Modeling the Release of Urea from Coated Urea: The Constant Release Stage

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Abstract. Controlled release fertilizer (CRF) plays an important role in nutrient loss prevention by plants and its utilization enhancement. This study uses multi-diffusion model to simulate the release of urea for two coating materials: modified polyolefin (MPO) and latex film, based on COMSOL Multiphysics software. Effective diffusivity and lag time (t_0) are determined based on experimental data. Modeling results well simulate the experimental data of "constant release" stage. Standard error of estimate (SEE) ranges from 0.012 - 0.017 for MPO and 0.0316 for Latex film. The validated model is then utilized to study the effect of coating thickness (l), saturated urea concentration (C_{sat}) and effective diffusivity (D_e) on the urea release profile. Release time increase with increasing coating thickness or decreasing saturated urea concentration, effective diffusivity. In addition, a change in effective diffusivity does not make significant change in percentage of urea at the end of "constant release" stage.

Introduction

The idea of controlled release fertilizer (CRF) is to prevent nutrient loss and enhance nutrient utilization efficiency of plants [1]. The amount of fertilizers recovered by plant when applied in conventional forms is only 30-50%. CRFs possess manifold advantages including fertilizer use economy through least possible losses of the fertilizer, prevention of the seedling damage and better protection of the ecosystem in the case of biodegradable carriers [2].

The application of controlled release technology to fertilizers was first conducted in 1962 by Ortil et al. [3]. The nutrient release from coated CRFs is usually controlled by the diffusion through the coating layer. In 1987, Glaser *et al.* studied the release of polymer-coated granule and applied one-dimensional coordinate diffusion system [4]. Gambash *et al.* used semi-empirical model in their study [5]. Lu and Lee applied the Fickôs law in spherical coordinate for the release of latex coated urea (LCU) [6]. Al-Zahrani modeled unsteady state of polymeric membrane particle and assumed a well-mixing condition inside sphere particle [2]. Most of modeling efforts were based on the assumption that nutrient release of nutrients from coated fertilizer is controlled by simple solute diffusion. In 2003, Rabanôs experiments showed that 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 stage of gradual decay of the release rate [3]. In 2007, Lu proposed a mathematical model for the release of a scoop of polymer coated urea which took into account the effect of granule population. This model was based on mass balance equation of pseudo-steady state of Fickôs law. However, the first stage of release process was neglected, and ñtrial and errorò method was used to estimate diffusion coefficient [7].

Understanding the release of urea through the coating layer is very important to predict nutrient release behavior. Therefore, 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 technologists [8]. This study investigates the urea release through coating layer into the outer environment (water) using multi-diffusion model on two coating materials: Modified Polyolefin (MPO) and Latex film. Effects of coating thickness, urea saturated concentration and effective diffusivity on the urea release is also studied in this study.

Methodology

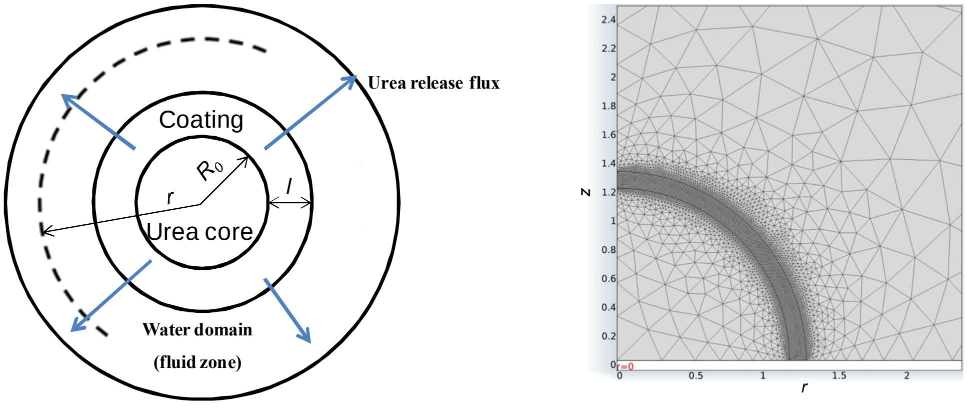
Model development and validation. Simulations are based on the multi-diffusion model developed in our previous studies [9, 10]. The dissolving model of a spherical urea is described in Fig. 1a. In this model, coated urea granule is surrounded by water environment. Urea granule consists of two parts: urea core and coating layer outside the urea core. Model is assumed that coating layer is saturated with water, and water at the surface of urea core quickly dissolves solid urea. Whenever solid urea presents in the core, urea concentration is kept at saturated level. Urea begins to release through the coating layer by mean of diffusion. There are two diffusion processes occuring in the release of urea. First, the diffusion of urea through the coating layer described by mass transport equation in porous medium as below [7, 11]:

