface of solid urea to environment through multilayer using finite element method (FEM). A multi-diffusion model was established to simulate the diffusion of urea through coating layer and to environment. Firstly, a comparison between analytical and numerical model was conducted to obtain accurate numerical model for the diffusion of urea. Secondly, model was applied to study the effect of diffusivity coefficient on urea releasing time. Modeling results indicated that releasing time increases as effective diffusivity coefficient decreases. Releasing time was 8.34 days with a diffusivity coefficient of $1.60 \times 10^{-13} \text{ m}^2/\text{s}$ and 132.96 days with diffusivity coefficient of $10^{-14} \text{ m}^2/\text{s}$. It demonstrated that material chosen for urea coating would have a diffusion coefficient of $1.49 \times 10^{-14} \text{ m}^2/\text{s}$ to obtain a suitable releasing time for effective fertilization.

Keywords: Urea Release; Urea Diffusion; Finite Element Method; multi-diffusion modeling.

1. Introduction

The aim of slow release or controlled release fertilizer (SRF/CRF) is to prevent nutrient loss and enhance nutrient utilization efficiency by plants (Trenkel, 1997). The amount of fertilizers recovered by plant when applied in conventional forms is only 30-50%, while CRFs make least possible losses of the fertilizer through volatilization or leaching, prevention of the seedling damage and full protecting of the ecosystem in the case of biodegradable carriers (Al-Zahrani, 1999).

Urea was selected as the material to be coated because of its high nitrogen content, low cost, and commercial availability (Kent, 2007). First study on the application of controlled release technology to fertilizers was conducted in 1962 by Ortil et al. (Avi Shaviv et al., 2003a). Coated CRFs usually controlled by the diffusion through the coating layer. One of the major factors controlling the release of first-type of CRFs is the rupture of the coating found in sulphur coated urea (SCU). Jarrell and Boersma developed a mathematical model for urea release for SCU particle (Jarrell and Boersma, 1980). Glaser et al. studied the release of polymer-coated granule and applied one-dimensional coordinate diffusion system in 1987 (Avi Shaviv et al., 2003a). They introduced nonlinearity into the release by assuming that the diffusion coefficient, D , is time dependent. Gambash et al. used semi-empirical model in their study. The release of CRF was considered as a first-order process and ignored the effect of geometry and size. Besides these assumptions, the lag period was not included (Gambash et al., 1990).

Gandeza built up a semi-empirical model using quadric equation to study the effect of temperature on CNR-polyolefin-coated urea in soil ($CNR = a + b(CT) + c(CT)^2$) (Gandeza et al., 1991). Lu and Lee applied the Fick's law in spherical coordinate for the release of latex coated urea (LCU) (Lu and Lee, 1992). Al-Zahrani modeled unsteady state of polymeric membrane particle and assumed a well-mixing condition inside sphere particle (Al-Zahrani, 1999). Most of the modeling efforts were based on the assumption that the release of nutrients from coated fertilizer is controlled by simple solute diffusion. 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 (Avi Shaviv et al., 2003a). They also extended the model to statistical model for population of granules (Avi Shaviv et al., 2003b). In 2007, Lu proposed a mathematical model for the release of a scoop of polymer coated urea which took into account on the effect of population. This model was based on mass balance equation of pseudo-steady state of Fick's law. However, first stage of release process was neglected, and "trial and error" method was used to estimate diffusion coefficient (Lu et al., 2007).

There are many efforts in understanding the controlling release mechanism and pattern to obtain a model which could be used for predicting the release of nutrients under laboratory and field conditions and also as a design tools for technologist (Aviv Shaviv, 2005). Most of the studies in this area only concentrated on the simple diffusion of urea through coating layer without considering the diffusion through multilayer. To get more details on the urea release process, this study investigates the diffusion of urea from its solid core to environment and base on FEMLAB software for modeling the diffusion process through multilayer.

2. Model development

This study consists of two parts. The first part describes how to choose an appropriate geometry for water domain by comparing results between numerical method and mathematical method. The second part investigates the diffusion of coated urea from solid core through coating layer and into water zone by mean of Finite Element Method. The releasing time then is calculated based on mass balance of one urea particle.

2.1. Choosing an appropriate water domain for diffusion models

2.1.1. Mathematical method

Assume that the urea particle is spherical in shape, and the dissolution rate is under steady state condition. Urea is quickly dissolved in the solvent and the sphere's surface (solid urea) is saturated with the solute (dissolved urea). Since the urea particle is immersed in a large volume of fluid, its concentration away from the sphere can be considered as zero (Cussler, 2009).

The mathematical solution for urea diffusion of non-coating particle is calculated as:

$$j_D = \frac{D_{urea} c_1(sat)}{R_0} = 5.3910^{-4} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \quad (1)$$

where D_{urea} is the "free" diffusivity of urea in water, R_0 , urea radius, $c_1(sat)$, saturate urea concentration.

