

Modelling and Simulation of Nutrient Release from Neem (*Azadirachta Indica*) Oil Coated Urea

Shiv Om Meena, Manish Vashishtha, and Ankush Meena

Department of Chemical Engineering, Malaviya National Institute of Technology, Jaipur-302017, India

Email: mvashishtha.chem@mnit.ac.in

Abstract—Urea is an important Nitrogenous fertilizer. However, uncoated Urea when applied to crops is prone to nutrient losses due to run off, volatilisation and leaching. Answer to this problem lies in application of controlled release urea which plays a dual role of enhancing nitrogen use efficiency by plants leading to improved crop yields and also controls environmental pollution by reducing hazardous gaseous emissions and water eutrophication. The present study aims to model and simulate the nutrient release from urea coated with Neem (*Azadirachta indica*) oil coating (NCU) unveiling the three stages of nutrient release as explained in literature for other coated fertilizers. Multi diffusion model is developed for multilayer including the Neem Oil coating, water domain and couples the Finite element approximation with 2D geometry, to improve the accuracy of simulation urea diffusivity in water is taken as a function of its concentration. The simulation results agree well with the experimental data with standard error of estimate varying from 0.016 to 0.023. The model not only predicted nutrient release from NCU but also described the internal release mechanism from the core to coating interface and coating interface to water environment. The model was also validated with experimental results for urea coated with other materials also differing from NCU in core and coating thickness.

Index Terms—Controlled Release Fertiliser (CRF), multi-diffusion modelling, nutrient Release, neem oil coated urea, urea diffusion

I. INTRODUCTION

Soil fertility is primarily determined by three major elements namely Nitrogen, Phosphorus & Potassium (N, P, K) of which Nitrogen plays a very important role. For this reason, Urea (containing 46% of N) consumption is very high all over the world. Unfortunately, more than half (up to 60%) of the nitrogen leaches out or vaporizes in the form of nitrogen gas, ammonia & nitrous oxide due to the presence of denitrifying bacteria in the soil [1]-[3]. Therefore, Controlled Release Fertilizers (CRF) conceptualized and introduced by Oertli [4] in 1962, provides a way to increase nutrient recovery and fertilizer management. In comparison to normal fertilizers, the nutrient release pattern from CRF meets plant requirement and minimizes leaching in an efficient manner whereby improving the overall fertilizer usage [5]. When uncoated urea is applied to the soil, the urea

(Amide) nitrogen is rapidly converted to ammonical nitrogen and subsequently to nitrite and nitrate forms. Nitrogen in these forms, besides being absorbed by plants, is also rapidly lost from the soil due to leaching, run off, volatilization and de-nitrification. When Neem Coated Urea (NCU) is applied to soil, the Neem Triterpenes inhibit the activity of nitrifying bacteria results in delayed transformation of ammonical nitrogen into nitrite nitrogen. This ensures slow and continuous availability of nitrogen throughout the crop growth. Coating urea with neem not only puts it into slow release mode but also prevents its misuse, nourish the saplings for a longer period, and helps in avoiding the repeated use of fertilizer. The process also reduces pollution of groundwater, increase the crop yield and provides an efficient pest control management leading to savings. It also increases the shelf life of the product [6]. Glaser et al. studied the release from polymer-coated granule and applied one-dimensional coordinate diffusion system [7]. Gambash et al. used semi-empirical model in their study but the effect of geometry and size was ignored apart from these assumptions, the lag period, during which no release is observed, was not included [6]. Lu and Lee applied the Fick's law in spherical coordinate for the release of Latex Coated Urea (LCU) [8]. Al-Zahrani modelled unsteady state release from polymeric membrane particle and assumed a well-mixed condition inside sphere particle [9]. Majority of the modelling studies were based on the assumption that the release of nutrients from coated fertilizer is controlled by simple solute diffusion. However, from Raban's experiments, it is established that the release from a single granule of a polymer coated CRF 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 [10]. Lu proposed a mathematical model for the release nutrient from a population of polymer coated urea. 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 [11].