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

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

Second, the diffusion of urea from the interface of coating to the liquid is calculated based on mass transport equation of urea in water. The equation for urea diffusion can be written as:

$$D_{urea}\frac{\partial^2 C}{\partial r^2}+\frac{2D_{urea}}{r}\frac{\partial C}{\partial r}=\frac{\partial C}{\partial t}. \tag{2}$$



(a) (b)

Fig. 1. (a) Urea dissolution models for coated urea and (b) mesh generation.

Four simulations are run following the input data in Table I. These data are based on previous publications from Lu & Lee, and Shaviv *et al.* [3, 6]. Geometry and meshing steps are done for urea granules with radius and coating thickness following Table I and Fig. 1b. Fluid zone, which is defined as the distance from center of the urea granule to outer boundary of water domain, is set 22 times of the radius of urea core [9]. 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), coating material (thickness and properties) and saturated concentration.

"Constant release" stage is considered from the beginning of the release to the time solid urea is totally dissolved. When solid urea totally dissolved, the amount of urea in the core is

$$m_{core} = m_{sat} = M_{urea} C_{sat} V_{core} \,. \tag{3}$$

where m_{sat} is mass of urea core when solid urea is totally dissolved in g, C_{sat} is saturated urea concentration in mol/m^3.

Equation 3 specifies as the stop condition for "constant release" stage. This model focuses on the "constant release" stage, and validates with Modified Polyolefin (MPO) and Latex coating material experiments. Lag time (t_0) is determined based on each experiment. Data are extracted using Engauge Digitizer 4.1. Based on information from these papers and extracted data, simulation and experiment data are overlaid to validate the model.

Effect of coating thickness, saturated urea concentration and effective diffusivity on the release of urea. After validation process, the model is used to study the effect of coating thickness, saturated urea concentration, and diffusive flux to urea released profile.

Effect of coating thickness is studied with three thicknesses as 0.0375, 0.0917 and 0.1833 mm respectively. Effective diffusivity for these simulations is 1× 10^{-5} cm^2/day, and urea core radius is 1.2mm.

For the effect of saturated urea concentration, the release of urea is conducted with concentrations as 10486, 11083, 12275, 13339 and 14403 mol/m^3. Core radius is 1.2mm, coating thickness is 0.0375mm, and effective diffusivity is 1 × 10^{-5} cm^2/day.

Five effective diffusivities (0.8, 1.0, 1.5, 2.0 × 10^{-5} cm^2/day) is used to study the relationship between diffusivity and release time. In this case, coating thickness is 0.0375 mm, and urea core radius is 1.2 mm.

Results and discussion

Model development and validation. At the beginning, urea core is solid so it keeps urea concentration in urea core at saturated level. As in Fig. 2, the urea core will decrease its mass by diffusion through coating layer (blue line). The constant release stage will end when solid urea is totally dissolved. At this moment, urea mass reaches the red dashed line, which is equivalent to saturated urea concentration.

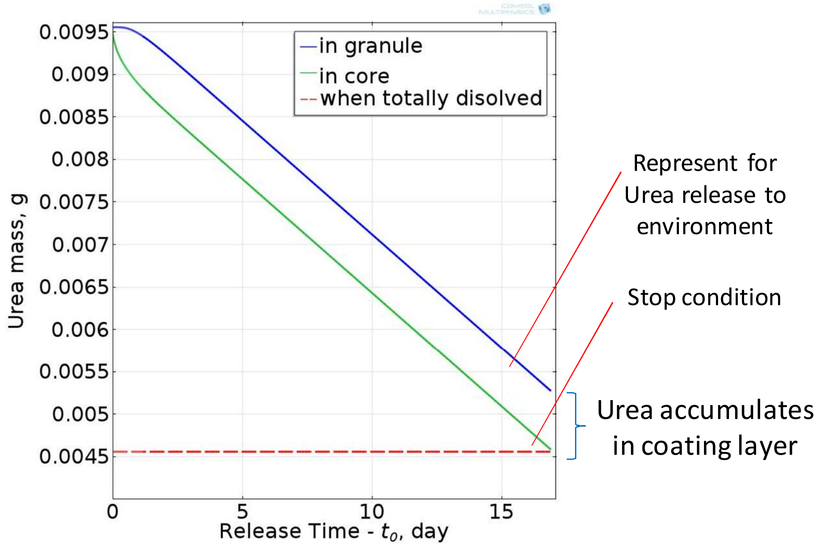


Fig. 2. Urea mass profiles in core and granule, and the stop condition for "constant release" stage