2.1.2. Numerical solution for Urea diffusion of non-coating particle

For simple cases, the mathematical solution can be solved for the diffusion of urea to the environment. However, in the case where complex factor involved, the FEM is used

instead. Figure 1 illustrates the dissolving model of a spherical urea. When urea particle is immersed in water, it begins to dissolve by mean of diffusion. Based on mass transport equation of urea in water, the steady state equation for urea diffusion can be written as:

$$D_{urea} \frac{\partial^2 C}{\partial r^2} + \frac{2D_{urea}}{r} \frac{\partial C}{\partial r} = \frac{\partial C}{\partial t} = 0 \quad (2)$$

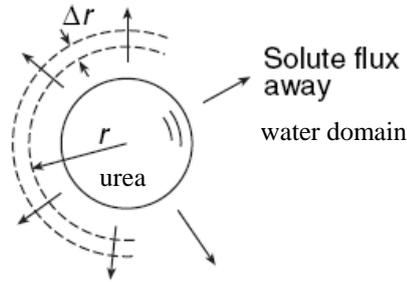


Figure 1. Dissolution model of a spherical urea

FEMLAB software is used to solve the dissolution model. Mesh was generated in a defined geometry of urea and surrounding water as in Figure 2a. Because water domain had to be defined, and could not reach infinity as in mathematical solution so we assumed concentration was zero at a distance far enough from the urea surface.

By varying this distance, we compared the errors between mathematical solution and numerical solutions to get an appropriate water domain (fluid size). Fluid size, the distance from center of urea particle to outer boundary of water domain, will be used for later simulations using FEM method.

2.2. Diffusion model for coated urea particle

When the coating layer is saturated, urea begins to release through the coating layer by mean of diffusion. Based on mass transport equation in porous medium, a transient stage for urea diffusion through the coating could be written as (Lu et al., 2007; Savithri S. and Manju M. S., 2009)

$$D_e \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] = \varepsilon \frac{\partial C}{\partial t} \quad (3)$$

where C is concentration of urea in mol/m^3 , D_e is effective diffusivity of urea in porous medium in m^2/s , ε is porosity of the coating in percentage (%).

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 in liquid, and calculated by equation (2). In this model, D_{urea} is a function of urea concentration: $D_{urea} = (1.380 - 0.0782c_1 + 0.00464c_1^2) \times 10^{-5} \text{ cm}^2/\text{s}$ (Cussler, 2009).

Geometry and meshing steps are made for a urea particle and coating thickness as shown in Figure 2b. In this case, radius of urea core is 3 mm, and coating thickness is

0.1 mm. Fluid size which is defined as the distance from center of urea particle to outer boundary of water domain is set to 22 times the radius of urea core. Initial values and boundary conditions are specified for the model. At the surface of urea core, urea concentration is saturated and depended on ambient temperature. Concentration is zero at the outer layer of fluid field.

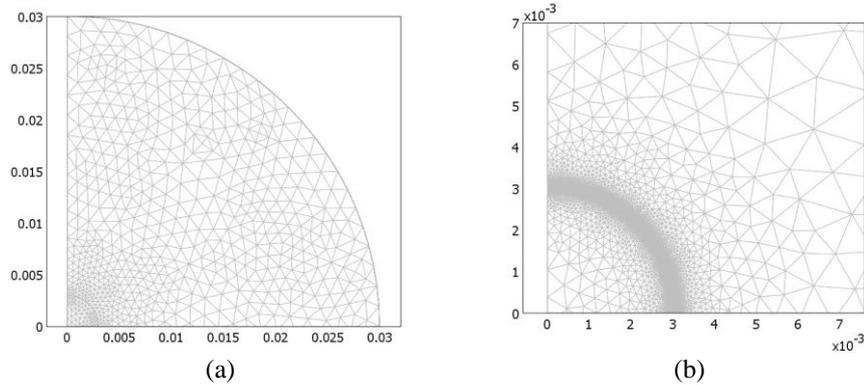


Figure 2. Mesh generation for urea dissolution models. a) Non-coating urea; b) Coated urea.

Simulations are conducted for different effective diffusivity coefficients (D_e) from 10^{-14} to 10^{-12} m^2/s with an interval of 5×10^{-14} . In the simulation, diffusive flux at the coating layer is used for releasing time calculation based on material balance. These data help to predict the appropriate effective diffusivity coefficient of coating layer.

3. Results and Discussion

3.1. Fluid size estimation

The diffusion of non-coating urea particles are simulated with different fluid sizes: $2x$, $10x$, $20x$, $22x R_0$ where R_0 is urea radius. As fluid size increases, memory usage and calculation time increase. From the result shown in Table 1 and Figure 3, fluid size $22R_0$ had a standard deviation (STD) of 3.91%. In technical term, STD less than 5% is acceptable so that fluid size $22R_0$ is chosen in all simulations which are used to predict the effective diffusivity coefficient of materials.

Table 1. Fluid size comparison

| Fluid size | $2R_0$ | $10R_0$ | $20R_0$ | $22R_0$ |
|--------------------------------|----------|----------|----------|----------|
| Diffusive flux ($mol/m^2/s$) | 0.001069 | 6.03E-04 | 5.76E-04 | 5.61E-04 |
| Standard deviation (%) | 98.16 | 11.84 | 6.74 | 3.91 |

R_0 is radius of urea particle.