Application of Finite-Element Method (FEM) for nutrient release modelling of CRF has been used since 2003 [12]. However, the geometry used in their model was not a particle type specific. Trinh *et al.* [13] used 2D geometry and the FEM model to simulate urea release from coated particle but this model only explained the second stage of release. Therefore, the objective of the present study is to unveil all the three stages of nutrient

release. So, a multi diffusion model was developed which yielded a sigmoidal release profile, the model results were validated by comparing them with experimental results from NCU. To establish universality and robustness of the model, it was also compared with experimental data of nutrient release from urea coated with other materials.

II. GENERATION OF EXPERIMENTAL DATA

A. Material

NCU used in the present study for obtaining the release profile was prepared in laboratory using drum coating technique. Commercial urea granules with a nitrogen content of 46.44% and with a distribution of particle diameter from 0.5 mm to 2.8 mm were supplied from Chambal fertilizer & Chemical limited (CFCL) Gadepan, Kota (India). Neem oil used in coating was supplied by Shubhra industries, Jaipur (India). The particle size distribution was determined for both uncoated urea and NCU using sieve analysis and it was seen that maximum particles are available in diameter range of 1.7 mm and 2.0mm (so a diameter of 2.0mm is used in simulation studies). Coating thickness range from 72 to 83 μ m as determined by scanning electron microscope (SEM) (Nova Nanosem-450 FEI company available in Materials Research Centre at Malaviya National Institute of Technology, Jaipur), as shown in Fig. 1. So an average coating thickness of 77.5 μ m is used in simulation.

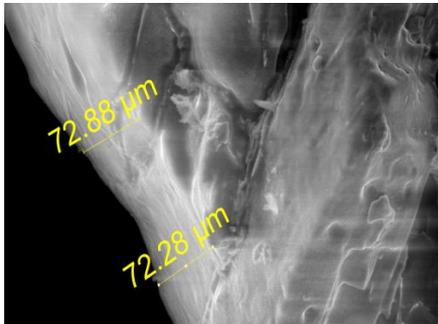


Figure 1. SEM of neem oil coated urea (magnified 500x)

B. Determination of Nutrient Release

The release test was performed in a beaker containing 2 \pm 0.001 gm of NCU in 250 ml distilled water at room temperature. At an interval of 2-4 days, urea concentration was measured using a UV-Vis double beam (Make Shimadzu, model UV-1800 available in research lab of the Chemical Engineering department at Malaviya National Institute of Technology Jaipur) at a wavelength of 210 nm. From this experimental data release profile was constructed.

III. DEVELOPMENT OF MATHEMATICAL MODEL

The dissolution model of a perfectly spherical urea particle surrounded by a water zone is shown in Fig. 2(a). NCU particle is divided into two regions viz. urea core (R_0) and Neem oil coating (thickness= Δr). For time, $t < t_0$ (t_0 , determined experimentally) which is called the lag

period, mainly water vapour penetrates into the NCU granule and dissolves a small fraction of solid fertilizer. The driving force responsible for this process is the vapour pressure gradient across the Neem oil coating. The volume available to the condensed vapour is basically limited to the voids present inside the solid core and those between the core and the coating. A reasonable explanation for the lag period is that some time is needed to fill the internal voids of the granule with a critical water volume.

The model assumes that the coating layer was saturated with water at the time (t_0) of initial release. Water within the core begins dissolving the solid urea where urea concentration is maintained at a saturated level as long as solid urea exists in the core. Nitrogen is released through the coating layer by diffusion with a constant rate. Hence, it is called “constant release” stage. When solid urea in the core is totally dissolved, urea concentration decreases, and a “decay release” stage begins and then continues till the end of the process.