Simulations are conducted using information in Table I. For MPO coating material, effective diffusivity, in all three simulations, is 1 × 10^{-5} cm^2/day. In Fig. 3a, simulation data corresponds with experiments from Shaviv *et al.* literature [3]. It means that the model well simulates the release of urea during "constant release" stage. Another simulation is run and validated with experiment from Lu and Lee which Latex film was used as coating material [6]. In Fig. 3b, red square markers and green line are experiment and simulation results from Lu and Lee; and blue line is simulation results obtained from our study. This plot also shows that modeling results are in good agreement with the experimental data. Standard error of the estimate (SEE) ranges from 0.012 - 0.017 for MPO and 0.0316 for Latex film.

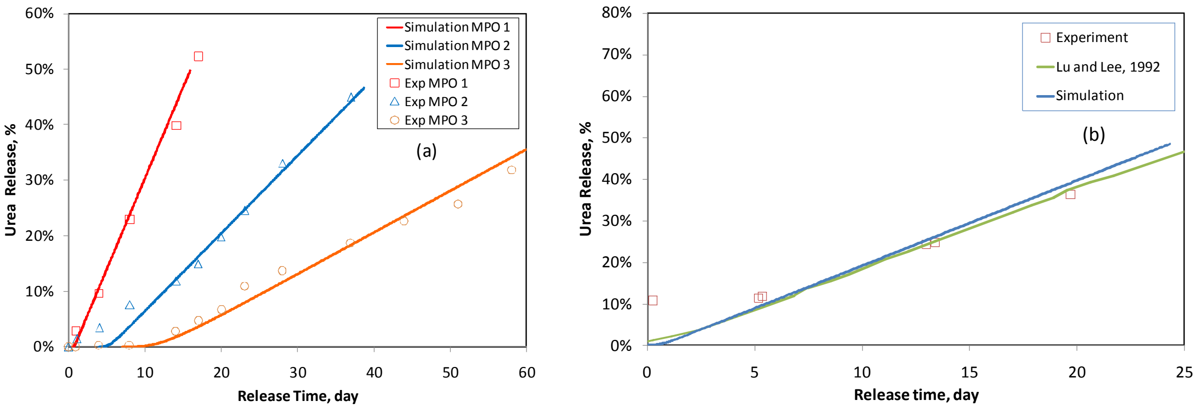


Fig. 3. Urea release profile during constant release stage for (a) MPO and (b) Latex film

Table I. Simulation input and output

No.	Coating Material	Urea Radius [mm]	Coating thickness [mm]	Lag time t_0 [days]	Release time [days]	Percentage release [%]	Source
1	MPO[a]	1.2	0.0375	0.5	15.89	49.71	Shaviv, 2003
2	MPO[a]	1.2	0.0917	4	38.72	46.66	
3	MPO[a]	1.2	0.1833	7	66.84	40.72	
4	Latex	15	0.3500	22	24.31[b]	48.48	Lu and Lee, 1992

[a] Modified Polyolefin

[b] Lag time t_0 is not included

Effect of coating thickness on urea release time. Simulation results are summarized as in Table I. As coating thickness increases, release time also increases. It causes by the increase in diffusion resistant. Beside, ñconstant releaseò stage ends at different percentage of urea released depending on coating thickness. Percentage of urea released decreases as coating thickness increases (Table I). This finding is very interesting because the percentage of the urea released is not the same in all cases although the stop condition does not change. Moreover, the coating thickness does not affect the stop condition.

This can be explained by the difference between amount of dissolved urea inside the core and amount of urea release to environment. In these simulations, stop condition is

$$m_{core} = m_{sat} = M_{urea} C_{sat} V_{core}. \tag{4}$$

Stop condition depends on mass of dissolved urea in core while the percentage release depends on mass of urea released to environment. The different amount is accumulated in the coating layer. This finding also shows that measured urea is not the actual urea dissolved in core, and release curve has late response to the urea dissolving curve. This phenomenon strongly affects the prediction of the end point of the release, amount of urea dissolved and urea released. Thus, it will lead to false modeling which increases error between simulation and experimental results.