3.2. Calculation of appropriate effective diffusivity of coating layer

As shown in Figure 4, diffusive flux at the coating layer was plotted, and releasing time was calculated base on material balance of urea particle. Releasing time increases when the effective diffusivity coefficient decreases. It is 8.34 days with a diffusivity coefficient of 1.60×10^{-13} m^2/s and 132.96 days with a diffusivity coefficient of 10^{-14} m^2/s . From simulation, the diffusivity coefficient is 1.49×10^{-14} m^2/s for a crop of which duration is 90 days. Shaviv et al. also found similar results on the solute permeability

which is equivalent to D_e in this study. Their results were based on the experiments with twenty granules of which the radius ranges between 0.12 and 0.14 cm, the coating thickness ranges between 0.004 and 0.0015 cm, and releasing time was more than 60 days. The solute permeability were $1.16 \times 10^{-14} \text{ m}^2/\text{s}$ and $2.89 \times 10^{-14} \text{ m}^2/\text{s}$ for modified polyolefin and polyurethane-like coating, respectively (Avi Shaviv et al., 2003a).

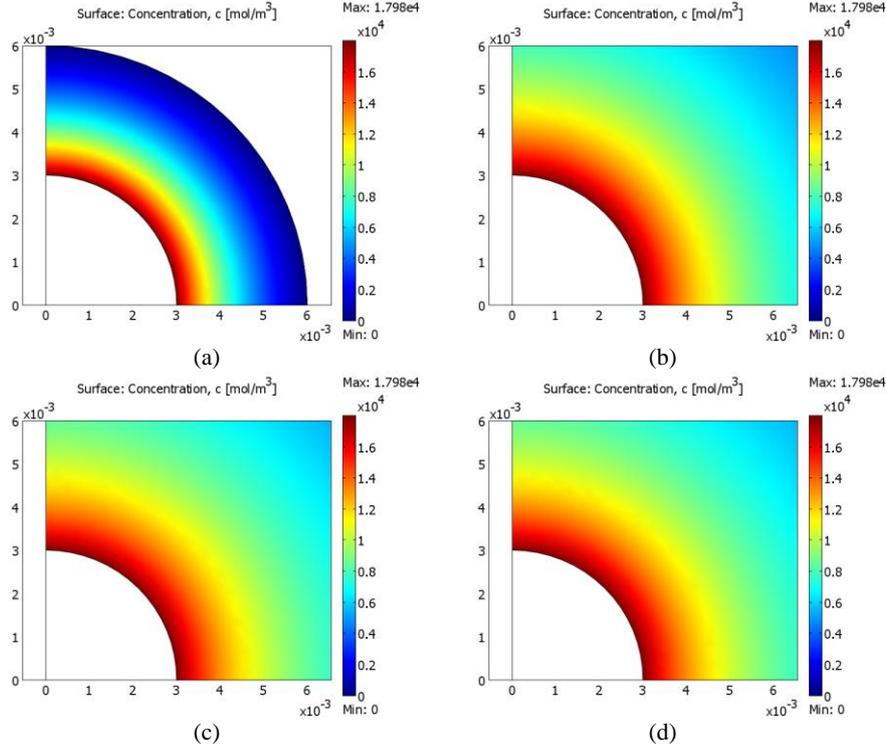


Figure 3. Concentration profile with different fluid sizes: a) fluid size = $2R_0$, b) fluid size = $10R_0$, c) fluid size = $20R_0$, d) fluid size = $22R_0$.

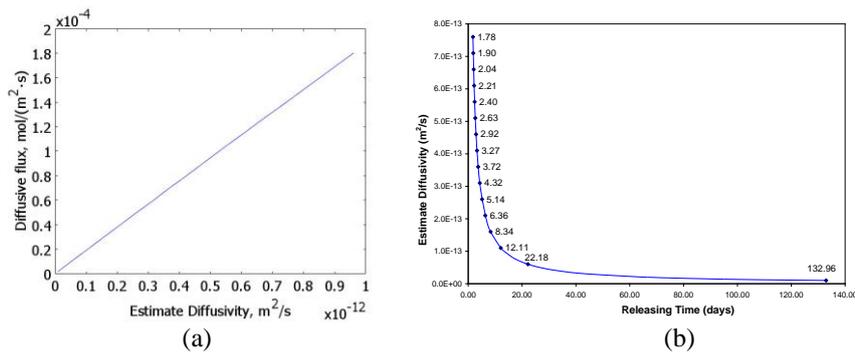


Figure 4. Effective diffusivity vs. diffusive flux at coating surface and estimated releasing time.

4. Conclusion

By applying FEM method to the urea diffusion model, a complicated diffusion process is solved, and it helps to predict the effective diffusivity coefficient for coating material. This model includes the diffusion of urea through the coating and water zones. It also couples diffusivity coefficient as a function of urea concentration. However, this model still not includes the characteristics of coating layer such as porosity, permeability, etc. Finally, coating materials chosen for urea coating should have a diffusivity coefficient of $1.49 \times 10^{-14} \text{ m}^2/\text{s}$ to get a releasing time suitable for crops.

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