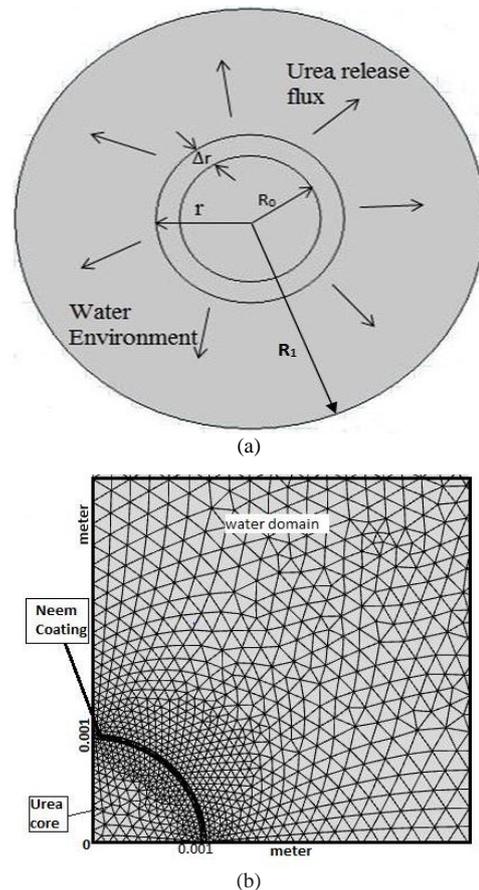


Figure 2. (a) Dissolution model of a spherical urea particle in water environment (b) Geometry and mesh generation of a urea dissolution model for coated urea in COMSOL.

Based on mass transport equation for porous medium, the transient stage of urea diffusion through the coating is represented by Eq. 1 [11]

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

As the urea particle is motionless, it is assumed that urea flux from the coating interface to the liquid

environment is controlled by the diffusion of urea in liquid. Thus, diffusion is calculated on the basis of mass transport equation of urea in water as follows:

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

Inside the water zone, urea diffusivity in liquid, D_{urea} , expressed in $cm^2 s^{-1}$ varies according to urea concentration as described by eq. (3) [14].

$$D_{urea}(r,t) = (1.380 - 0.0782C(r,t) + 0.00464C(r,t)^2) \times 10^{-5} \quad (3)$$

To solve the model, Finite Element Method (FEM) and 2D geometry was applied. COMSOL Multiphysics version 5.3 was used to find urea release behaviour. Since NCU particle under consideration is spherical, due to symmetry considerations the model's geometry was based on one quarter of a sphere. Geometry and meshing for single urea particle is shown in Fig. 2b. Fluid zone diameter, i.e. the distance from the centre of the urea particle centre to the **water boundary** (R_1), was set at twenty-two times of the **core radius** (R_0) [15]. Parameters used in modelling for four different coatings namely Neem oil (NCU), Modified Polyolefin (MPO1 and MPO2) and latex coated urea (LCU) are given in Table I. Initial values and boundary conditions specified for the model are presented in Table II.

At time t_0 (obtained from experiment), urea solution at the surface of urea core is saturated, and concentration is zero at the outer layer of fluid field. In these simulations, urea release time depends on the amount of urea (size and shape) and coating material properties (thickness, diffusivity, porosity). A stop condition is specified for the constant release whenever solid urea core is totally dissolved. At this time, the whole urea core is liquid and equivalent to saturated urea concentration ($m_{core} = m_{sat}$).

Mesh convergence analysis was performed to estimate the accuracy of simulation. Percent released converged to the second decimal place for mesh size factors from 0.6 to 1.2 which is close to the accuracy achieved from experiments. Error between mesh size factor of 0.6 and 1.0 was 0.0013%, hence the factor of 1.0 was chosen for the model. At this factor 19364 elements were chosen for applying backward and central difference scheme for discretization and solving eqns (1-3).

TABLE I. PARAMETERS USED IN THE MODEL

| Type→ | NCU | MPO 1 | MPO 2 | LCU |
|--|---------------------|-----------------------|-----------------------|------------------------|
| Data Source→ | Experimentally | From Literature [10] | From Literature [10] | From Literature [8] |
| Parameter↓ | Determined | | | |
| Radius (mm), R_0 | 1.0 | 1.2 | 1.2 | 7.06 |
| Coating thickness (mm), Δr | 0.0775 | 0.0375 | 0.0917 | 0.353 |
| Lag time, t_0 (day) | 19 | 1.0 | 5.0 | 25 |
| Effective diffusivity, D_e (m^2/s) | 3×10^{-14} | 1.2×10^{-14} | 1.2×10^{-14} | 39.5×10^{-14} |