Effect of saturated urea concentration on the release. Based on the model of urea release, effect of saturated urea concentration on the release of urea has been investigated as in Fig. 4a. Table II shows that the higher the saturated urea concentration, the shorter the "constant release" stage is. Release time is 15.89 days when saturated concentration is 10486 mol/m^3. It becomes 7.68 days as saturated concentration is 14403 mol/m^3. Simulations also show a linear relationship between saturated urea concentration and percentage of urea release during "constant release" stage.

$$Percentage\ released\ (\%) = 4\times10^{-11}C_{sat}^{2} - 5\times10^{-5}C_{sat} + 0.997\ ;\ R^2 = 1. \tag{5}$$

Effect of effective diffusivity on the release. Effect of diffusivity on the release has also been studied and results are shown in Fig. 4b. The smaller the diffusion coefficient, the longer the ñconstant releaseò stage is. Release time decreases from 19.83 to 8.14 days when effective diffusivity changes from 0.8 × 10^{-5} to 2.0 × 10^{-5} cm^2/day. However, there is no significant change in the percentage release at the end of ñconstant releaseò stage as effective diffusivity changes. Meanwhile, this change is significant in case of coating thickness or saturated urea concentration.

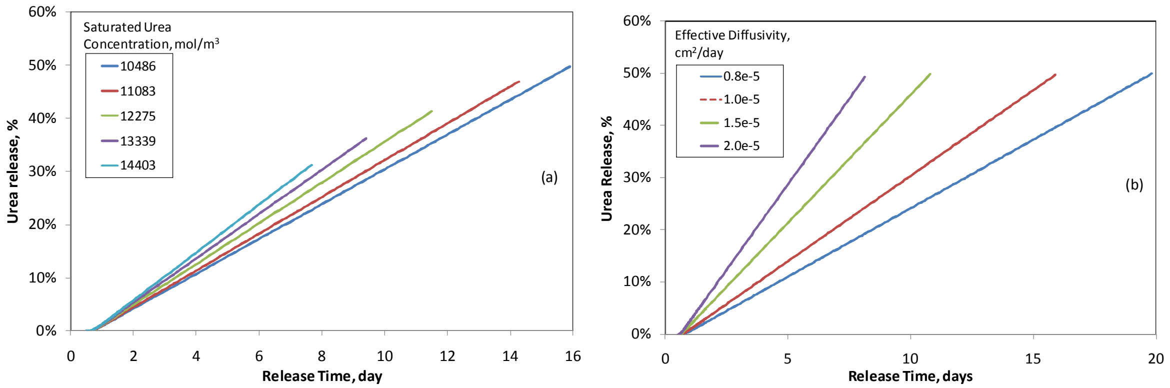


Fig. 4. Release profile of urea for (a) different saturated urea concentration (10486, 11083, 12275, 13339, 14403 mol/m^3); (b) different effective diffusivities (0.8, 1.0, 1.5, 2.0 *x* 10^{-5} cm^2/day)

Table II. Release time and percentage release vs. saturated urea concentration

Saturated Urea Concentration [mol/m^3]	**Release time [days]**	**Percentage release [%]**
10486	15.89	49.71
11083	14.27	46.92
12275	11.50	41.31
13339	9.41	36.20
14403	7.68	31.27

Conclusion

The "constant-release" stage of urea release has been modeled by applying finite element method to the urea diffusion model. This model is validated with experimental data and is shown to successfully simulate the release of urea. However, this model focuses mainly on the constant release stage. It needs to enhance to suit with three stages of the release.

Effect of parameters like coating thickness, saturated urea concentration and effective diffusivity has been studied on "constant release" stage. Increase in urea coating thickness results in longer release time, and óconstant releaseô stage ends at lesser percentage of urea release. This can be explained by the fact that the reduced amount of urea release is due to retention of urea in the coating layer. This factor should always be taken into account for the modeling urea release.

Saturated urea concentration has a linear relationship with the percentage of urea released. An increase in saturated urea concentration decreases the duration of óconstant releaseô stage. Decrease in effective diffusivity increases the duration of óconstant releaseô stage, however, it does not have any effect on the percentage of urea released at the end of óconstant releaseô stage.

Although this model simulates well the óconstant releaseô stage of urea fertilizer, it needs modification to simulate the overall urea release process including all the three-stage release.

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