TABLE II. INITIAL AND BOUNDARY CONDITIONS

| Stage→ | Constant release | Decay release |
|------------------------------|---|--|
| Initial Condition | $C_{const.}(r,t_0) = 0$ ($R_0 \leq r \leq R_1$) | $C_{decay}(r,t_1) = C_{cont.}(r,t_1)$ ($0 \leq r \leq R_1$) |
| Boundary Condition -1 | $C_{const.}(R_0,t) = C_{sat.}$ ($t_0 \leq t \leq t_1$) | $D_{urea} \nabla C_{decay}(R_1, t) = 0$ ($t \geq t_1$) |
| Boundary Condition -2 | $C_{const.}(R_1,t) = 0$ ($t_0 \leq t \leq t_1$) | |

where, $C_{decay}(r, t_1)$ = the initial urea concentration of decay release stage, $mol m^{-3}$

$C_{const.}(r, t_1)$ = urea concentration at the end of constant release stage, $mol m^{-3}$

$C_{sat.}$ = saturated concentration $mol m^{-3}$

IV. RESULTS AND DISCUSSION

Although an experimental analysis uncovers the real behaviour of any process, however it involves time and cost. So Simulation becomes an obvious choice. For ease of understanding and presentation, the results are presented in three subsections. In first subsection, the model validation using experimental data for nutrient release from NCU is presented. Second subsection aims to check reliability and robustness of the model, hence experimental results of nutrient release from urea coated with other materials (MPO1, MPO2 and LCU taken from the literature) were compared with the model. The third subsection, presents modelling results regarding the internal mechanism of nitrogen release from the NCU particle.

A. Model Verification Using Experimental Data Of Nutrient Release From NCU

The simulation result plotted in Fig. 3 corresponded well with our experimental data. The Standard Error of Estimate (SEE) used to determine the accuracy between simulation and experimental [16] results was found to be 0.023, which is acceptable for the prediction of nutrient release. The small mismatch between the experimental and simulation results occurs due variations in particle shape, imperfection in coating and presence of surrounding particles. Both modelling and experimental data follows a sigmoidal release trends in agreement with the cited literature [8], [10], [14], [17], [18].

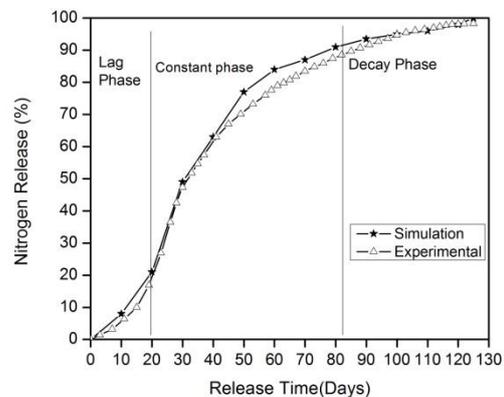


Figure 3. Experimental and simulation release profile for NCU

B. Comparison with Literature Data

Simulation runs were also done for three samples of two other types of coating material also viz. Modified Polyolefin (two samples: MPO 1 and 2) and Latex (LCU) which represent both small and large particles in which release time ranged from hours to days. Data from literature was extracted using webplot digitizer 2.0. The results are shown in Fig. 4.

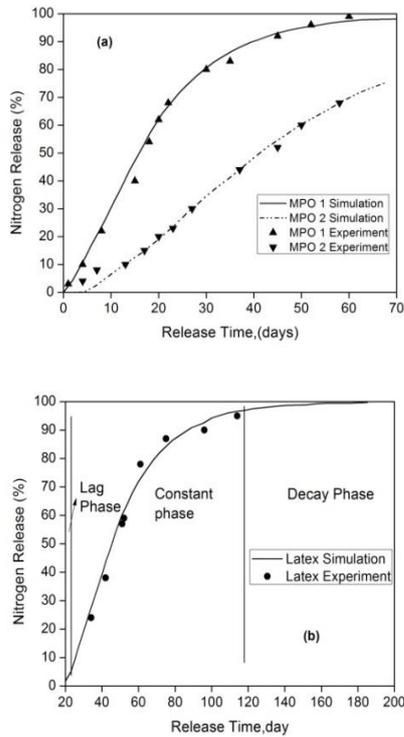


Figure 4. Experimental and simulation release profile (a) MPO1 and 2 (b) LCU

Fig. 4(a) shows simulation results compared with experimental data from [10] for MPO1 and 2 where R_0 was taken as 1.2 mm and coating thickness as given in Table I. A constant release phase extends upto sixty days in both these case. The Standard Error of Estimation (SEE) ranged from 0.016 to 0.018. Thus, the model satisfactorily predicts the three staged release behaviour

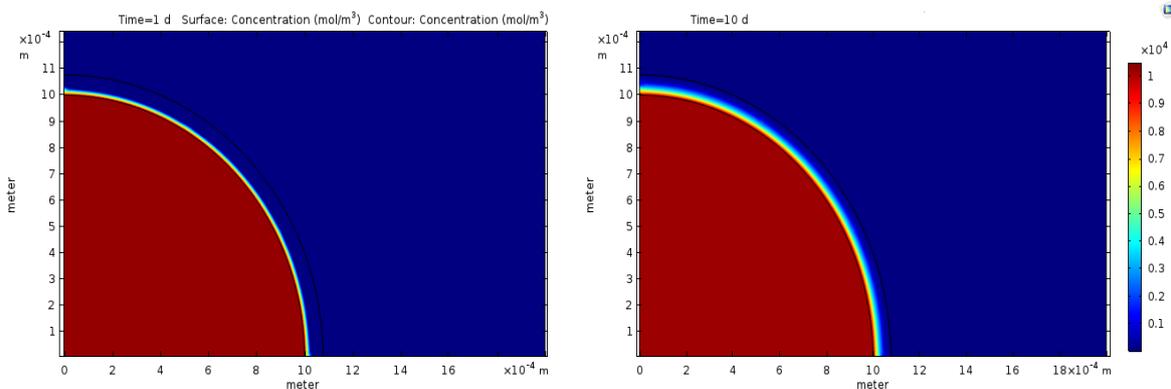
and proves to be sufficiently robust in estimating the release for coated urea particles with release time less than that in NCU but these release characteristics are shown by commercial products used. The developed model also proved equally suitable in explaining the experimental release behaviour of a large ($R_0=7.06$ mm) LCU [8], where release time extends upto 120 days which greater than NCU as shown in Fig. 4(b). Thus our model proved to be reliable and robust in accurately predicting the nutrient release behaviour and explaining the release stages from coated urea particle over a wide range of sizes, coating thickness and release intervals.

C. Release of Nutrient from NCU (2D Results)

The three staged nutrient release process from NCU can be more easily understood by COMSOL 2D results. The Lag phase or the first phase (upto 19 days) as shown in Fig. 5 is characterized by the feature in which the urea core gets dissolved while the mass of urea remains constant and thus very little release is observed during this period.

Fig. 6 presents results for constant and decay release stages. Starting from 20th day the release percentage rises rapidly and reaches to 89.65% at the end of 90th day. This corresponds to the second stage, called the *constant release stage*, which begins when a critical volume of saturated solution accumulates inside the NCU granule. The rate remains constant as long as the saturated solution in the granule is equilibrated with the non dissolved solid fertilizer. The constant, saturation concentration, yields a constant driving force for fertilizer transport since the concentration of the fertilizer in the external solution is negligible.

The release becomes somewhat slower from 90th day to 120th day, and the amount of nitrogen release reaches 98.27% at the end of experiment. This is the third stage of the release and named as the *decay stage*. This occurs due to the fact that once the solid fertilizer in the core is dissolved the concentration of the internal solution decreases due to the continuing concomitant fluxes of nutrient release out and water flow into the granule. Accordingly, the driving force for the release decreases and the release rate decays.



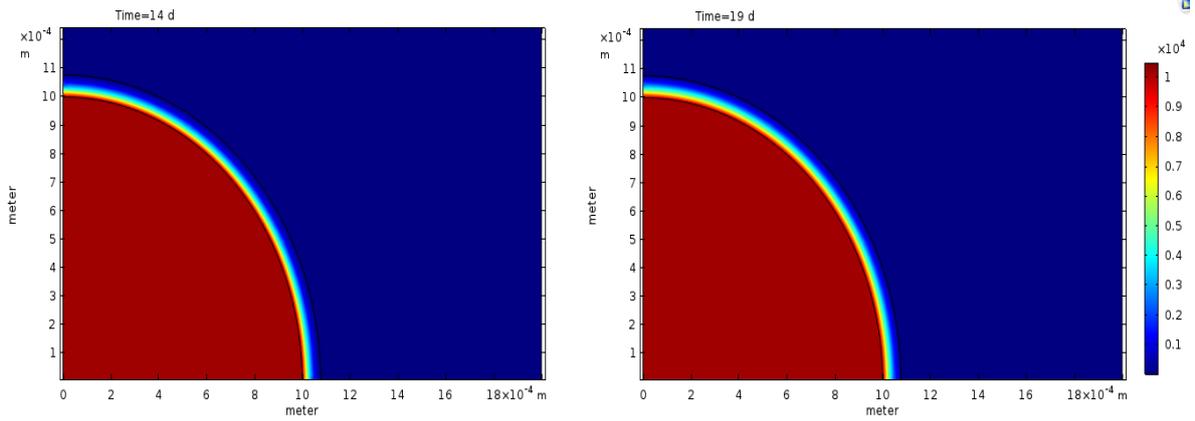


Figure 5. 2D release profile in NCU during lag phase. Colour legend represents urea concentration in range of 0-10500 mol/m³

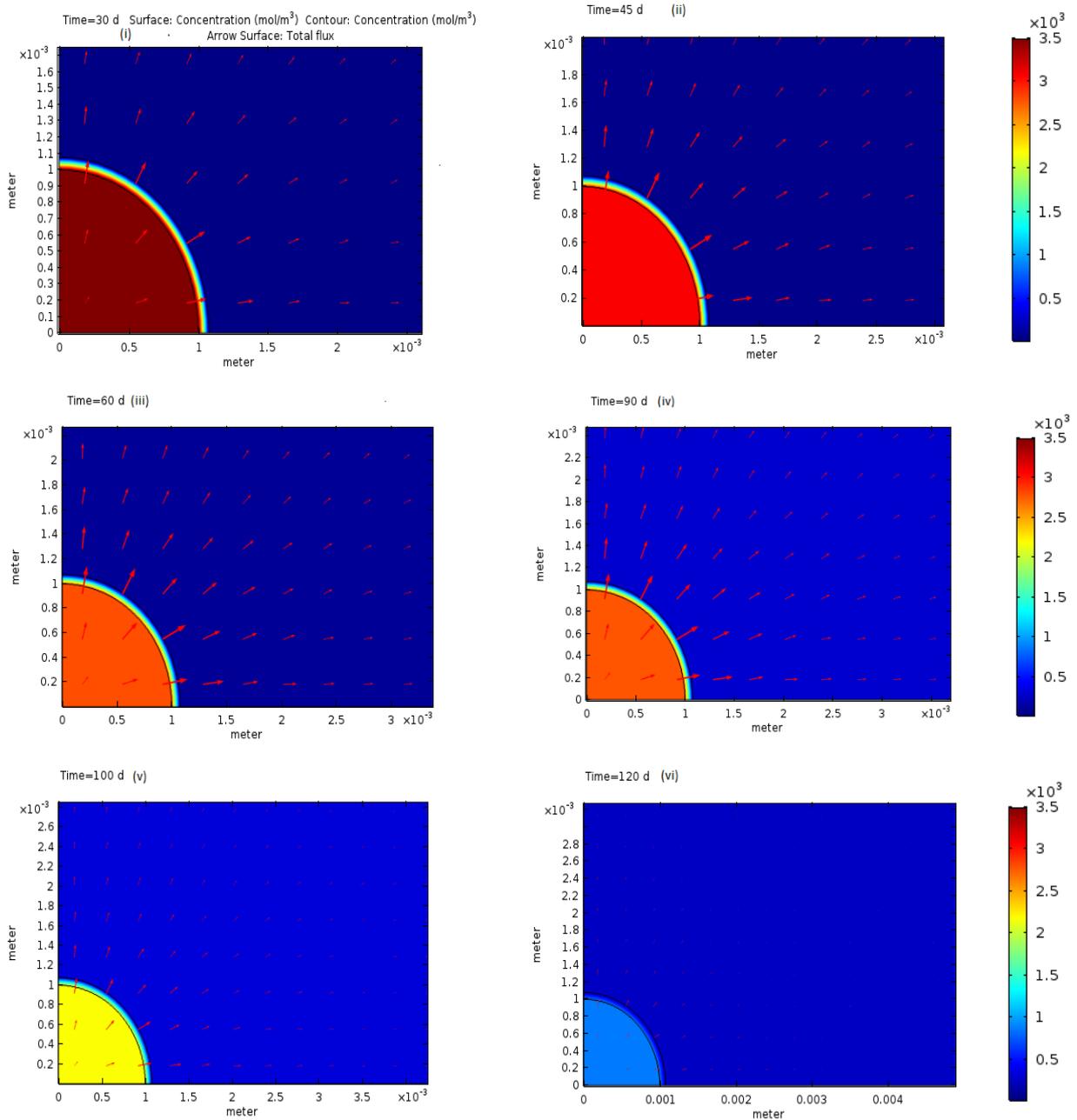


Figure 6. 2D release profile in NCU during Constant and Decay release phase. Colour legend represents urea concentration in range of 0-10500 mol/m³

V. CONCLUSION

In present work the experimental and simulation study on nutrient release from NCU is carried out, results show that nutrient release follows a sigmoidal behavior, following a three stage process. The nutrient release data also shows that NCU match the requirement for controlled release fertilizer. The FEM based 2D model using COMSOL multiphysics was validated with NCU and other coated urea like MPO1, MPO2 and latex. This model successfully predicted nutrient release for most of the commercially used coated urea spanning over different sizes, coating thicknesses and release intervals. However, for further refinement of model is required to incorporate the effect of urea concentration on effective diffusivity as well as effect of particle shape and population.

REFERENCES

- [1] B. Azeem, K. KuShaari, Z. B. Man, A. Basit, and T. H. Thanh, "Review on materials & methods to produce controlled release coated urea fertilizer," *Journal of Controlled Release*, vol. 181, pp. 11–21, 2014.
- [2] Y. Z. Shen, C. W. Du, J. M. Zhou, and F. Ma, "Modeling nutrient release from swelling polymer-coated urea," *American Society of Agricultural and Biological Engineers*, vol. 31, no. 2, pp. 247–254, 2015.
- [3] T. H. Trinh, K. KuShaari, A. S. Shuib, L. Ismail, and B. Azeem, "Modelling the release of nitrogen from controlled release fertiliser: Constant and decay release," *Biosyst. Eng.*, pp. 130–134, 2015.
- [4] J. J. Oertli and O. R. Lunt, "Controlled release of fertilizer minerals by encapsulating membranes: I. Factors influencing the rate of release," *Soil Sci. Soc. Proc.*, vol. 26, pp. 579–583, 1962.
- [5] O. R. Kathrin, "Enhanced efficiency fertilizers," *Montana State University, Bozeman*, cp. 5, pp. 1–16, 2011.
- [6] S. Gambash, M. Kochba, and Y. Avnimelech, "Studies on slow-release fertilizers: II. A method for evaluation of nutrient release rate from slow-releasing fertilizers," *Soil Sci.*, vol. 150, pp. 446–450, 1990.
- [7] V. Glasser, P. Stajer, J. Vidensky, P. Svandova, and V. Knor, "Urea-formaldehyde resins as packaging materials for industrial fertilisers with protracted action," *Part 4. Rubber and Plastics Research Association of Great Britain*, vol. 14, no. 7–12, 127, 1987.
- [8] S. M. Lu and S. F. Lee, "Slow release of urea through latex film," *J. Controlled Release*, vol. 18, pp. 171–180, 1992.
- [9] S. M. Al-Zahrani, "Controlled-release of fertilizers: Modelling and simulation," *International Journal of Engineering Science*, vol. 37, no. 10, pp. 1299–1307, 1999.
- [10] A. Shaviv, S. Raban, and E. Zaidel, "Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules," *Env. Sci. Technol.*, vol. 37, no. 10, pp. 2251–2256, 2003.
- [11] S. M. Lu, S. L. Chang, W. Y. Ku, H. C. Chang, J. Y. Wang, and D. J. Lee, "Urea release rate from a scoop of coated pure urea beads: Unified extreme analysis," *J. Chin. Inst. Chem. Eng.*, vol. 38, no. 3–4, pp. 295–302, 2007.
- [12] U. Shavit, M. Reiss, and A. Shaviv, "Wetting mechanisms of gel-based controlled-release-fertilizers," *Journal of Controlled Release*, vol. 88, no. 1, pp. 71–83, 2003.

- [13] T. H. Trinh, K. KuShaari, A. Basit, B. Azeem, and A. Shuib, "Use of multi-diffusion model to study the release of urea from urea fertilizer coated with polyurethane-like coating (PULC)," *APCBEE Procedia*, vol. 8, pp. 146–150, 2014.
- [14] E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, 3rd ed., Cambridge University Press, 2009.
- [15] H. T. Trinh, K. Z. K. Shaari, A. S. Shuib, and L. Ismail, "Modeling of urea release from coated urea for prediction of coating material diffusivity," in *Proc. 6th International Conference on Process Systems Engineering*, Kuala Lumpur, Malaysia, 2013, p. 20.
- [16] B. S. Grewal, *Higher Engineering Mathematics*, 43rd ed., 2017, pp. 213–216.
- [17] N. Xiaoyu, W. Yuejin, W. Zhengyan, W. Lin, Q. Guannan, and Y. Lixiang, "A novel slow-release urea fertiliser: Physical and chemical analysis of its structure and study of its release mechanism," *Biosyst. Eng.*, vol. 115, no. 3, p. 274, 2013.
- [18] M. Vashishtha, P. Dongara, and D. Singh, "Improvement in properties of urea by phosphogypsum coating," *International Journal of Chem. Tech. Research*, vol. 2, pp. 36–44, 2010.



Dr. Manish Vashishtha was born in Karauli (Rajasthan, India) and obtained his Bachelor of Engineering (with Honours) in Chemical Engineering, from Malaviya National Institute of Technology (MNIT), Jaipur (India) and Master of Technology (M.Tech.) and Doctor of Philosophy (Ph.D.) degrees in Chemical Engineering, from Indian Institute of Technology (IIT), Delhi, New Delhi (India). He is currently working as Associate Professor in Department of Chemical Engineering, at MNIT, Jaipur. He has more than 19 years of teaching and research experience. His areas of research include Interfacial Engineering, Thin liquid films, Modelling and Simulation, Environmental engineering, Particle Science and Thermodynamics. He has published about 60 research papers in various Journals and conferences.



Shiv Om Meena was born at Karauli District in Rajasthan, India, in 1986. He received his B.E. degree in Chemical Engineering from the Jai Narain Vyas University of Rajasthan, India, in 2008 and M.Tech. in Chemical Engineering from Indian Institute of Technology, Kharagpur, India, in 2010. Currently he is research scholar and Assistant Professor at Department of Chemical Engineering, M.N.I.T Jaipur. He has 7 years of teaching and research experience. His area of interest includes Modeling and simulation of applied chemical engineering problems, Petroleum Engineering, Process Control and Environmental Engineering.



Ankush Meena was born at Baran in Rajasthan, India, in 1991. He received his B.Tech. degree in Chemical Engineering from National Institute of Technology, Calicut, Kerala, India, in 2014 and is currently pursuing M.Tech in Chemical Engineering from Malaviya National Institute of Technology, Jaipur, India. His area of interest includes Chemical Reaction Engineering, Heat Transfer, Process Dynamics and Control.